

Law (Education) (1925) Department.

Ordinary SERIES.

G.O. No. 142

DATED 30-1-1925

[Despatch Abstract.]

Gandhekar, Mr. S.S.

Application for appointment to the Indian
Educational Service - Not entertained

BACK PAPERS.

G.O.	No.	Department.	Date.	G.O.	No.	Department.	Date.

FURTHER PAPERS.

G.O.	No.	Department.	Date.	G.O.	No.	Department.	Date.

C.A.
No. 1 (Men).

Educational Appointments in India and the Colonies.

FORM OF APPLICATION to be filled up by persons desiring Educational Employment in India or the Colonies. It is requested that this form may be returned in a cover marked "C.A." to The Secretary, Board of Education, London, S.W. 1.

1. Name in full:—	GANDHEKER, Sitaram Sadasiv. <i>L-10054</i>
2. Address:—	Wrangei Str. 48, Kiel, Germany. <i>57/24</i>
3. Age last birthday with date and place of birth:—	Nellore, India. 23 rd Nov. 1894. 29 years age
4. Married or Single (Number and ages of children, if any):—	Single.
5. Health (past and present):—	very good
6. Father's name, nationality, and occupation (State whether living or dead):—	Sadasiva Row, B.A., B.L. British subject Retired lawyer.
7. Permanent domicile of candidate's family:—	Mayavaram, Madras, India.
8. Post and approximate salary desired:—	as Professor of Organic & inorganic chemistry to start on the regular service scale is 600 Rs a month
9. Duration of visits or residence abroad:—	In the United States of America from January 1919 to July 2 1922 In Europe 1922 - to date.
10. Names of districts abroad of which the applicant has special knowledge:—	Bombay and Madras Provinces
11. Particulars and dates of any important appointments, e.g., Headmasterships or Principalships, Administrative posts, University Professorships, Lectureships, or the like, for which the applicant has stood or is standing:—	
12. Athletics—(a) experience in organising games; (b) proficiency in athletics:—	good.
13. Date of application:—	8 th April 1924

	Name of School or College.	Name of Principal or Employer.
14. School education :—	Kalyanasundaram High School	
	Pachaiyappas High School	Venkatarambhaaya
15. University education, if any :—	Pachaiyappas College	J. C. Rollo.
	University of Illinois, Urbana, Ill. U.S.A.	President: Edmund J. James.
	Harvard University, Cambridge, Mass. U.S.A.	President: A. Lawrence Lowell.
	University of Kiel, Kiel, Germany.	Rector: Prof. Wedemeyer.

	Name of School (or place) where employed.	Name of Principal or Employer.
17. Teaching employment :—		
18. Other employment :— (All employment to be entered in order of time).	Illinois State Water Survey, Urbana, Ill.	State of Illinois.

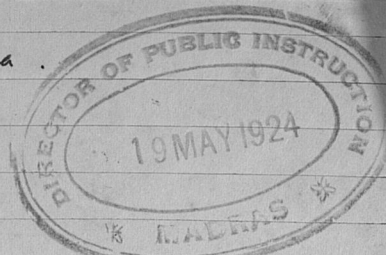
Dates of joining and leaving.	Scholarships, Certificates, Degrees and other Honours. It should be stated whether the degree is Honours or Pass, also in what class and Division the candidate was placed in the examination qualifying for degree.
up to 1913.	
1913 - 1914.	School Final Examination
1914 - 1916.	Intermediate
Feb. 1917 - Feb. 1920.	B. Sc. in chemistry.
Apr. 1920 - June 1922.	M. A. in chemistry with distinction
Oct. 1922 - to date.	Candidate for Doctor's degree.

Dates of joining and leaving.	Position and character of work done, also salary received.
Summer 1918.	as water analyst in the Chemical Laboratory of samples of water from different parts of the State.

19. References:

1. Name,
Address,
Occupation or position,
2. Name,
Address,
Occupation or position.

V. P. Madhava Row, C.I.E.
Ex-Dewan of Mysore & Baroda.
Bangalore, India.



INDIA

(These should be persons resident in the United Kingdom, who have known the applicant intimately, and are in a position to answer any enquiries that may be made of them. They should not be relations, and should be holders of responsible positions who are acquainted with the applicant's character and work in recent years. The names of Officers of the Board of Education should not be given.)

20.*Copies of testimonials from :— If desired references are to be made to—

1. Prof. A. Skita, Hohenbergstr. 20. III. Kiel
2. Prof. James B. Conant, Harvard University, Cambridge, Mass. U. S. A.
3. Prof. William A. Noyes, University of Illinois, Urbana, Ill. U. S. A.
4. Prof. Arthur R. Seymour, ex-Dean of Foreign Students, Urbana, Ill. U. S. A.

*Two sets of copies of testimonials should be submitted with the application form. Original testimonials should not be forwarded unless asked for by this Office.

21. Observations.

[Subjects the applicant is prepared to teach and any special qualifications or experience (e.g., in music and singing, commercial subjects, languages, literary work, organization or inspection) not mentioned under heads 14-18 above, should be given here.]

The applicant desires position as professor of Organic or inorganic chemistry especially in an institution where facilities for Organic Research are to be found. He prefers above all to be located in the Bombay Pres. or Central Provinces or the United Provinces or in the new University of Delhi. He would be thankful if the Government of Madras will recommend him to any of the abovementioned places, in case there should be any vacancy. The Rules of the Indian Education Service prohibit him from sending his application to any province other than his, and he trusts the Madras Government will do the rest. As a second choice he would like either Madras or Bengal.

The applicant has done considerable work in Organic Chemical Research and part of this work for his Master's degree at the Harvard University is published in the Journal of the American Chemical Society, vol 45, March 1923, under the joint authorship of Conant, Wallingford and Gandheker. His thesis for Ph. D. at Kiel which is a study of Stereomerism resulting from the catalytic hydrogenation of trisubstituted aromatic compounds, he expects, will be published later in the German Chemical Journal. He has done considerable work in Biological Chemistry & Bacteriology. He has a very good knowledge of German & a working knowledge of French.

S. J. Gandheker

Aus dem Chemischen Institut der Universität Kiel.

Referenten: Prof. Dr. A. Skita
Prof. Dr. O. Diels

Tag der mündlichen Prüfung: 21. Juni 1924.

Zum Druck genehmigt: Kiel, den 9. Juli 1924.

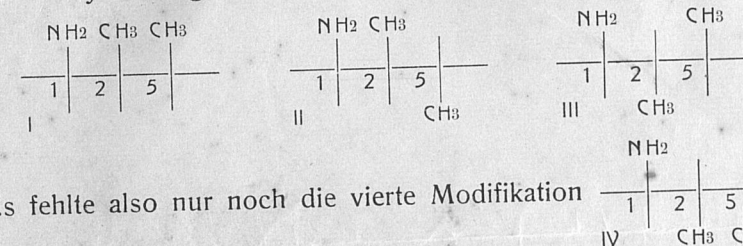
Prof. Dr. Wüst, Dekan.

Zur Stereochemie der Hexahydro-p-Xylidine.

Auszug aus der Inaugural-Dissertation
zur Erlangung der Doktorwürde
der Hohen Philosophischen Fakultät der Christian-Albrechts Universität
zu Kiel

vorgelegt von
Seturam Sadasiv Gandheker
aus Nellor (Indien).

Von den vier theoretisch möglichen Konfigurationen des Hexahydro-p-Xylidins $C_6H_9(CH_3)_2NH_2$ waren vor kurzem die ersten drei verwirklicht worden.¹⁾ Sie entstehen bei der katalytischen Hydrierung des as-p-Xylidins $C_6H_8NH_2(CH_3)_2$ (1, 2, 5)



Es fehlte also nur noch die vierte Modifikation

welche sich nach den bisherigen Erfahrungen durch die niedrigsten Werte in Dichte und Brechungsexponent als extremste trans Form kenntlich machen sollte.

Um diese Lücke auszufüllen, sollte nach einem Hydrierungsverfahren das bisher nur an einzelnen Vertretern der aromatischen Säureamide ausgeführt worden war, das Amid der p-Xylylsäure in das Amid der Hexahydro-p-Xylylsäure überführt werden, welches dann zu dem gewünschten Amin abgebaut werden sollte.

Zur Ausgestaltung des Verfahrens wurde sowohl N-Diäthylbenzamid als auch der Benzoylharnstoff durch katalytische Hy-

46 6
drierung mit kolloidem Platin in saurer Lösung in das neuer cyclischen Amid das N-Diäthylhexahydrobenzamid $C_6H_{11}CON(C_2H_5)_2$ und den Hexahydrobenzoylharnstoff $C_6H_{11}CONHCONH_2$ umgewandelt. Im Anschluß daran gelang auch die Hydrierung des Xylylamids $C_6H_3CONH_2(C_2H_5)_2$ (1, 2, 5) nach dem selben Verfahren. Zu diesem Zweck wurde aus p-Xylol mit Acetylchlorid das Xylylmethylketon hergestellt und dieses über Xylylsäure in das Amid überführt.

Der Abbau des Amids der Hexahydroxylylsäure zu dem Amin wurde nach der von E. Jeffries²⁾ verbesserten Hoffmann'schen Methode ausgeführt. Dieses Vorgehen gab eine befriedigende Ausbeute, so daß dieses Amin nunmehr aus dem p-Xylol in guten Ausbeuten aufgebaut werden kann.

Die neue Base zeigte die Zusammensetzung des Hexahydro-p-Xylidins einen Skdp. $168^{\circ}-9^{\circ}$ bei 760 mm und gab Derivate, von welchem das Pikrat, Hydrochlorid, Benzoat, Thioharnstoff als charakteristisch hervorgehoben werden können und welche die sichere Gewähr bieten, daß es sich um einen von der bisher dargestellten Hexahydro-p-Xylidinen verschiedenen Körper handeln muß, dem nicht die Konfig. I, II oder III zukommen kann. Die Dichte und Brechungsexponent des neuenamins besitzen die kleinsten Werte von den bisher dargestellten Basen, welcher Befund die Annahme berechtigt, daß der neuen Substanz die extremste trans Form - Konfig. IV-, die des 1^t amino 2^c 5^c Dimethylcyclohexans zuzuerteilen ist.

1) Winterhalder Diss. Kiel 1922.

2) B. 30 900 (1897).

Addition Reactions of the Phosphorus Halides. VII. The Addition of Alkoxy and Aroxy Chlorophosphines to Carbonyl Compounds

By J. B. Conant, V. H. Wallingford and S. S. Gandhekar

[Reprinted from the Journal of the American Chemical Society,
Vol. XLV, No. 3. March, 1923.]

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

ADDITION REACTIONS OF THE PHOSPHORUS HALIDES. VII. THE ADDITION OF ALKOXY AND AROXY CHLOROPHOSPHINES TO CARBONYL COMPOUNDS

By J. B. CONANT, V. H. WALLINGFORD AND S. S. GANDHEKER

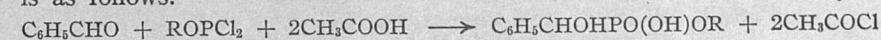
Received November 3, 1922

Introduction

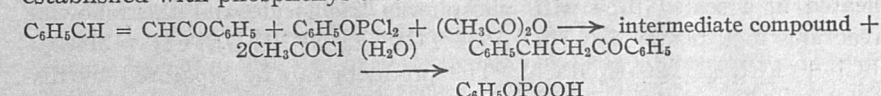
The previous papers of this series¹ have dealt with the 1,2 and 1,4 addition of phosphorus trichloride and its aryl derivatives, phosphenylchloride ($C_6H_5PCl_2$) and diphenylchlorophosphine. As a continuation of this work we have investigated the action of substances of the general type $ROPCl_2$ and $(RO)_2PCl$ on simple ketones and aldehydes and on an α,β unsaturated ketone. By carrying out the reaction in the usual manner in the presence of acetic acid or acetic anhydride we have prepared the mono- and di-esters of the phosphonic acids which are formed by the reaction of phosphorus trichloride with the corresponding aldehyde or ketone. This investigation completes the study of the various types of chlorophosphines in regard to their addition reactions with aldehydes, ketones and α,β unsaturated ketones. In general it may be said that phosphorus halides of the type $APCl_2$ and A_2PCl , where $A = R$ or RO , combine with carbonyl compounds in the same manner as phosphorus trichloride. As would be expected, compounds of the type A_3P do not

give this reaction. It is interesting to note that while phosphorus tribromide behaves in a similar manner to the trichloride,² no addition reaction could be brought about with the tri-iodide. This is undoubtedly connected with the fact that phosphorus tri-iodide, unlike the trichloride and tribromide, does not combine with a further molecule of halogen to form compounds of the type PI_3X_2 .

The addition of monophenoxy-, monomethoxy- and mono-ethoxydichlorophosphine to benzaldehyde was effected by bringing the reactants together in glacial acetic acid at room temperature; acetyl chloride was formed and, after pouring the material into water, the mono-esters were isolated as oils insoluble in water but soluble in sodium carbonate solution. Their structure was shown by hydrolysis to the well-known hydroxyphosphonic acid, $C_6H_5CHOHPO_3H_2$, which was isolated and identified as the aniline salt which has a sharp melting point. The general reaction is as follows.



The 1,4 addition of monophenoxy-dichlorophosphine to benzalacetophenone yielded the crystalline monophenyl ester previously prepared from the ketophosphonic acid.³ Somewhat better yields were obtained by using acetic anhydride instead of acetic acid; the mechanism of the reaction with this reagent is undoubtedly the same as that previously established with phenenyl chloride.^{1d}



Abnormal results were obtained on attempting to add ethoxy-dichlorophosphine to benzalacetophenone although normal results were obtained with benzaldehyde. Crystalline compounds containing phosphorus were obtained, but they could not be transformed into the ketophosphonic acid. It is hoped to investigate this reaction at some later time.

Diphenoxy-chlorophosphine

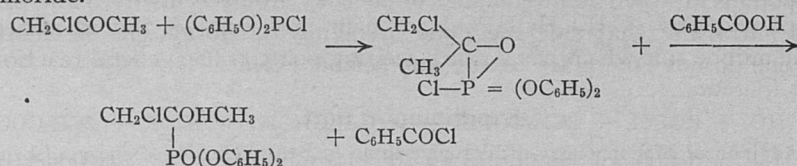
Diphenoxy-chlorophosphine was added to a number of aldehydes and ketones and gave crystalline diphenyl esters. The constitution of the ester formed from benzaldehyde was shown by hydrolysis, the known phosphonic acid being formed; the ester prepared from benzalacetophenone was identified by a mixed melting point with the ester previously prepared from the known ketophosphonic acid.³ Crystalline esters were formed by the reaction with benzaldehyde, acetone, methylethyl ketone, acetophenone and chloro-acetone. In the case of this last substance it was found impossible to obtain any reaction in acetic acid or acetic an-

² THIS JOURNAL, 43, 1713 (1921); PBr_3 also reacts in the usual way with C_6H_5CHO .

³ Ref. 1b, p. 839.

¹ THIS JOURNAL, (a) 39, 2679 (1917); (b) 42, 830, (c) 2337 (1920); (d) 43, 1665, (e) 1677, (f) 1928 (1921); (g) 44, 165 (1922).

hydride; however, by using benzoic acid and allowing the mixture to stand for several days at room temperature a low yield of the desired diphenyl ester was obtained. In the light of our previous work with benzophenone and phosphorus trichloride, a probable explanation of these results can be formulated. The speed of the primary addition reaction is very slow,⁴ and the diphenoxy-chlorophosphine is decomposed by the acetic acid or anhydride before it has reacted appreciably with the ketone. Benzoic acid, on the other hand, does not react with the phosphorus halide at room temperature and thus the addition reaction can proceed slowly when benzoic acid is present; as fast as the primary addition product is formed it reacts with the acid, producing the desired diphenyl ester and benzoyl chloride.⁵



Preparation of Diphenoxy-chlorophosphine

It was found convenient to prepare diphenoxy-chlorophosphine by a somewhat novel reaction. Triphenoxy-phosphine was prepared in the usual way from phenol and phosphorus trichloride; this substance was then heated in a sealed tube with phosphorus trichloride and the following reactions took place: $2(\text{C}_6\text{H}_5\text{O})_3\text{P} + \text{PCl}_3 \rightleftharpoons 3(\text{C}_6\text{H}_5\text{O})_2\text{PCl}$; $(\text{C}_6\text{H}_5\text{O})_2\text{PCl} + \text{PCl}_3 \rightleftharpoons 2\text{C}_6\text{H}_5\text{OPCl}_2$. The products can be separated by distillation. The following figures (the average of several experiments) indicate the effect of increasing the concentration of phosphorus trichloride.

TABLE I
REACTION BETWEEN TRIPHENOXY-PHOSPHINE AND PHOSPHORUS TRICHLORIDE AT 150° FOR 8 HOURS

Moles of PCl ₃ per mole of (C ₆ H ₅ O) ₃ P	Approximate percentages of products			
	PCl ₃	C ₆ H ₅ OPCl ₂	(C ₆ H ₅ O) ₂ PCl	(C ₆ H ₅ O) ₃ P
0.5	negligible	12	55	32
1.0	0.5	25	50	23
2.0	13	47	27	9

It is obvious that the results are such as would be expected if the two reversible reactions written above were involved; increasing the amounts of trichloride increases the conversion of the triphenoxy-phosphine into chlorophosphines. However, as the ratio of trichloride to phosphine is increased the yield of monophenoxy compound increases at the expense of

⁴ Unpublished work on the action of other phosphorus halides on α -chloro ketones indicates that the addition reaction proceeds with difficulty.

⁵ Compare Ref. 1f, p. 1929.

the diphenoxy-chlorophosphine. The diphenoxy compound is best prepared by using only 0.5 mole of phosphorus trichloride per mole of triphenoxy-chlorophosphine and using over again the recovered triphenoxy compound. The yields so obtained (90%, based on the material used up) were far superior to those we were able to obtain by the direct action of 3 moles of phenol and 1 of trichloride.⁶ Equilibrium is apparently reached at 150° in 8 hours as longer heating produced no appreciable change in the composition of the mixture. Essentially the same results were obtained at 110° (16 hours) and at 225° (8 hours). Similar reversible reactions have been found to occur when aryl arsines are heated with arsenic trichloride.⁷ It is interesting that this reaction should also take place with phosphorus compounds in which an interchange of phenoxy groups is involved and perhaps surprising that side reactions involving the formation of chlorobenzene do not take place to any appreciable extent.

Experimental Part

Addition of Monophenoxy-dichlorophosphine to Benzaldehyde.—Nine g. of benzaldehyde, 16.5 g. of monophenoxy-dichlorophosphine (b. p. 213–217°) and 15 g. of acetic acid were mixed and allowed to stand for 5 hours in a flask fitted with a calcium chloride tube. The fumes of acetyl chloride were noticed when the flask was opened from time to time. The mixture was poured into water and extracted with ether; the ether layer was in turn extracted with an aqueous solution of sodium carbonate and, on acidification of the aqueous solution, the monophenyl ester of the hydroxyphosphonic acid was obtained as an oil. The yield of dry oil was 20 g. or 90%; it slowly hardened on standing, but could not be obtained crystalline. Seven g. of the oil was hydrolyzed by boiling it for 5 hours with 15% hydrochloric acid under a return condenser. The solution was then extracted with ether to remove the phenol and any unchanged ester. On evaporation of the hydrochloric acid solution, 4 g. of somewhat impure hydroxybenzylphosphonic acid was obtained. This was dissolved in a little alcohol; the solution was diluted with ether and treated with a slight excess of aniline. The aniline salt of the hydroxyphosphonic acid separated as a white precipitate which, after recrystallization from alcohol, melted at 199° and was identified by a mixed melting point with a pure sample of the aniline salt of the hydroxyphosphonic acid.

Addition of Monomethoxy-dichlorophosphine to Benzaldehyde.—This reaction was carried out exactly as described above for the phenoxy compound. Ten g. of benzaldehyde and 12.5 g. of the monomethoxy-dichlorophosphine (b. p., 95–96°) yielded 7.5 g. of the monomethyl ester as an oil, insoluble in water but soluble in sodium carbonate solution. It could not be obtained crystalline. It was hydrolyzed by boiling with hydrochloric acid; 3.5 g. of the ester yielded 1.6 g. of crude hydroxyphosphonic acid and 1.9 g. of the aniline salt which was identified by a mixed melting point. The formation of methyl alcohol as the other product of hydrolysis was proved by the usual qualitative tests.

Addition of Ethoxy-dichlorophosphine to Benzaldehyde.—Five g. of benzaldehyde, 7 g. of ethoxy-dichlorophosphine (b. p., 117–118°) and 8 g. of acetic acid yielded, after the usual treatment, 9.3 g. of the mono-ethyl ester as an oil which could not be crystallized. It was converted into the hydroxyphosphonic acid by hydrolysis with hydro-

⁶ Noack, *Ann.*, **218**, 85 (1883).

⁷ Michaelis and Reese, *Ber.*, **15**, 2876 (1882).

chloric acid, ethyl alcohol being identified as the other product. The acid was identified as the aniline salt; 4.5 g. of pure aniline salt was obtained from 3.8 g. of the oily ester.

Addition of Monophenoxy-dichlorophosphine to Benzalacetophenone.—The addition to benzalacetophenone can be carried out in the presence of either acetic acid or acetic anhydride. The best results are obtained by working with the latter reagent. Five g. of benzalacetophenone, 4.7 g. of the chlorophosphine and 7.3 g. of acetic anhydride were mixed and allowed to stand for 2 hours; the temperature was then raised to 35° in the course of 5 hours and finally to 40° during 1 hour and then the mixture allowed to stand overnight at room temperature. It was then poured into water and the insoluble oil formed was dissolved in ether. The ethereal solution was extracted with sodium bicarbonate solution and this solution was then acidified. The monophenylester was thus precipitated as an oil which was dissolved in ether; after drying, the ethereal solution was evaporated and the product was obtained as a crystalline mass weighing 5.5 g. After 2 recrystallizations from alcohol, 1.3 g. of pure monophenyl ester was obtained which melted at 145–146°. It was identified as the monophenyl ester of α -phenyl- β -benzoyl-ethyl-phosphonic acid by a mixed-melting-point determination. About 2 g. of unchanged benzalacetophenone was recovered from the first ethereal solution showing that the initial reaction had been far from complete.

Diphenyl Ester of Hydroxybenzyl-phosphonic Acid, $C_6H_5CHOHPO(OC_6H_5)_2$.—To a mixture of 9.2 g. of diphenoxy-chlorophosphine (prepared as described below) and 3.9 g. of benzaldehyde was added 8 g. of acetic acid. The mixture became slightly warm and within an hour crystals began to separate. After standing overnight the crystals were filtered off, washed with ether and dried; they weighed 4.8 g. After recrystallization from methyl alcohol, the compound melted at 146°. It was insoluble in benzene, in water and in sodium carbonate solution. It was hydrolyzed to the hydroxyphosphonic acid by boiling it with hydrochloric acid and the acid was identified in the usual manner.

Analysis. Calc. for $C_{19}H_{17}O_4P$: P, 9.1. Found: 9.2.

Diphenyl Ester of α -Hydroxyisopropyl-phosphonic Acid, $(CH_3)_2COHPO(OC_6H_5)_2$.—Ten g. of diphenoxy-chlorophosphine was treated with 2.5 g. of acetone (a slight excess); heat was evolved during the mixing. Glacial acetic acid (6 cc.) was then added and a fairly rapid reaction took place, judged by the evolution of heat and formation of acetyl chloride. After standing for 12 hours, the mixture was poured into water, and the ester dissolved in ether. Evaporation of the ethereal solution yielded 13 g. of a pasty mass which was spread on a porous plate. After recrystallization of the resulting crystals from petroleum ether, 4.5 g. of the compound was obtained which melted at 113–114°.

Analysis. Calc. for $C_{15}H_{17}O_4P$: P, 10.6. Found: 10.8.

Acetyl Derivative of the Diphenyl Ester of α -Hydroxyisopropyl-phosphonic Acid, $(CH_3)_2C(OCOCH_3)PO(OC_6H_5)_2$.—The mother liquor from the crystallization of the diphenyl ester just described yielded on evaporation a small amount of a crystalline compound which melted at 71–73.5°. This was the acetyl derivative of the diphenyl ester formed by the action of the acetyl chloride during the reaction as the following experiment shows. One g. of diphenyl ester was allowed to stand overnight with acetyl chloride; there was thus obtained a substance which after recrystallization from petroleum ether melted at 72–72.5° and was identical with the compound just described.

Analysis. Calc. for $C_{17}H_{19}O_5P$: P, 9.3. Found: 9.3.

Diphenyl Ester of α -Hydroxy- α -methylpropyl-phosphonic Acid, $C_2H_5C(CH_3)(OH)PO(OC_6H_5)_2$.—Three g. of methylethyl ketone was mixed with 10 g. of diphenoxy-chlorophosphine and then 3 cc. of glacial acetic was added during 1 hour. The whole was allowed to stand for 2 days at room temperature when the mixture had become a

crystalline mass. The crystals were washed several times with water by decantation, filtered and washed with ether. Five g. of diphenyl ester was thus obtained which after crystallization from alcohol melted at 128.5°.

Analysis. Calc. for $C_{16}H_{19}O_4P$: P, 10.2. Found: 10.2.

Diphenyl Ester of α -Hydroxy- α -methylbenzyl-phosphonic Acid, $C_6H_5C(CH_3)(OH)PO(OC_6H_5)_2$.—A mixture of 5 g. of diphenoxy-chlorophosphine, 2.5 g. of acetophenone and 1.1 g. of glacial acetic acid was allowed to stand for 4 days at room temperature. At the end of this time the crystalline product was filtered from the reaction mixture, washed with ether and recrystallized from alcohol. The yield of crude ester was 4.5 g.; the compound melted at 143.5°.

Analysis. Calc. for $C_{20}H_{19}O_4P$: P, 8.8. Found: 8.9.

Diphenyl Ester of α -Hydroxy- α -methyl- β -chloro-ethyl-phosphonic Acid, $CH_3CIC(CH_3)(OH)PO(OC_6H_5)_2$.—Attempts to add diphenoxy-chlorophosphine to chloroacetone in the presence of acetic acid were without success. By using benzoic acid, however, the desired ester was obtained in a small yield. Five g. of chloroacetone, 14 g. of diphenoxy-chlorophosphine and 6.5 g. of benzoic acid were mixed and allowed to stand for 2 days; at the end of this time white cubic crystals were visible in the mixture. These crystals were collected and washed with ether; they weighed 1 g. and melted sharply at 119°.

Analyses. Calc. for $C_{16}H_{16}O_4PCl$: Cl, 10.9. Found: 10.4, 10.9.

Addition of Diphenoxy-chlorophosphine to Benzalacetophenone.—Two g. of diphenoxy-chlorophosphine and 2.3 g. of benzalacetophenone were mixed with 1 cc. of glacial acetic acid. The mixture was allowed to stand for 3 days, then poured into water and the solid material crystallized from ether. A solid (1.3 g.) melting at 116–117° was thus obtained; it was identified by a mixed melting point with the known diphenyl ester of α -phenyl- β -benzoyl-ethyl-phosphonic acid.

Attempts to add diphenoxy-chlorophosphine to acetaldehyde, enanthole, cinnamic aldehyde, methylisopropyl ketone and pinacolone resulted only in oily products which could not be obtained crystalline. Apparently in these cases, however, the addition reaction had proceeded at least to some extent.

The Preparation of Diphenoxy-chlorophosphine.—Triphenoxy-phosphine was prepared from phenol and phosphorus trichloride by the method of Noack; the yield of crude product which boiled above 210° at 10 mm. varied from 78 to 81%. This material, in 20g. portions, was heated with various proportions of phosphorus trichloride in sealed tubes in a furnace for a definite time. The tubes were opened and the contents distilled under atmospheric pressure until the thermometer recorded 150° and then at 10 mm. pressure. The fractions boiling at 130–150°, 130–210°, and 210–235° at 10 mm. were considered as $C_6H_5OPCl_2$, $(C_6H_5O)_2PCl$ and $(C_6H_5O)_3P$, respectively; the largest portion of each fraction boiled over a much narrower range (about 10°) than that indicated. Essentially the same equilibrium is attained at 110°, 150° and 225° as shown by the following percentages of $C_6H_5OPCl_2$ and $(C_6H_5O)_2PCl$ obtained with a mixture of 1 mole of triphenoxy-phosphine with 2 moles of trichloride: 110° for 16 hours, ratio of $C_6H_5OPCl_2$ to $(C_6H_5O)_2PCl$, 51:31; 150° for 8 hours, ratio 55:24; 225° for 8 hours, ratio 40:32. Other experiments showed that 12 to 14 hours was necessary to obtain equilibrium at 110° and only 6 or 7 hours at 150° or 225°. For preparative purposes, the most convenient temperature is 150° and the best proportions are 0.5 mole of trichloride to 1 of triphenoxy-phosphine; the unchanged triphenoxy-phosphine which is recovered is then used in another run. In a typical run which was made on a larger scale for preparative purposes, 76 g. of triphenoxy-phosphine and 13.7 g. of trichloride yielded 18 g. of crude $C_6H_5OPCl_2$, 38 g. of $(C_6H_5O)_2PCl$ (boiling over a 10° range) and

23.5 g. of $(C_6H_5O)_3P$. The yield of $(C_6H_5O)_2PCl$ based on the $(C_6H_5O)_3P$ used up is 90%.

Table I given in the introduction to this paper summarizes the average of some 10 final experiments and shows the effect of varying the proportions on the yields of the various products.

Summary

1. Monophenoxy-, monomethoxy- and mono-ethoxy-dichlorophosphine were added to benzaldehyde in the presence of acetic acid. Mono-esters of the hydroxyphosphonic acid were formed.

2. Monophenoxy- and monomethoxy-dichlorophosphine were similarly added to benzalacetophenone giving mono-esters of the ketophosphonic acid.

3. Diphenoxy-chlorophosphine was added to benzaldehyde, several ketones and benzalacetophenone, yielding diphenyl esters of the corresponding phosphonic acids.

4. Diphenoxy-chlorophosphine was prepared by heating mixtures of phosphorus trichloride and triphenoxy-phosphine in sealed tubes. An equilibrium is thus established; the composition of the equilibrium mixture varies with the proportion of the 2 reactants employed.

CAMBRIDGE 38, MASSACHUSETTS



Q. D. B. V.

RECTORE MAGNIFICO

GVERNERO WEDEMEYER

IVRIS VTRIVSQVE DOCTORE ET PROFESSORE PVBLICO ORDINARIO

EGO

EVALDUS WUEST

PHILOSOPHIAE DOCTOR ET PROFESSOR PVBLICVS ORDINARIVS PHILOSOPHORVM ORDINIS H.T. DECANVS

IN VIRVM ORNATISSIMVM OPTIMEQVE INSTRVCTVM

SETURAM SADASIV GANDHEKER

NELLORENSEM

EXHIBITA DISSERTATIONE QVAE INSCRIBITUR

Zur Stereochemie der Hexahydro-p-Xylidine

SPECIMINE ERVDITIONIS ET DILIGENTIAE IDONEO

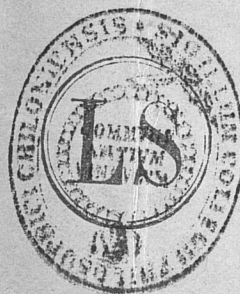
EXAMINE LEGITIMO RITE PERFVNCTVM

EX DECRETO ORDINIS PHILOSOPHORVM

SUMMOS IN PHILOSOPHIA HONORES DOCTORISQVE NOMEN
DIGNITATEM IURA

RITE COLLATA ESSE TESTOR

DATVM KILIAE HOLSATORVM DIE XIV MENSIS JVLII
ANNI MCMXXIV



Dr. Ewald Wüst
H. t. decanus.

KILIAE TYPIS EXPRESSERVNT SCHMIDT & KLAVNIG

UNIVERSITY OF ILLINOIS
DEPARTMENT OF CHEMISTRY
URBANA

9 10 23
Mi 15.11.24
October 9, 1924.

Mr. R. Littlehales, Esq., M. A.
Director of Public Instruction,
Madras, India.

Dear Sir:

Mr. S. S. Gandheker graduated with the degree of B. S. in chemistry at the University of Illinois in February, 1920. He was an earnest student of good ability and was faithful and reliable in his work. His thesis work was on a subject in organic chemistry, under the direction of Dr. Roger Adams. I consider him a man who is thoroly reliable, and with the additional training which he has received in Germany he should be very competent for a position as a teacher. I take pleasure in recommending him heartily for such a position.

Very sincerely,

W. A. Noyes

Director of Chemical Laboratory

ARTHUR MICHAEL
THEODORE WILLIAM RICHARDS
ELMER PETER KOHLER
GEORGE SHARP MAYMER
GREGORY PAUL BAXTER, Chairman
LAWRENCE JOSEPH HENDERSON
ARTHUR BECKET LAMB, Director
GEORGE SHANNON FORBES
GRINNELL JONES
JAMES BRYANT CONANT
NORRIS FOLGER HALL

HARVARD UNIVERSITY

DIVISION OF CHEMISTRY

Cambridge 38, Massachusetts, U.S.A.

October 14, 1924.

Mr. R. Littlehales,
Director of Public Instruction,
Madras, India

Dear Sir:

Dr. S. S. Gandheker studied organic chemistry under my direction at Harvard University for one year. He received the degree of A. M. from this University for this work.

Mr. Gandheker carried out a piece of original investigation in connection with a problem in theoretical organic chemistry. I found him to be a skillful and intelligent worker. His knowledge of organic chemistry and general chemistry was good and his method of working showed his ability as an original thinker.

Dr. Gandheker has since continued his work in organic chemistry at Kiel. With this additional training I am sure that he is well equipped to carry on research work and give university or school instruction in organic chemistry or any other branch of the subject. I feel certain that he will give a good account of himself in whatever capacity he is employed.

Sincerely yours,

James B. Conant
Assistant Professor of Chemistry

c/c

ROMANCE LANGUAGES

Nov. 5, 1924.

Mr. R. Littlecharles, M. A.
Director of Public Instruction,
Madras, India,

Dear Sir:

I take great pleasure in writing to you in regard to the qualifications and character of Mr. Seturam S. Gandheker, with whom I was acquainted when he was in the United States.

During the years of my contact with Mr. Gandheker he showed himself to be a very earnest student, always very thorough in his work and eager to gain an accurate knowledge of his specialty. His scholastic work was of a high character.

As a man, Mr. Gandheker has a pleasing personality and a character above reproach. I always found him very dependable and able to do what was requested of him. He is willing to help others with the heartiest cooperation. He possesses a determination to succeed in his chosen profession which should make him a valuable man to any institution which might employ him. A keen sense of humour is an estimable quality in the character of Mr. Gandheker, a quality sometimes wanting in the thorough scientific scholar that he is.

All in all, I consider Mr. Gandheker an unusually well equipped man in his specialty, and I am pleased to recommend him most heartily to anyone who may wish to employ him.

Yours sincerely,

Arthur R. Seymour

[Cno. 1805A]

(Law/Education)

13

Memo. 1805A-1 dt 17-5-24

The accompanying application from Mr. S.S. Gandhekar for an appointment in the D.S.S. ~~is forwarded~~ is forwarded to the D.P.O. who is requested to obtain and forward to Government, ~~the opinion of the local Selection Committee as to the applicant's fitness for the appointment~~ the opinion of the local Selection Committee as to the applicant's fitness for the appointment ~~to the post.~~

Sis
12/5/24

14.5.24

NH
12/5

The D.P.O.
(Link - appn in reg)
The record copy)

D.P.O. 25/6/24



May be submitted to M2 for approval

NH
12/5

14.5.24

to place appn -

But the D.P.O. has to send the application to the Central D.P.O.

M
The applicant passed B.A. & U.P. & does not study. See his line - this



REMINDER.



Department.

Education Branch

REPLY.

To

The Director of Public Instruction

To

The Secretary to Govt, Law (Edn) Deptt

The undersigned ~~has the honour to invite~~
is directed to invite
invites

attention to the communication noted in the
No. 18059-1, dated 7.5.24 margin and to
request that
this reminder may be returned at once with
information as to—

- (1) the stage at which the matter now is,
- (2) the date by which a reply may be expected
- (3) the circumstances which have caused the delay

2. It is requested that the reply to this
reminder may be sent not later than

Chandrasekharaiah
1876

Office Law Department
Station 21st George
Dated 21st June '24

Signature.
Under Secretary
Designation. Govt

SUBJECT.

Application of Mr. S. S.
Gandhekar for an
appointment in the
P.S.

The application of Mr
S.S. Gandhekar for an
appointment in the Indian
Educational Service is
~~we forwarded to~~
~~now before~~ the Selection
Committee and will be
submitted to Government
on receipt.

J.R. Sundaram
for Director of Public
Instruction

Trs
20.6.24



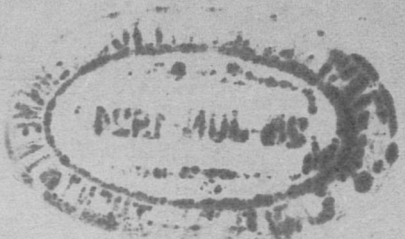
(Law/Edn)

The D.P.I. may be
reminded again a
month hence if no
reply is received
till then.

Trs
21/7/24

R
47

D.P. examined
on 6.8.24



14

O.F. 84

15

Law Department.
Education Branch.

L. Cu 3472A
17/9/24

REMINDER.

REPLY.
Application No. 16/24 d/11.9.24

To

The Director of
Public Instruction

To

The Secretary to Govt.,
Law (Edn) Deptt

The undersigned ~~has the honour to invite~~
is directed to invite
invites

attention to the communication noted in the
No. 1805A-1, dated 17.5.24 margin and to
request that
this reminder may be returned at once with
information as to

- (1) the stage at which the matter now is,
- (2) the date by which a reply may be expected and
- (3) the circumstances which have caused the delay.

2. It is requested that the reply to this
reminder may be sent not later than

At the Committee's request,
Mr S.S. Gandhekar
was requested to furnish
certain copies of
testimonials from
certain Professors
under whom he was
educated. A reply
will be submitted to
Government ~~after the~~ receipt
of the documents &
the consideration of the case
by the Committee

Accompanied by the Committee
Gg

Old

Office Law Department
Station Fort St George
Dated 6th Sept 24

Signature.
Under Secretary
Designation. B. J. S.

for Director of Public
Instruction

Recd
6.9.24

SUBJECT.

Application of Mr S.S.
Gandhekar for an
appointment in the
J. E. S.

MS
11.9.24

Recd
12.9.24

Note: The matter has not
been decided as
the fact of his not in
town at the time

further appointments to the
Indian Educational Service

File
12.8.24



G.F. 30-41,000-8-9-24.

LAW (EDUCATION) DEPARTMENT.

16

Received.....192 . Registered.....192 .



L. E. 2114
20/1/25

Mr. S.S. Gandhekar.

Application for appointment to the Indian Educational Service.

ENCLOSURES.
No.
.....
Spare copies.

Application No. 16/24.

Station M a d r a , Dated the 19th January 1925.

From (Name) R. Littlehailes Esquire. M.A..
(Designation) DIRECTOR OF PUBLIC INSTRUCTION.

To The Secretary to the Government of Madras,
LAW (EDUCATION) Department.

Sir,

In resubmitting herewith the application of Mr. S.S. Gandhekar forwarded with Memorandum No. 1805 A-1, dated 17th May 1924, I have the honour to state that the Selection Committee which considered his application and interviewed him on the 17th instant was not prepared to recommend his appointment to the Indian Educational Service.

I have the honour to be,
Sir,
Your most obedient servant,

Chd
for Director of Public Instruction.

(Law/Education) DEPARTMENT. 17

Date.	Initials.
-------	-----------

25/1/28

8/8

--	--

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118	119	120	121	122	123	124	125	126	127	128	129	130	131	132	133	134	135	136	137	138	139	140	141	142	143	144	145	146	147	148	149	150	151	152	153	154	155	156	157	158	159	160	161	162	163	164	165	166	167	168	169	170	171	172	173	174	175	176	177	178	179	180	181	182	183	184	185	186	187	188	189	190	191	192	193	194	195	196	197	198	199	200	201	202	203	204	205	206	207	208	209	210	211	212	213	214	215	216	217	218	219	220	221	222	223	224	225	226	227	228	229	230	231	232	233	234	235	236	237	238	239	240	241	242	243	244	245	246	247	248	249	250	251	252	253	254	255	256	257	258	259	260	261	262	263	264	265	266	267	268	269	270	271	272	273	274	275	276	277	278	279	280	281	282	283	284	285	286	287	288	289	290	291	292	293	294	295	296	297	298	299	300	301	302	303	304	305	306	307	308	309	310	311	312	313	314	315	316	317	318	319	320	321	322	323	324	325	326	327	328	329	330	331	332	333	334	335	336	337	338	339	340	341	342	343	344	345	346	347	348	349	350	351	352	353	354	355	356	357	358	359	360	361	362	363	364	365	366	367	368	369	370	371	372	373	374	375	376	377	378	379	380	381	382	383	384	385	386	387	388	389	390	391	392	393	394	395	396	397	398	399	400	401	402	403	404	405	406	407	408	409	410	411	412	413	414	415	416	417	418	419	420	421	422	423	424	425	426	427	428	429	430	431	432	433	434	435	436	437	438	439	440	441	442	443	444	445	446	447	448	449	450	451	452	453	454	455	456	457	458	459	460	461	462	463	464	465	466	467	468	469	470	471	472	473	474	475	476	477	478	479	480	481	482	483	484	485	486	487	488	489	490	491	492	493	494	495	496	497	498	499	500	501	502	503	504	505	506	507	508	509	510	511	512	513	514	515	516	517	518	519	520	521	522	523	524	5
---	---	---	---	---	---	---	---	---	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	---

Sandhekar, Mr J.S.

Application for
appointment to the I. E. S. —
not entertained

READ AGAIN G.O. No., dated 192 ..

” ” ” ” ” 192 .

READ ALSO:—

C. No. 1805 A From the 2638 A, No. 124, dated 192.

” ” ” ” ” ” 192

” ” ” ” 192

ORDER.

Mis

No. 142 dated 30-1- 1925

The Government are unable to recommend the inclusion of the name of Mr S. S. Ganshekar in the list of candidates eligible for appointment to the Indian Educational Service.

90

DW/ky 30/1

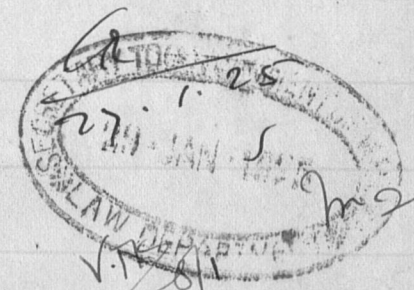
This
2.6.25

✓
Per S. S. Gaudhekar
40 W. R. R. Y. Sadhanika Rao Avasal B. B. B.

(copy to the D. J. Maynard farm)

(with ref. to his

Letter Appln no
16/24 of 19.1.25)



8
29/25

(containing 3/10)

102 100 100 100

100 100 100 100

100 100 100 100

100 100 100 100

A 208
A 208
A 208
A 208

100

When given for copying—
When copied—
When examined—
When signed—

192

READ AGAIN G.O. No.
192

DATED

CURRENT No.

ENCLOSURES TO G. No.

ORDER OF GOVERNMENT ..

.. A A A A A A A

LETTER OF GOVERNMENT.

STATEMENT WITH DITTO.

PAPERS NOT FILED OF, BEING MEANT FOR DESPATCH
IN ORIGINAL.

N.B.—

- A = Copy in full.
- B = Not to be copied.
- P = Copy abstract only.
- Q = Copy heading only.