Continued elution with chloroform produced 321 mg of an oil which consisted predominantly of 2-hydroxylmethyl-2-methyl-1-tetralone (**6**) as evidenced by infrared and nmr spectra and trimethylsilanation and gas chromatographic analysis.

Rearrangement of *threo*-Epoxy Alcohol 5. A. Reaction with Boron Trifluoride Etherate in Methylene Chloride. Treatment of 196 mg (1.03 mmole) of the *threo*-epoxy alcohol **5** with boron trifluoride etherate in methylene chloride by the same procedure as described above for the *erythro* isomer **4** afforded 180 mg of a pale yellow oil. The infrared spectrum of this material contained carbonyl bands at 1691 and 1725 cm^{-1}, with the latter the more intense. Trimethylsilanation by the same procedure described above followed by gas chromatography indicated the presence of only two components with retention times of 17.1 (major) and 20.8 min (minor) in a ratio of 89.6:10.4 by integration of peak areas. Distillation provided the mixture of keto trimethylsilyl ethers **19** and **20** as a colorless oil, bp 80–84° (0.03 mm).

Anal. Calcd for $C_{15}H_{22}O_2Si$: C, 68.65; H, 8.45. Found: C, 68.57; H, 8.42.

B. Reaction with Acidic Alumina. The *threo* isomer **5** was rearranged on treatment with acidic alumina under exactly the same conditions as described above for the *erythro* isomer **4**. Concentration of the benzene solution afforded 64 mg of a pale yellow oil whose infrared spectrum indicated a single carbonyl band at 1725 cm^{-1}. Examination of the gas chromatogram of the trimethylsilanated material indicated the presence of three components with retention times of 9.3, 16.8, and 21.1 min. These peaks had planimetrically integrated ratios of 9:9:1 and were assigned the structures **22**, **16** + **19**, and **20**, respectively, by comparison with authentic samples. The position of the second peak (**16** and **19**) is only approximate since a mixture of these two compounds appears as a single nonsymmetric peak whose maximum depends on the ratio of the two components. For analytical purposes the entire peak is integrated and no effort was made to determine the ratio of **16** to **19**, although in all cases the deformylation product **16** was present in large excess.

When the rearrangement was carried out for a period of 16 hr employing 950 mg (5 mmoles) of the *threo* isomer and 5 g of alumina in 100 ml of benzene, filtration and evaporation of the solvent left 645 mg of a pale yellow oil which on distillation yielded 227 mg of 1-methyl-2-tetralone (**16**) as a colorless oil, bp 136–140° (15 mm) (lit.[20] bp 138–142° (20 mm)). The infrared and nmr spectra of the distillate were identical with that of an authentic sample.[20] The semicarbazone crystallized from ethanol had mp 189–193° (lit.[21] mp 177–178 and 200–203°). The melting point was not depressed on admixture with an authentic sample.[21]

***erythro*-1-Methyl-1-(1′-trimethylsilanoxyindanyl)oxirane (21).** To 100 mg (0.53 mmole) of *erythro*-epoxy alcohol **4** in a 5-ml flask was added a freshly made solution of 0.2 ml of hexamethyldisilazane and 0.1 ml of trimethylchlorosilazane in 1.0 ml of pyridine and the flask was stoppered and allowed to stand for 30 min at room temperature with occasional shaking. The crude reaction mixture was then concentrated under reduced pressure, triturated with methylene chloride, filtered, and reconcentrated to leave 114 mg of the trimethylsilyl ether **23** as a colorless oil. The material eluted as a symmetrical peak with a retention time of 8.8 min. Short-path distillation provided an analytical sample: bp 78–80° (0.03 mm); $n^{25}\mathrm{D}$ 1.5004.

Anal. Calcd for $C_{15}H_{22}O_2Si$: C, 68.65; H, 8.45. Found: C, 68.74; H, 8.41.

***threo*-1-Methyl-1-(1′-trimethylsilanoxyindanyl)oxirane (22).** Application of the above described trimethylsilanation procedure to 100 mg (0.53 mmole) of the epoxy alcohol **5** produced 110 mg of crude trimethylsilyl ether **22**. The ether was homogeneous on gas chromatographic analysis and had a retention time of 9.0 min. Short-path distillation provided the pure trimethylsilyl ether **22** as a colorless oil: bp 76–78° (0.03 mm); $n^{25}\mathrm{D}$ 1.5024.

Anal. Calcd for $C_{15}H_{22}O_2Si$: C, 68.65; H, 8.45. Found: C, 68.64; H, 8.38.

Chemical Shift of Hydroxyl Protons. The data exhibited in Figure 2 were obtained by the procedure of Ouellette.[8] The Varian A-60 spectrometer was equipped with a V-6020 closed-loop water circulator and operated at probe temperature of 45°. The samples were prepared gravimetrically. The chemical shifts were measured after the sample had equilibrated to probe temperature with an average value of five to ten scans for each concentration. Deviations are less than ±0.5 cps.

Acknowledgment. The authors wish to thank Mr. W. S. Anderson and Mrs. Leslie Lynch of the Air Force Rocket Propulsion Laboratory for the high dilution infrared spectra. We also wish to express our appreciation to Captain Jack Penick and Dr. John Sharp for timely suggestions.

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(20) G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrell, *J. Am. Chem. Soc.*, **85**, 207 (1963).

(21) H. Hock, S. Lang, and G. Knauel, *Chem. Ber.*, **83**, 227 (1950).

A Novel Rearrangement of Some Phenoxyphosphonium Salts[1]

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Contribution from the Department of Chemistry, Rutgers, The State University, New Brunswick, New Jersey. Received July 27, 1967

Abstract: Treatment of tris(diethylamino)phenoxyphosphonium chloride (Ia) and tris(diethylamino)-*p*-methoxyphenoxyphosphonium chloride (IIa) with lithium diethylamide in benzene–hexane led to the rearranged betaines (III and VI). The structures of these materials were demonstrated by alternate syntheses of derivatives of them. Treatment of the hexafluorophosphate (Ib) in benzene–hexane and hexane alone with lithium diethylamide yielded III in the benzene–hexane reaction; however, in hexane alone, N,N-diethylaniline and tris(diethylamino)phosphine oxide were formed along with III. The amine and oxide probably arise by benzyne formation. The mechanism of the reaction is discussed.

The preparation and chemistry of pentasubstituted phosphorus compounds is of considerable interest from both the theoretical and practical points of view.[2] Compounds with five nitrogens bonded to phosphorus are not known, although some compounds with three nitrogens and two oxygens bonded to phosphorus have been prepared recently.[3]

A possible route to pentadialkylaminophosphoranes involves preparation of a tetrakis(dialkylamino)phos-

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[1] This research has been supported by the National Science Foundation under NSF GP 4997X.

[2] (a) F. Ramirez, *Bull. Soc. Chim. France*, 2443 (1966); (b) F. Ramirez, *Pure Appl. Chem.*, **9**, 337 (1964); (c) R. F. Hudson, "Structure and Mechanism in Organo-Phosphorus Chemistry," Academic Press Inc., New York, N. Y., 1965, Chapter 3.

[3] F. Ramirez, A. V. Patwardhan, and C. P. Smith, *J. Am. Chem. Soc.*, **87**, 4973 (1965).

phonium salt which could then be allowed to react with a dialkylamide ion. Interestingly reaction of tris(dialkylamino)phosphines with N-chlorodialkylamines did not yield the expected tetrakis (dialkylamino)phosphonium chlorides.[4] The results of this study indicated that the reaction proceeded by nucleophilic displacement on halogen to give a tris(dialkylamino)chlorophosphonium dialkylamide ion pair which underwent further reaction without the production of the desired salt.

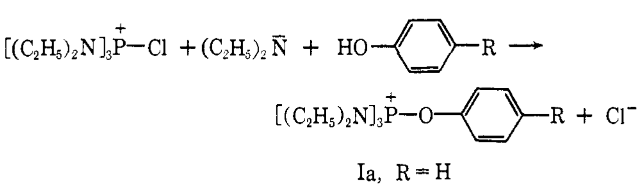
$$(R_2N)_3P + R_2N{-}Cl \longrightarrow (R_2N)_3\overset{+}{P}{-}Cl + R_2N^-$$

This reaction involves reversal of the initial displacement reaction and subsequent decomposition of the N-chlorodialkylamine by amide ion.

It was hoped that replacement of the halogen by phenoxy would lead to a salt which would react with dialkylamide ion to give a tetrakis(dialkylamino)phosphonium cation. Preparation of such salts has now been accomplished and it is the purpose of this report to describe their reactions with dialkylamide ions.

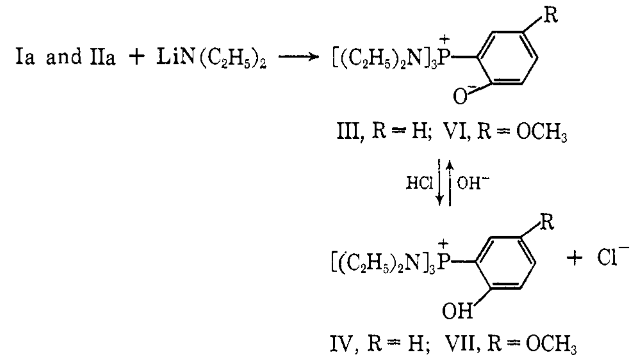
Results and Discussion

The phenoxyphosphonium salts, Ia and IIa, were prepared by allowing the appropriate phenol to react with the initial reaction product of the tris(dialkylamino)phosphine and the N-chlorodialkylamine. The salts were extremely hygroscopic and were most easily characterized as the corresponding hexafluorophosphates, Ib and IIb, which were much less hygroscopic and could be crystallized without difficulty. The chlorides, Ia and IIa, usually contained some phenol or *p*-methoxyphenol as contaminents. These could not be removed easily from the chlorides, but they were not present in the hexafluorophosphates.



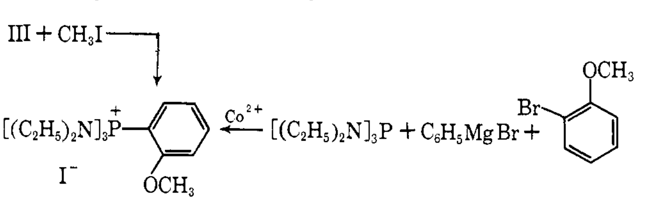
Ia, R = H
IIa, R = OCH$_3$

Reaction of Ia with lithium diethylamide in benzene–hexane at room temperature proceeded smoothly with the production of a red solution. The product of the reaction, III, showed typical absorptions in the nmr for N-(CH$_2$CH$_3$)$_2$ groups attached to phosphorus. Aromatic absorptions were also present and these could not be removed by a variety of purification techniques. It seemed apparent that tetrakis(diethylamino)phosphonium cation was not the product and that the phenoxy group was still present. Of the possible structures, III seemed to be reasonable and this structure is favored on the basis of several pieces of evidence. Treatment of III with hydrochloric acid yielded a hydrochloride, IV, which could be converted back into III with a strongly basic ion-exchange resin. Reaction of III with methyl iodide afforded the iodide, Va, which was most conveniently characterized by conversion to the hexafluorophosphate, Vb. This same material was obtained by condensing tris(diethylamino)phosphine with *o*-bromoanisole in the presence of phenylmagnesium bromide and cobalt chloride. This condensation reaction has been studied in detail by Horner and Hoffmann[5] and the structural assignment is in accord with their results.



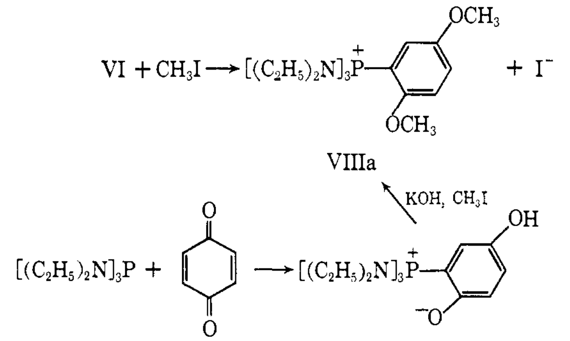
III, R = H; VI, R = OCH$_3$

IV, R = H; VII, R = OCH$_3$



Va

A similar reaction of IIa with lithium diethylamide yielded a betaine whose structure has been assigned as VI. The evidence for this structure follows from the nmr spectrum and chemical properties along with the following conversions. Reaction of VI with methyl iodide provided VIIIa. Condensation of tris(diethylamino)phosphine with *p*-benzoquinone gave the adduct, IX. The structure of this material is assigned on the basis of the studies of Ramirez and Dershowitz,[6] who showed that triphenylphosphine condenses with *p*-benzoquinone to give an adduct whose structure is entirely analogous to that of IX. Treatment of IX with methyl iodide and potassium hydroxide yielded VIIIa. Conversion of the two salts prepared by the different routes into the hexafluorophosphates, VIIIb, gave materials which were identical in all respects. The structural assignments for III and VI are based then on these alternate methods of preparation and the properties of the rearrangement products.



VIIIa

IX

It is of interest to consider the mechanism for the production of these materials. The first step undoubtedly involves hydrogen abstraction by amide ion to give X and XI (Scheme I). The abstraction is assisted by

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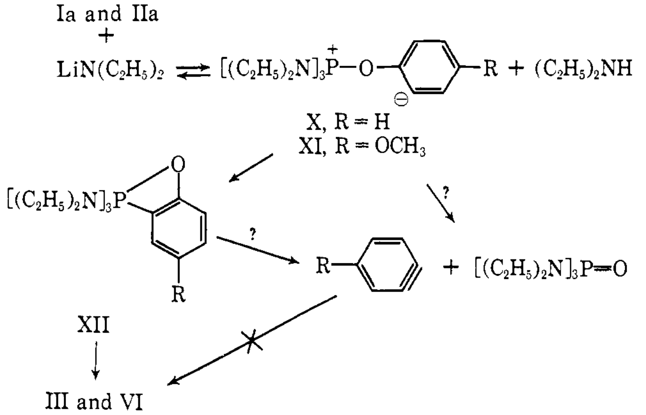
[4] (a) S. R. Jain, L. K. Krannich, R. E. Highsmith, and H. G. Sisler, *Inorg. Chem.*, **6**, 1058 (1967); (b) D. B. Denney and S. Felton, in preparation.

[5] L. Horner and H. Hoffmann, *Ber.*, **91**, 50 (1958).

[6] F. Ramirez and S. Dershowitz, *J. Am. Chem. Soc.*, **78**, 5614 (1956).

Scheme I



the positive charge which acidifies the *ortho* protons on the aromatic ring.[7] Two paths for the final production of III and VI need consideration. The first involves dissociation into a benzyne and tris(diethylamino)phosphine oxide. This is not believed to be the path for the production of rearranged product for the following reasons: (1) recombination of the methoxybenzyne from IIa should lead to two betaines rather than one[8] (no evidence for an isomeric betaine was ever obtained), and (2) production of the methoxybenzyne by reaction of *p*-bromoanisole with lithium diethylamide in the presence of tris(dimethylamino)phosphine oxide did not yield any betaine.

Evidence for the production of benzyne during the reaction of Ia was obtained when hexane was substituted as solvent for the benzene–hexane solvent system which was normally used. Under these conditions tris(diethylamino)phosphine oxide was formed in considerably greater amounts than in the mixed solvent system. The possible dual mode of decomposition has been studied in greater detail. Reaction of Ib with lithium diethylamide in benzene–hexane (8:1) and in hexane alone led to substantially different product ratios. The product from the benzene–hexane was essentially all betaine, III, while the hexane reaction yielded N,N-diethylaniline, tris(diethylamino)phosphine oxide, and III. The latter two substances were formed in a ratio of 2:3. It appears therefore that the intermediate ion, X, can undergo two modes of reaction, one of which leads to benzyne and the other to rearranged product.

The rearrangement reaction most probably proceeds through an intermediate or transition state XII. This species might also decompose to benzyne and phosphine oxide as well as opening up to the betaines. Similar intermediates must be involved in the conversion of certain phosphoranes into acetylenes and phosphine oxides.[9]

The lack of attack by lithium diethylamide on phosphorus can be due to a number of factors. It is clear that steric and electronic factors tend to stabilize phosphonium salts with dialkylamino groups bonded to phosphorus and thus when alternate reaction paths are available they often become the favored mode of reaction.

Experimental Section[10]

Preparation of Tris(diethylamino)phenoxyphosphonium Chloride (Ia). Tris(diethylamino)phosphine (9.88 g, 0.04 mole) was added to a stirred ice-cold solution of 0.043 mole of N-chlorodiethylamine[11] in *ca.* 50 ml of hexane. A white cloudy suspension formed and to this there was added 3.76 g (0.04 mole) of phenol. The solution warmed and after 10 min a dull gray viscous oil had formed. After 16 hr in a refrigerator a yellow-orange oil had separated. The hexane was decanted and the oil was washed with two 50-ml portions of dry ether. The oil was heated at 75° (1 mm) for 2 hr. Titration with perchloric acid in acetic acid in the presence of mercuric acetate[12] gave an equivalent weight of 387 (theory for Ia is 375). This material was dried at 150° (0.1 mm) to give 13.2 g (87%) of a gray-white solid, equivalent weight 376. The salt is extremely hygroscopic and difficult to recover in crystalline form from solvents. The nmr spectrum in methylene chloride showed a triplet at 1.18 ppm (J = 7 cps), an octet at 3.25 ppm (J_{PH} = 11.5 cps), and an absorption at 7.05–7.67 ppm. The relative areas under these absorptions were 18:12:5, respectively. The ^{31}P nmr spectrum had one absorption at −34.5 ppm.

Treatment of the supernatent hexane layer with anhydrous hydrogen chloride precipitated 5.80 g of material whose infrared spectrum was identical with that of diethylamine hydrochloride.

Salt Ia (0.80 g in 10 ml of acetone) was added to a solution of 0.40 g (0.0022 mole) of potassium hexafluorophosphate in 20 ml of acetone. The solution was filtered and the acetone was concentrated to a paste. Trituration of this paste with dry ether caused crystallization. The solid was crystallized twice from ethanol to give material, mp 88–89°.

Anal. Calcd for $C_{18}H_{35}F_6N_3OP_2$: C, 44.53; H, 7.21. Found: C, 44.32; H, 7.05.

The nmr spectrum in acetonitrile showed a triplet at 1.12 ppm (J = 7 cps), an octet at 3.21 ppm (J_{PH} = 11.5 cps), and absorption between 7.05 and 7.57 ppm. The relative areas were 18:12:5.

Preparation of Tris(diethylamino)-*p*-methoxyphenoxyphosphonium Chloride (II). A 90% yield of an oil, equivalent weight 413, theory 405.5, was obtained by the above procedure except *p*-methoxyphenol was substituted for phenol and N-chlorodimethylamine was use in place of N-chlorodiethylamine. The oil did not crystallize. The nmr spectrum in methylene chloride had a triplet at 1.15 ppm (J = 7 cps), an octet at 3.22 ppm (J = 11.5 cps), a singlet at 3.79 ppm, a singlet at 3.68 ppm, and complex absorption between 6.52 and 7.36 ppm. The absorptions at 1.15, 3.22, and 3.79 ppm are due to the salt whereas the absorption at 3.68 ppm is due to the -OCH$_3$ of unreacted *p*-methoxyphenol.

The oil (3.4 g) was dissolved in 50 ml of water and this solution was treated with a saturated aqueous solution of potassium hexafluorophosphate. The gummy precipitate was recrystallized twice from ethanol to yield 2.2 g of white crystals, mp 88–90°. The nmr spectrum in methylene chloride had a triplet at 1.17 ppm (J = 7 cps), an octet at 3.20 ppm (J_{PH} = 11.0 cps), and a singlet at 7.05 ppm. The relative areas were 18:12:3:4. No *p*-methoxyphenol could be detected as a contaminant.

Rearrangement of Ia. A suspension of lithium diethylamide in benzene–hexane was prepared by adding 40 ml of 1.6 *M* butyllithium in hexane to 100 ml of dry benzene followed by the slow addition of 9 ml of of diethylamine. To this was added 11.18 g (0.0297 mole) of Ia. A slightly exothermic reaction took place and the solution underwent a series of color changes and it finally became red. After 16 hr of vigorous stirring at room temperature the reaction mixture was light orange and it contained a white precipitate. The reaction mixture was concentrated to a dark viscous oil which was dissolved in 50 ml of benzene. The benzene solution was washed with 50 ml of water and concentrated to yield 9.5 g of an orange-yellow paste. The nmr spectrum of the crude material indicated that tris(diethylamino)phosphine oxide was present, *ca.* 15%, along with a new material, III. Purification was most

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(7) R. Huisgen, "Organometallic Chemistry," H. Zeiss, Ed., Reinhold Publishing Corp., New York, N. Y., 1960, Chapter 2.

(8) H. Gilman and R. H. Kyle [*J. Am. Chem. Soc.*, **70**, 3945 (1948)] have shown that *p*-bromoanisole with lithium diethylamide in ether gave a mixture of *p*- and *m*-methoxy-N,N-diethylanilines.

(9) S. T. D. Gough and S. Trippett, *J. Chem. Soc.*, 2333 (1962).

(10) The proton nuclear magnetic resonance spectra were recorded with a Varian Associates A-60 spectrometer at 60 MHz. The spectra were run in a variety of solvents with tetramethylsilane as an internal standard. The chemical shifts are reported in parts per million relative to tetramethylsilane. The phosphorus-31 nmr spectra were recorded at 40.5 MHz with a Varian Associates HA-100 spectrometer. The chemical shifts are reported in parts per million with 85% phosphoric acid as an external standard. Infrared spectra were recorded with Perkin-Elmer Models 21 and 137 and a Beckman IR-5A instrument. Melting points are uncorrected.

(11) G. H. Coleman, *J. Am. Chem. Soc.*, **55**, 3001 (1933).

(12) S. T. Ross and D. B. Denney, *Anal. Chem.*, **32**, 1896 (1960).

easily effected by conversion to the hydrochloride, IV. The orange-yellow paste was suspended in 100 ml of water and treated with concentrated hydrochloric acid until the mixture remained acidic. The aqueous solution was extracted with four 30-ml portions of methylene chloride. The methylene chloride was concentrated to yield a paste which gave 8.2 g (73%) of crystalline material on washing with ether. Titration gave an equivalent weight of 381 (theory of IV is 375.5). The material could be further purified by recrystallization from methylene chloride–tetrahydrofuran, mp 184.5–185.5°.

Anal. Calcd for $C_{18}H_{35}N_3OPCl$: C, 57.52; H, 9.32. Found: C, 57.04; H, 9.25.

The nmr spectrum showed a triplet at 1.20 ppm (J = 7 cps), an octet at 3.18 ppm (J_{PH} = 11 cps), and a broad aromatic absorption between 6.79 and 7.84 ppm. Integration gave relative areas 18:12:4:3. The hydrochloride was converted into the hexafluorophosphate by reaction of IV with potassium hexafluorophosphate in acetone. It had mp 157–159° after crystallization from water. The nmr spectrum was identical with that of IV except for slight differences in chemical shifts.

Preparation of III from IV. Salt IV (8.22 g, 0.00215 mole) was dissolved in 100 ml of water and passed through a column of Dowex 1-X8 ion-exchange resin in the basic form. The aqueous solution was evaporated to a light tan solid which was washed with 75 ml of petroleum ether (bp 30–60°). The dried product, mp 119–122°, 5.75 g (79%), gave an equivalent weight of 339 (theory 339) on titration. More of the betaine was obtained from the petroleum ether on standing for a few days. The nmr spectrum in methylene chloride showed a triplet at 1.12 ppm (J = 7 cps), an octet at 3.21 ppm (J_{PH} = 11 cps), and a broad absorption band at 5.95–7.33 ppm. The areas under these absorptions were in the ratio 18:12:4. The betaine was soluble in carbon tetrachloride, tetrahydrofuran, and benzene and gave a blue fluorescence in solution. The betaine was very difficult to crystallize.

Reaction of III with Methyl Iodide. The betaine (III), 1.0 g (0.00295 mole), was dissolved in 50 ml of methylene chloride. Methyl iodide (3.0 g) was added and the reaction mixture was allowed to stand at room temperature for 2 days. The methylene chloride solution was concentrated to half its volume and 50 ml of diethyl ether was added. An oil separated which could not be crystallized. The nmr spectrum indicated that a methyl ether was present. The oil was dissolved in 50 ml of water and this solution was treated with a saturated aqueous solution of potassium hexafluorophosphate until precipitation ceased. A white solid (1.51 g) was isolated and recrystallized twice from ethanol: yield, 0.98 g; mp 292–293°.

Anal. Calcd for $C_{19}H_{37}F_6N_3OP_2$: C, 45.70; H, 7.41. Found: C, 45.28; H, 7.41.

The nmr spectrum in methylene chloride showed a triplet at 1.17 ppm (J = 7 cps), an octet at 3.18 ppm (J_{PH} = 11 cps), a singlet at 3.96 ppm ($-OCH_3$), and a broad absorption between 6.98 and 7.86 ppm. The ratio of areas was 18:12:3:4.

Preparation of IV from Tris(diethylamino)phosphine and *o*-Bromoanisole. A vigorously stirred mixture of 12.35 g (0.050 mole) of tris(diethylamino)phosphine, 18.7 g (0.100 mole) of *o*-bromoanisole, and 0.650 g (0.005 mole) of anhydrous cobalt chloride in 75 ml of ether was treated with 33 ml (0.05 mole) of phenylmagnesium bromide in ether. The mixture was stirred for 16 hr and then treated with 100 ml of 2 *N* hydrochloric acid. The two-phase mixture was filtered and the aqueous solution was treated with 16 g of sodium iodide. The aqueous solution was extracted with four 40-ml portions of methylene chloride. Concentration afforded a brown oily paste, 5.6 g (23% based on phosphine). This material could not be crystallized. An aqueous solution was treated with a saturated solution of potassium hexafluorophosphate. The solid which formed had nmr and infrared spectra identical with the compound obtained above. The melting point after three crystallizations was 290–293°. There was no depression of the melting point on admixture with the sample obtained from the rearrangement reaction.

Anal. Calcd for $C_{19}H_{37}F_6N_3OP_2$: C, 45.70; H, 7.41. Found: C, 45.56; H, 7.48.

Rearrangement of II. Tris(diethylamino)*p*-methoxyphenoxyphosphonium chloride (13.0 g, 0.032 mole) was added slowly with vigorous stirring to 0.064 mole of lithium diethylamide in benzene. After 16 hr the reaction mixture was orange-red and a gummy precipitate had formed. The mixture was washed with 50 ml of water and the benzene was concentrated to yield a dark orange viscous oil with a blue fluorescence. The yield of this material was 11.0 g (93%). Titration gave an equivalent weight of 421 (theory 369). The nmr spectrum showed some *p*-methoxyphenol was present along with a new compound. Crystallization occurred on standing and trituration with ether gave material, mp 120–122°.

The oil (2.0 g) was suspended in 50 ml of water and treated with concentrated hydrochloric acid. The acidic solution was extracted with three 30-ml portions of chloroform. Concentration of the chloroform extracts yielded an oil which was triturated with dry ether to give a solid, 1.9 g (96%). This material was recrystallized from diethyl ether–tetrahydrofuran to give 1.51 g (76%) of a white solid, mp 155–156°. The nmr spectrum in methylene chloride had a triplet at 1.19 ppm (J = 7 cps), an octet at 3.21 ppm (J_{PH} = 11 cps), a singlet at 3.72 ppm ($-OCH_3$), and broad aromatic absorptions at 6.58–7.81 ppm. The integrated areas were 18:12:3:3.

Anal. Calcd for $C_{19}H_{37}ClN_3O_2P$: C, 56.22; H, 9.14. Found: C, 57.19; H, 9.35.

Reaction of VI with Methyl Iodide. A solution of 4.0 g of VI in 75 ml of benzene was treated with 10 ml of methyl iodide. The purple-blue fluorescence disappeared. The reaction mixture warmed and an oil formed. The reaction mixture was heated under reflux for 1 hr and then concentrated to a dark oil which on trituration gave a brown solid, 4.6 g (95%). Titration gave an equivalent weight of 555 (theory 511). This material was recrystallized from tetrahydrofuran and diglyme to give material, mp 116–117°. The nmr spectrum in methylene chloride exhibited a triplet at 1.12 ppm (J = 7 cps), an octet at 3.19 ppm (J_{PH} = 11 cps), a singlet at 3.85 ppm, and a singlet at 3.95 ppm and aromatic absorption. The relative areas were 18:12:3:3:3.

Anal. Calcd for $C_{20}H_{39}IN_3O_2P$: C, 46.96; H, 7.63. Found: C, 46.13; H, 7.58.

The salt (VIII) was converted into the hexafluorophosphate which after two recrystallizations from ethanol had mp 195–196°. The nmr spectrum was essentially the same as that of VIII except for small differences in chemical shift.

Anal. Calcd for $C_{20}H_{39}F_6N_3O_2P$: C, 45.37; H, 7.37. Found: C, 46.08; H, 7.67.

Condensation of Tris(diethylamino)phosphine with *p*-Benzoquinone. Tris(diethylamino)phosphine (10.9 g, 0.044 mole) in 30 ml of ice-cold benzene was treated dropwise with 3.3 g (0.031 mole) of *p*-benzoquinone in 70 ml of benzene. Addition of each drop gave a bright red color. After the addition, the reaction mixture was black-red and a viscous oil had formed. The benzene was evaporated to give a brown solid which was triturated with ether to yield 10.0 g (95%) of material which was triturated with tetrahydrofuran and acetone. This treatment gave a white solid, mp 222–226° dec. Titration gave an equivalent weight of 357 (theory 355). The product was very insoluble in common solvents. No effective solvent was found for crystallization.

Reaction of IX with Methyl Iodide and Potassium Hydroxide. A solution of 3.00 g (0.00846 mole) of IX, 0.474 g (0.00846 mole) of potassium hydroxide, and 5 ml of methyl iodide was stirred in the dark for 3 weeks. The reaction mixture was concentrated and the resulting paste was extracted with 50 ml of methylene chloride. The methylene chloride was evaporated and the residue was converted into the hexafluorophosphate derivative. Two crystallizations from ethanol gave material, mp 194–195°, no depression on admixture with the material obtained from VIII. The nmr and infrared spectra of the two samples were identical.

Anal. Calcd for $C_{20}H_{39}F_6N_3O_2P_2$: C, 45.37; H, 7.37. Found: C, 45.82; H, 7.89.

Rearrangement of Ib in Benzene–Hexane. A suspension of 0.016 mole of lithium diethylamide in 80 ml of benzene and 10 ml of hexane was allowed to react with 3.00 g (0.0062 mole) of Ib. After 16 hr of stirring at room temperature, the reaction mixture was filtered and the solid was washed with several portions of benzene. The combined benzene solutions were concentrated to a gummy yellow-orange product, 3.10 g. A portion of this material was dissolved in a small amount of benzene and investigated by glpc on a 6-ft silicone grease column at 192° with a helium flow of 60 ml/min. Two components were present in very small amounts. Their retention times were the same as those of N,N-diethylaniline and tris(diethylamino)phosphine oxide and the peaks were augmented by the addition of these two materials.

The remaining material was treated with concentrated hydrochloric acid to give IVa, 2.02 g. The infrared spectrum was identical with that obtained before. Titration indicated a purity of 96% and thus an 84% yield was obtained.

Rearrangement of Ib in Hexane. The quantities used above were used in this experiment except 80 ml of hexane was substituted for the benzene. Both N,N-diethylaniline and tris(diethylamino)phosphine oxide were present. The ^{31}P nmr spectrum showed absorptions at −24.1 ppm, tris(diethylamino)phosphine oxide, and −57.7 ppm, III. The integrated proton nmr spectrum showed these materials to be present in the ratio 2:3.

Reaction of *p*-Bromoanisole and Lithium Diethylamide in the Presence of Tris(dimethylamino)phosphine Oxide. Lithium diethylamide, 0.064 mole, was prepared as a suspension in 150 ml of benzene and 48 ml of hexane. Tris(dimethylamino)phosphine oxide (5.83 g, 0.0325 mole) was added with stirring and this was followed by the slow addition of 6.09 g (0.0325 mole) of *p*-bromoanisole. After 16 hr the mixture was concentrated and treated with 30 ml of water and 100 ml of ether. The aqueous phase was extracted with 80 ml more of ether. Concentration of the ether gave 9.29 g of liquid which was examined by glpc. Tris(dimethylamino)phosphine oxide and two other components, presumably *p*- and *m*-methoxy-N,N-diethylanilines, were present. Quantitative glpc indicated 2.27 g of oxide. The aqueous layer was concentrated and extracted with 75 ml of methylene chloride. Concentration afforded 6.48 g of impure tris(dimethylamino)phosphine oxide: 54% by glpc; 60% by nmr. The total recovery of oxide was *ca.* 100%.

A Sulfone α-Elimination Rearrangement and a Related Diazoethane Decomposition

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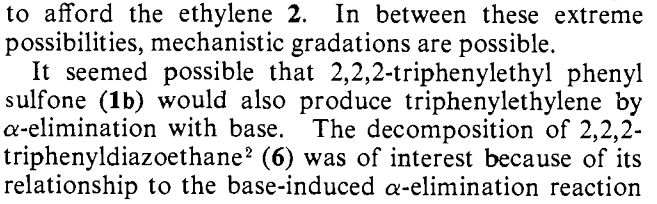
Abstract: The reaction of 2,2,2-triphenylethyl phenyl sulfone with phenyllithium and phenylsodium was found to give triphenylethylene. In the similar reaction of 2-anisyl-2,2-diphenylethyl phenyl sulfone, the statistically corrected anisyl migratory aptitude for this reaction was found to be 0.86. This contrasts with the 1.9 value found for the thermal rearrangement of 2-anisyl-2,2-diphenyldiazoethane in hydrocarbon solvents. The nature of the rearranging divalent species is considered.

The research described here concerns a novel α-elimination reaction of 2,2,2-triarylethyl phenyl sulfones and a parallel study of the reactions of an analogous diazo compound. Interest in the α-elimination reactions of sulfones was prompted by our finding[1] of the α-elimination rearrangement of 1-chloro-2,2,2-triphenylethane (**1a**) by treatment with amylsodium to give triphenylethylene (**2**). For this reaction two extreme mechanisms may be considered. In path A (note Scheme I), after proton removal by base, the carbanion **3a** rearranges, followed by loss of chloride to give the olefin. In path B, the same carbanion loses chloride to yield a carbene (**5a**), which then rearranges to afford the ethylene **2**. In between these extreme possibilities, mechanistic gradations are possible.

Scheme I



It seemed possible that 2,2,2-triphenylethyl phenyl sulfone (**1b**) would also produce triphenylethylene by α-elimination with base. The decomposition of 2,2,2-triphenyldiazoethane[2] (**6**) was of interest because of its relationship to the base-induced α-elimination reaction under consideration. Hellerman[2] found that this diazoethane (**6**) lost nitrogen under a variety of conditions, both thermal and acidic, to give triphenylethylene.

$$\underset{\mathbf{6}}{Ph_3C-\overset{-}{C}H-\overset{+}{N}\equiv N} \xrightarrow[-N_2]{\Delta} \underset{\mathbf{2}}{Ph_2C=CHPh}$$

Synthesis of Starting Materials. For the study of the sulfone α-elimination, both 2,2,2-triphenylethyl phenyl sulfone (**1b**) and a *p*-methoxy-substituted analog were needed. 2-Anisyl-2,2-diphenylethyl phenyl sulfone (**1c**) was selected for the latter. Both compounds were prepared by the oxidation of the corresponding sulfides (**9b** and **9c**) with peracetic acid. The sulfides, in turn, were obtained from the reaction of α-chlorothioanisole[3] with triphenylmethylsodium (**8b**) and anisyldiphenylmethylsodium (**8c**), respectively. These organosodium derivatives were conveniently prepared from the corresponding triarylchloromethanes by treatment with a 0.75% (liquid) sodium amalgam using high-speed stirring.[4] The synthetic scheme is outlined in Scheme II.

The synthesis of 2-anisyl-2,2-diphenyldiazoethane (**6c**) started with anisyldiphenylacetonitrile[5] (**10**). This was reduced with lithium aluminum hydride to give a 54% yield of the previously unknown 2-anisyl-2,2-diphenylethylamine (**11**), mp 92.0–93.5°. The latter was treated with ethyl chloroformate and triethylamine to afford ethyl N-(2-anisyl-2,2-diphenylethyl)carbamate (**12**), mp 74.5–76.0°, in 70% yield. Nitrosation of **12** with sodium nitrite in acetic anhydride–acetic acid using

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(1) H. E. Zimmerman and F. J. Smentowski, *J. Am. Chem. Soc.*, **79**, 5455 (1957).

(2) L. Hellerman and R. L. Garner, *ibid.*, **57**, 139 (1935).

(3) F. G. Bordwell and B. M. Pitt, *ibid.*, **77**, 572 (1955).

(4) See H. E. Zimmerman and V. R. Sandel, *ibid.*, **85**, 915 (1963), for the general method.

(5) I. Lifschitz and G. Girbes, *Ber.*, **61**, 1463 (1928).