[Contribution from the Department of Chemistry, Baylor University]

On the Structure of Couper's Compound[1]

A. G. PINKUS, P. G. WALDREP, and W. J. COLLIER

Received September 10, 1959

It has been conclusively established that the following reactions all yield Couper's compound (I): (1) reaction of salicylic acid and phosphorus pentachloride; (2) reaction of salicylic acid and phosphorus trichloride followed by reaction of this product (II A) and (a) chlorine or (b) phosphorus pentachloride. These results correct previous reports in the literature. Partial hydrolysis of compound I yields compound IV which was also obtained by direct oxidation of compound II A. On the basis of various considerations, the cyclic structure (I A) is favored over the open possibility (IB) for the structure of Couper's compound.

The basis for the structural theory of organic chemistry was conceived independently by Kekulé and Couper in 1858.[2] Couper formulated his brilliant ideas on structure while investigating the reaction of methyl salicylate and salicylic acid with phosphorus pentachloride.[2,3] The importance of Couper's contributions has been recently reemphasized in connection with the Kekulé-Couper Centennial Celebration.[4] Although earlier observations had been made on the reaction, Couper[5] was the first investigator who correctly interpreted the course of the reaction and also proposed a cyclic structure (IA) for the final reaction product in connection with his newly formulated structural theory.[6] However, it is noteworthy that the correct structure has not been conclusively decided up to the present time. Anschütz at a later time[7] studied the reaction of salicylic acid and phosphorus pentachloride and after an extended series of investigations on this and related problems, came to the conclusion in his final paper on the subject[8] that an alternate structure, IB, was the correct structure for this compound, which could also be prepared by two further methods: reaction of salicylic acid and phosphorus trichloride to form compound II, followed by treatment of compound II with (1) chlorine or (2) phosphorus pentachloride (see Chart I). More recently, the problem has been reinvestigated by Atherton[9] who reported that although the product from phosphorus pentachloride and salicylic acid was miscible with cyclohexane, that obtained by the action of chlorine on compound II was not. As the infrared spectra of both products showed characteristic carbonyl bands, he concluded that the compounds were isomeric (IA *and* IB). In the discussion of the paper (Ref. 9, p. 90), he stated the belief that the compound formed by phosphorus pentachloride is IB whereas that formed by the action of chlorine on IIA is IA.

Our interest in this problem was aroused by our finding that an intermediate compound (III) was produced in the reaction of methyl salicylate and phosphorus pentachloride which on subsequent heating, produced compound I and methyl chloride. In this work[1] it was found that the pyrolysis product from the methyl salicylate–phosphorus pentachloride reaction was identical with the product from the reaction of salicylic acid and phosphorus pentachloride on the basis of the respective infrared curves and other properties. As the solution of the structure of this compound was related to the possible solution of our original problem on the structure of the product from the phenyl salicylate–phosphorus pentachloride reaction,[10] further work was done in attempting to relate the results of our work to those obtained by Atherton. As Atherton[9] had checked Anschütz's preparation of compound I by treating compound II with chlorine,[11] it was pertinent to check Anschütz's other method of preparation,[11] *viz.*, the reaction of compound II with phosphorus pentachloride, to see whether or not this product was the same as that obtained from the salicylic acid–phosphorus pentachloride reaction. It was found that the products of these two reactions were identical on the basis of the infrared curves (Figs. 1 and 2). This result was

---

(1) Presented in part at the 134th ACS Meeting, Atlantic City, N. J., Sept. 13–18, 1959. (Inadvertently in the abstract, p. 100 P, the Roman numerals IIB and III A have been misplaced with respect to the intended structures and should be interchanged.)

(2) A. S. Couper, *Compt. rend.*, 46, 1157 (1858); *Phil. Mag.*, [4], 16, 104 (1858); Alembic Club Reprints No. 21, *On a New Chemical Theory and Researches on Salicylic Acid*, Edinburgh, 1933; A. Kekulé, *Ann.*, 106, 129 (1858).

(3) A. S. Couper, *Ann.*, 109, 369 (1859).

(4) H. C. Brown, *J. Chem. Educ.*, 36, 104 (1959); O. T. Benfey, *J. Chem. Educ.*, 36, 319 (1959); see also, J. C. Irvine, *J. Chem. Educ.*, 7, 2808 (1930); and L. Dobbin, *J. Chem. Educ.*, 11, 331 (1934).

(5) C. Gerhardt, *Ann.*, 89, 360 (1854); C. Drion, *Ann.*, 92, 313 (1854); C. Drion, *Compt. rend.*, 39, 122 (1854).

(6) A. S. Couper, *The Edinburgh New Philosophical Journal*, 8, 213 (1858).

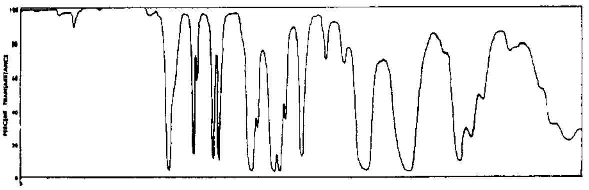
(7) R. Anschütz, *Ann.*, 228, 308 (1885).

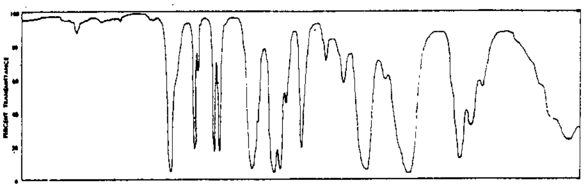
(8) R. Anschütz, *Ann.*, 346, 286 (1906).

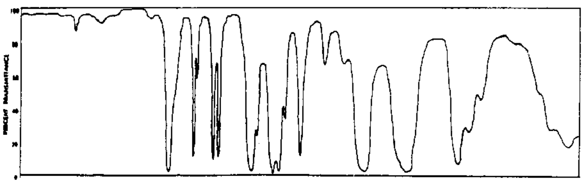
(9) F. R. Atherton in *Phosphoric Esters and Related Compounds*, Special Publication No. 8, The Chemical Society, London, England, 1957, pp. 475 ff. (Report of a Symposium held at the Chemical Society Anniversary Meeting, Cambridge, April 9–12, 1957.)

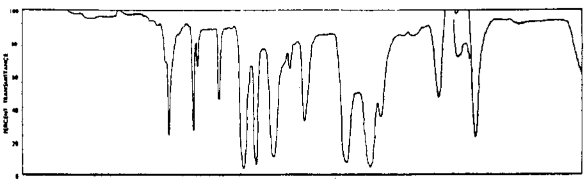
(10) A. G. Pinkus, P. G. Waldrep, and P. H. Ko, Abstracts, 132nd Meeting, American Chemical Society, Chicago, Ill., Sept. 7–12, 1958, p. 48P.

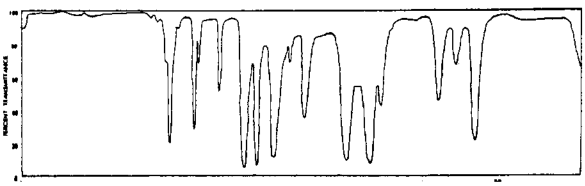
(11) R. Anschütz and W. O. Emery, *Ann.*, 239, 301 (1887).

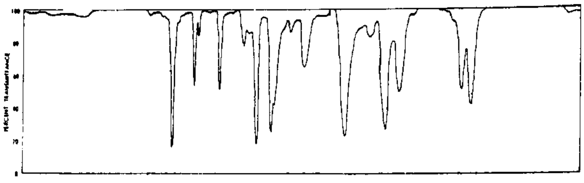












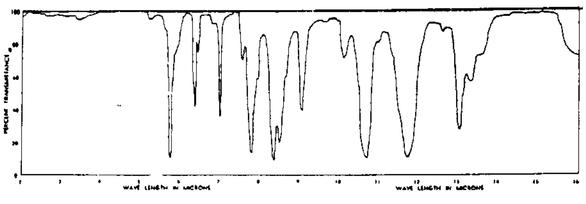


Fig. 1. Infrared spectrum of product from reaction of salicylic acid and phosphorus pentachloride (pure liquid)

Fig. 2. Infrared spectrum of product from reaction of compound II and phosphorus pentachloride (pure liquid)

Fig. 3. Infrared spectrum of product from reaction of compound II and chlorine (pure liquid)

Fig. 4. Infrared spectrum of product from partial hydrolysis of compound I (benzene solution)

Fig. 5. Infrared spectrum of product from oxidation of compound II (benzene solution)

Fig. 6. Infrared spectrum of product (compound II) from reaction of salicylic acid and phosphorus trichloride (benzene solution)

Fig. 7. Infrared spectrum of product from reaction of salicylic acid and phosphorus pentachloride (benzene solution)

somewhat unexpected since on the basis of Atherton's results with compound II and chlorine we had also expected the spectra to differ. Because of this unexpected result, the reaction of compound II and chlorine was then investigated. Under various conditions of preparation, (see Experimental) the compound obtained in our work was identical (as evidenced by infrared spectra, Fig. 3, and other properties) with that obtained in our previous work. On checking the miscibility with cyclohexane, the product of the reaction of compound II and chlorine was found to be completely miscible, contrary to the results of Atherton. It seemed possible that Atherton may have been working with a partially hydrolyzed sample since this would be a possible explanation of the nonmiscibility and differing infrared spectra. Indeed, compound I was found to react with the stoichiometric amount of water to produce compound IV (Fig. 4) which was identical with the product (Fig. 5) obtained by the direct oxidation of compound IIA. Compound IV is insoluble in cyclohexane.[12]

A conclusive decision between the two possible structures for Couper's compound is not yet possible. On the basis that the compound did not react with sulfur dioxide at room temperature and is volatile, Atherton expressed the belief that the compound probably has the open structure, IB.[9] However, the following considerations appear to make the cyclic structure, IA, more probable.

(1) The nonreactivity with sulfur dioxide at room temperature does not appear to be a reliable criterion for the absence of the $>PCl_3$ or $—PCl_4$ groupings. In other work[10] it was found that the product from the reaction of phenyl salicylate and phosphorus pentachloride did not react noticeably with sulfur dioxide at room temperature, whereas the reaction is reported to take place at higher temperatures.[13] Also, there does not appear to be any valid reason to expect the cyclic structure (IA) to be nonvolatile.

(2) It is possible to explain the reaction of chlorine or phosphorus pentachloride with IIA to produce the cyclic structure (IA) whereas a reasonable explanation is lacking for going from IIA to the open structure, IB. Thus, the reaction with chlorine

---

(12) Dr. Atherton, in a letter, states that on repeating the reaction of chlorine with freshly prepared 1,2-benzoylene phosphorochloridite (IIA), no cyclohexane-immiscible compound was produced. He was able to reproduce the observed effect of cyclohexane immiscibility by deliberately adding traces of 1,2-benzoylene phosphorochloridate (IV). However, Dr. Atherton stated that he did not believe that the contaminant was produced by hydrolysis since anhydrous conditions were used. He felt that the contaminant most likely arose either by direct oxidation of 1,2-benzoylene phosphorochloridite by interruption of the nitrogen supply during its distillation or by the use of phosphorus trichloride contaminated with phosphorus oxychloride in the initial preparation of the phosphorochloridite. The authors express their appreciation to Dr. Atherton for his letter furnishing this helpful information.

(13) A. Michaelis and W. Kerrhof, *Ber.*, 31, 2172 (1898).

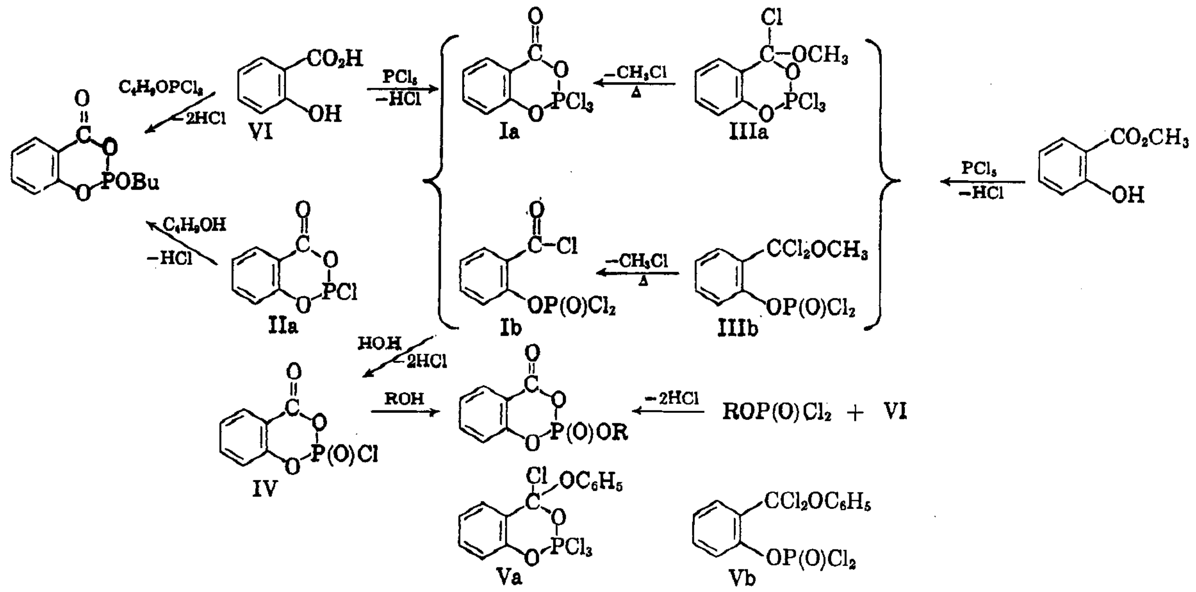


CHART I

to produce the cyclic structure, IA, is analogous to the well studied reaction of phosphorus trichloride and chlorine to form phosphorus pentachloride. In fact, one would expect the reaction with IIA to occur more readily, as the two oxygen atoms attached to phosphorus would tend to make the phosphorus more electron-deficient as compared with phosphorus trichloride, as oxygen is more electronegative than chlorine. The observation that this reaction is highly exothermic (see Experimental)is evidence for this expectation. The reaction of phosphorus pentachloride with IIA can be rationalized as a competition between IIA and phosphorus trichloride for chlorine (the phosphorus pentachloride being in equilibrium with phosphorus trichloride and chlorine). A recent analogous example is the reaction of triaryl phosphites with phosphorus pentachloride[14]:

$$(ArO)_3P + PCl_5 \longrightarrow (ArO)_3PCl_2 + PCl_3$$

By the same reasoning as above, the more electron-deficient phosphorus atom in IIA would be expected to react preferentially with the chlorine. Another point to be made here is that the reaction of structure IIA with chlorine is closely analogous to its reaction with oxygen to produce the cyclic compound, IV, the structure of which has been conclusively proved by Atherton[9,15] (Chart I). Both reactions can be classified as oxidation reactions with respect to phosphorus.

(3) As various considerations favored a cyclic structure (VA) for the phenyl salicylate–phosphorus pentachloride reaction product,[10] by analogy the cyclic structure (IIIA) is favored over the open structure (IIIB) for the methyl salicylate–phosphorus pentachloride reaction product. Structure IIIA, on pyrolysis, can form only the cyclic structure (IA) and not the open structure (IB) (Chart I).

(4) There is a very close resemblance between the infrared curves of the known cyclic structures, II A,[16] IV,[9,15] and that of compound I (Figs. 5, 6, and 7) that might be expected for two compounds having similar structures. It seemed that a definite decision between the two structures should be possible on the basis of the presence or absence of the well studied phosphoryl (P—O) stretching frequency which is usually found in the region, 1300–1250 cm.$^{-1}$ (7.7–8.0 μ)[17] as an intense but narrow band. Although the infrared spectrum of compound I shows a many shouldered band having its maximum peak at 7.71 μ, it was noted that compound II which does not contain a P—O grouping, also showed a similar band with a maximum peak at 7.82 μ. The infrared spectrum of compound IV shows a band at 7.81 μ which may be the P—O stretching band. It seemed that it might be possible to distinguish the P—O stretching band definitely by making use of the recent results of Sheldon and Tyree.[18] These authors showed that various metal halides formed addition compounds with phosphoryl halides and triphenylphosphine oxide which showed a shift of the P—O stretching band to lower

---

[14] I. N. Zhmurova and A. V. Kirsanov, *J. Gen. Chem., U.S.S.R.*, 29, 1664 (1959).

[15] F. R. Atherton, British Patents, 793,722, April 23, 1958; 806,879, Jan. 7, 1959 [*Chem. Abstr.*, 52, 20063 (1958); 53, 14125 (1959)].

[16] This structure was established conclusively by the work of R. W. Young, *J. Am. Chem. Soc.*, 74, 1672 (1952) and J. A. Cade and W. Gerrard, *Chem. & Ind.* (*London*), 402 (1954) by reactions such as those shown in Chart I.

[17] L. J. Bellamy, *Infrared Spectra of Complex Molecules*, 2nd edition, Wiley, New York, 1958, pp. 312 ff. Occasionally, the phosphoryl stretching frequency falls outside of these limits, as for trimethyl phosphine oxide at 1176 cm.$^{-1}$ (8.5 μ) or for the highly electronegatively substituted phosphorus oxyfluoride at 1404 cm.$^{-1}$ (7.12 μ).

[18] J. C. Sheldon and S. Y. Tyree, *J. Am. Chem. Soc.*, 80, 4775 (1958).

frequencies. However, in the present work, the spectra of various mixtures of titanium tetrachloride with compound IV or I showed deep-seated changes indicating the occurrence of reactions.

The P—O—C (aromatic) bands are usually found in the region, 8.0 to 8.4 μ (1240–1190 cm.$^{-1}$) (intense band) and at 9.71 μ (1030 cm.$^{-1}$) (weak band).[17] For compounds I, II, and IV, these are probably the bands at 8.27, 8.18, and 8.22 μ (intense) and 9.57, 9.65, and 9.65 μ (weak), resp. Although P—O—C (aliphatic) bands usually occur in the region 9.5 to 10.0 μ (1050–995 cm.$^{-1}$),[17] it might be expected that for compounds I, II, and IV the corresponding P—O—C (carbonyl) might be shifted to a different region. Thus, it is difficult to make this assignment at present.

EXPERIMENTAL

Operations were carried out in a dry-box wherever necessary to avoid possible hydrolysis.

Preparation of compound II. Compound II was prepared by heating together by means of an oil bath at 85°, a mixture of salicylic acid (72.0 g., 0.521 mole) and redistilled reagent grade phosphorus trichloride (118 g., 0.860 mole) in a Claisen flask tilted so as to be in reflux position. The apparatus was protected from moisture by means of a calcium chloride drying tube and arranged so as to allow for absorption of hydrogen chloride by sodium hydroxide solution. After cessation of the hydrogen chloride evolution (overnight heating), the flask was adjusted for vacuum distillation, a stream of dry nitrogen being passed through the capillary during distillation. The excess of phosphorus trichloride was distilled first and then the product was obtained in three fractions (96.8% based on salicylic acid): b.p. 107.5–108.5° (3.0 mm.) (main fraction).[19]

Preparation of compound I. 1. *Reaction of salicylic acid and phosphorus pentachloride.* The procedure was similar to that used above for the reaction with phosphorus trichloride. The quantities of reactants used were: salicylic acid, 55.2 g., 0.400 mole; phosphorus pentachloride, 91.0 g., 0.437 mole. Heating for 1 hr. in an oil bath at 100° brought about liquefaction of the mixture and evolution of hydrogen chloride. After cessation of hydrogen chloride evolution (1 hr.), the mixture was distilled and yielded the following fractions at 3 mm.: 12.2 g., b.p. 162°, $n_D^{20.1}$ 1.5553; 45.6 g., b.p. 162–164°, $n_D^{20.1}$ 1.5555; 14.9 g., b.p. 164°, $n_D^{20.0}$ 1.5556; total yield, 66.5% based on salicylic acid.[20]

2. *Reaction of compound* II *and phosphorus pentachloride.* Compound II (10.5 g., 0.0518 mole) was mixed with phosphorus pentachloride (10.8 g., 0.0518 mole) in a Claisen flask fitted for distillation and protected from moisture by means of a calcium chloride drying tube. The flask was heated by means of an oil bath at 58°. After a brief initiation period, a vigorous reaction took place and in a short time, went to completion. The mixture was then distilled, the phosphorus trichloride being first collected in a Dry Ice–acetone trap. The following fractions were collected: 0.4 g. of forerun, b.p. 165–169° at 13.0 mm.; 8.5 g., b. p. 169–176° at 13.0–13.5 mm.

3. *Reaction of compound* II *and chlorine.* Compound II (24.7 g., 0.122 mole) was dissolved in 91 ml. of carbon tetrachloride in a Claisen flask which was immersed in an ice bath. The apparatus was arranged for the introduction of chlorine which was generated by the reaction of potassium permanganate and concentrated hydrochloric acid. The chlorine was dried by bubbling through concentrated sulfuric acid before being passed through the reaction mixture. The reaction was followed to completion by observation of sequential infrared spectra. The carbon tetrachloride was removed *in vacuo* and the product distilled: 2.3 g., b. p. 125–134° at 1.5 mm., $n_D^{20.0}$ 1.5606; 11.6 g., b. p. 141–148° at 1.0–1.5 mm., $n_D^{20.0}$ 1.5560; 12.4 g., b. p. 145–148° at 1.5 mm., $n_D^{20.0}$ 1.5544. In an earlier run, the chlorination was carried out at room temperature without any essential difference in results. During this run, it was noted that the reaction was very exothermic.

Reaction of compound II *with oxygen.* Dry oxygen was passed through a solution of 22.7 g. (0.112 mole) of compound II dissolved in 350 ml. of dry redistilled ACS grade benzene for a period of about 8 hr. As the reaction was quite exothermic, the completion of the reaction was evidenced by a cooling of the reaction to room temperature. The benzene was removed *in vacuo*, leaving 24.6 g. (quantitative yield) of nearly pure product (as evidenced by comparison of the infrared spectrum with that of recrystallized material). The product was dissolved in a minimum quantity of benzene and filtered to remove a small quantity of insoluble material (possibly a small amount of hydrolyzed product). Dry petroleum ether (b.p. 30–60°) was then added. On standing crystals of compound IV deposited, m.p.[21] 95.5–96.0°.[22]

Partial hydrolysis of compound I. Compound I (15.25 g., 0.05577 mole) was dissolved in 40 ml. of absolute ether in a 500-ml. 3-neck flask equipped with a dropping funnel, stirrer, and condenser. The calculated equivalent (1:1 ratio) quantity of water (1.005 g., 0.05577 mole) was added to 365 ml. of absolute ether and anhydrous pyridine (4.41 g., 0.05577 mole) was added to the mixture to dissolve the water and to facilitate the hydrolysis reaction. The ether-water-pyridine solution was added slowly over a 1.5-hr. period to the stirred solution of compound I. The precipitated pyridine hydrochloride was separated from the mixture by means of a specially constructed set-up embodying a sintered disc which made possible a vacuum filtration without exposing the mixture to moist air. The ether solvent was removed from the filtrate *in vacuo* in a dry box. As the residue was found to be completely soluble in benzene, this indicated the absence of a further hydrolysis product, salicyl phosphate, which is insoluble in benzene. However, an infrared spectrum revealed the presence of a small amount of unhydrolyzed compound I which was removed by washing the residue with petroleum ether (b. p. 30–60°) in which compound IV is insoluble. The yield of residue was 9.5 g. (62.3%). The residue was dissolved in a minimum quantity of benzene and petroleum ether was then added. On standing, crystals had formed, m. p.[21] 95.0–95.2°.

Before developing the procedure used above for hydrolysis, the following experiments were performed. It was found that the hydrolysis of compound I by using anhydrous oxalic acid gave a mixture containing compound IV, a benzene-insoluble substance (possibly salicyl phosphate), and starting material. When the hydrolysis was carried out by adding water to a benzene solution of compound I, a similar mixture was also obtained. This is in contrast to the clearcut stepwise hydrolysis obtained[10] by a similar procedure used to hydrolyze Michaelis and Kerkhof's compound.[13] Also when the hydrolysis was carried out using wet ether with or without heating, a mixture was obtained. Apparently there is

---

(19) R. Anschütz and W. O. Emery, (Ref. 11) report b. p. 127° at 11 mm.; J. A. Cade and W. Gerrard (Ref. 16) report 123–125° at 9 mm.

(20) R. Anschütz (Ref. 7) gives b. p. 168° at 11 mm. Yields of 84% and 71.6% were obtained in other experiments.

(21) A technique for avoiding possible hydrolysis of the m.p. sample was used: A. G. Pinkus and P. G. Waldrep, *Mikrochim. Acta*, 772, 1959. Total immersion thermometers were used.

(22) R. Anschütz (Ref. 8) reports m.p. 95°.

not much of a difference in the ease of hydrolysis of the three chlorines under the conditions used.

Infrared spectra. Spectra were obtained on a KM-1 Baird-Atomic infrared spectrophotometer. Matched 1 mm. sodium chloride cells were used for the solution spectra. Pure liquids were run as thin films between two sodium chloride plates. All bands reported were calibrated against the nearest polystyrene peaks run on each chart. Because all of the compounds were found to be sufficiently soluble in benzene, it was the common solvent used to compare the spectra of the various compounds. The compounds were also run in other solvents in order to examine the regions of the spectra that were masked by strong benzene absorbing bands. Thus, the spectrum of compound I was also obtained in carbon tetrachloride, compound II in carbon tetrachloride, and phosphorus trichloride, and compound IV in phosphorus trichloride. There are a few extra bands that appear in these latter spectra that do not appear in the benzene spectra.

Acknowledgment. The authors express appreciation to the Public Health Service, National Institutes of Health for support of this work under Research Grant No. CY-3753.

WACO, TEX.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Pyrolysis of γ-Hydroxyalkyl Quaternary Ammonium Hydroxides and Alkoxides. Acyclic Systems[1,2]

VINCENT J. TRAYNELIS AND JAMES G. DADURA[3]

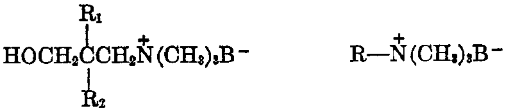
Received June 9, 1960

The decomposition of hydroxyneopentyltrimethylammonium hydroxide proceeds by dequaternization to produce 2,2-dimethyl-3-dimethylaminopropanol-1 (34%) plus the corresponding methyl ether (15%) and by a 1,3-cleavage (40%) to isobutylene, trimethylamine, and formaldehyde (although this undergoes further reaction in base). As the anion in this pyrolysis was changed to *n*-pentyl oxide and *t*-butoxide, the 1,3-cleavage increased up to 80%. When 3-hydroxypropyl- or 3-hydroxyisobutyltrimethylammonium hydroxide or *t*-butoxide was decomposed, Hofmann elimination was the predominant reaction leading to allyl alcohol and methallyl alcohol, respectively. The yield of elimination in these compounds appeared to be independent of the base used which was not the case for isobutyltrimethylammonium hydroxide (63%) and *t*-butoxide (20%). Apparently the hydroxyl group in the 3-position facilitates the Hofmann elimination. When Hofmann elimination is possible in these acyclic systems, this reaction predominates over the 1,3-cleavage.

When a hydroxylalkyl group is present in a quaternary ammonium base, the following equilibrium may arise:

$$\underset{\text{I}}{HO{-}(CH_2)_n{-}\overset{+}{N}(CH_3)_3B^-} \rightleftarrows \underset{\text{II}}{{}^-O{-}(CH_2)_n{-}\overset{+}{N}(CH_3)_3} + BH$$

One effect of the hydroxyl or alkoxide group in the decomposition reaction has been the formation of 3-,[4-7] 5-,[8] and 7-[9]membered oxygen heterocycles; while in the 2-hydroxyalkyl ($n = 2$) group it also enhances elimination by an inductive effect.[10] In the case of 3-hydroxyalkyl quaternary ammonium hydroxides[11-13] only olefin formation was observed in unreported yields. This paper deals with the decomposition of the following 3-hydroxyalkyl quaternary ammonium hydroxides and alkoxides.



$$HOCH_2\overset{R_1}{\underset{R_2}{C}}CH_2\overset{+}{N}(CH_3)_3B^- \qquad R{-}\overset{+}{N}(CH_3)_3B^-$$

III. $R_1 = R_2 = H$ $B = OH^-, n\text{-}C_5H_{11}O^-, t\text{-}C_4H_9O^-$
IV. $R_1 = CH_3, R_2 = H$ VI. $R = CH_2CH_2CH_3$
V. $R_1 = R_2 = CH_3$ VII. $R = CH_2\underset{CH_3}{CH}CH_3$

The various types of reactions one could consider for the decomposition of 3-hydroxyalkyltrimethylammonium bases are summarized in the equations below.

---

[1] This work was supported by a Frederick Gardner Cottrell Grant from Research Corp. for which grateful acknowledgement is made.

[2] Presented at the 134th Meeting of the American Chemical Society at Chicago, Ill., in September, 1958.

[3] Abstracted from the Ph.D. Dissertation of J. G. D., May 1960.

[4] S. Winstein and R. B. Henderson, "Ethylene and Trimethylene Oxide" in R. C. Elderfield, *Heterocyclic Compounds*, Vol. I, John Wiley & Sons, Inc., New York, 1950, p. 13.

[5] H. W. Bersch and G. Hubner, *Arch. Pharm.*, **289**, 673 (1956).

[6] B. Witkop and C. M. Foltz, *J. Am. Chem. Soc.*, **79**, 197 (1957).

[7] M. Svoboda and J. Sicher, *Collection Czechoslov. Chem. Commun.*, **23**, 1540 (1958).

[8] N. R. Easton and V. B. Fish, *J. Am. Chem. Soc.*, **77**, 1776 (1955).

[9] H. B. Bersch, R. Meyer, A. V. Mletzko, and K. H. Fischer, *Arch. Pharm.*, **291**, 82 (1958); H. B. Bersch and G. Hubner, *Arch. Pharm.*, **291**, 88 (1958).

[10] W. Hanhart and C. K. Ingold, *J. Chem. Soc.*, 997 (1927).

[11] C. Mannich and O. Salzmann, *Ber.*, **72B**, 506 (1939).

[12] J. Lichtenberger and R. Lichtenberger, *Bull. soc. chim. France*, 1002 (1948).

[13] C. Schopf, G. Dummer, W. Wust, and R. Rausch, *Ann.*, **626**, 134 (1959).