When 1,3-dichloro-2-benzenesulfonamidopropane (IV) was treated with alkali at 21°, determination of both chloride ion liberated *and* base consumed showed constant values of 1 equiv for each after 5–10 min of reaction. After 30 min, 1.07 equiv of chloride ion and 1.1 equiv of alkali were observed, an indication that the halide in the 1-benzenesulfonyl-2-chloromethylethylenimine cyclization product was not altogether inert to substitution or elimination. However, this process is slow relative to cyclization. Thus, at the same temperature (21°) cyclization was 78% complete in 3 min; at 15°, cyclization was 89% complete in 8 min.

The analytical procedure did not affect the 1,3-dibromo substrate V. After a mixture of the 1,3-dibromo compound, mp 93–94.5°, with aqueous-alcoholic silver bromide, silver nitrate, and nitric acid had been allowed to stand at room temperature for 0.5 hr, 95% of the starting material (mp 92–94°) could be recovered.

Under the conditions used for ring closure, the process was irreversible. Thus, solutions of 1×10^{-2} *M* 1-benzenesulfonyl-2-bromomethylethylenimine (I) and sodium bromide in 95% ethanol were allowed to stand for 30 min at 0°. Bromide ion was determined in the usual way to give the results in Table IX. The fact that 97, 100, and 99% of the added bromide remained uncombined showed that, once formed, the ring does not consume bromide ion. Whether this indicates a failure to react with bromide ion or whether it is the result of a favorable equilibrium remains to be seen.

TABLE IX

$10^2 \times$ NaBr added, *M*	$10^2 \times$ bromide found, *M*
2.45	2.38
2.14	2.13
2.02	1.99

The Structure of Couper's Compound. Chemical Studies and P^{31} Nuclear Magnetic Resonance Spectra on Couper's Compound and Related Structures[1]

A. G. PINKUS[2] AND P. G. WALDREP

Department of Chemistry, Baylor University, Waco, Texas 76703

Received July 20, 1965

Couper's compound, obtained from the reaction of salicylic acid and phosphorus pentachloride, has the phosphorodichloridate structure Ib rather than the cyclic structure Ia originally proposed by Couper. The structural evidence consists of the following: P^{31} nmr chemical shifts are in the general range found for other phenyl phosphorodichloridates; the infrared spectrum shows absorption bands in the regions expected for benzoyl chloride and phosphorodichloridates. The reaction of Couper's compound with 3 equiv of phenol forms a triphenylphosphate (VIIb) which is also produced in unambiguous fashion from the reaction of the phosphorodichloridate VIII with 2 equiv of phenol. Structure VIIb for this product is confirmed by the closeness of the P^{31} nmr shift to that of triphenylphosphate. Further chemical evidence for Couper's compound as Ib was obtained by the straightforward synthesis of Ib by the reaction of salicyloyl chloride and phosphorus oxychloride in the presence of an equivalent of pyridine. The interrelationships between Couper's compound and various related structures are clarified. The ring-opening and -closing reactions involved, as well as the formation of structure Ib, are rationalized. The infrared spectrum confirms structure XVIa for salicyl phosphate.

The compound obtained from the reaction of salicylic acid and phosphorus pentachloride[3] was designated as a cyclic structure Ia by Couper in his brilliant formulation of a structural theory of organic chemistry[4] in 1858. This structure is one of the first three[5] cyclic structures ever published; however, the correct structure has been a subject of controversy for over 100 years. Anschütz,[9] in 1885, proposed an open structure (Ib). Subsequently,[10] he also independently proposed the cyclic structure in 1887; he did not become aware[11] of Couper's neglected papers on the structural theory of organic chemistry until 1906. In his final paper[11] on the subject after a series of investigations extending over 20 years, Anschütz stated that structure Ib was probably correct, although he could not obtain conclusive evidence to support this structure. More recently, Atherton[7] considered this problem and also favored structure Ib but again furnished no conclusive evidence. In a recent paper,[8] the cyclic structure seemed the most probable on the basis of the available evidence. In the present paper, further chemical evidence and P^{31} nmr spectra of Couper's compound, *meta* and *para* analogs of structure Ib, cyclic structures related to structure Ia, and appropriate reference compounds are reported, enabling a definitive assignment of structure.

Results

P^{31} Nmr and Infrared Spectra.—The results are listed in Table I along with data on pertinent compounds for which P^{31} shifts have been published. The listing is in order of increasing magnitude of the chemical shift. The negative value of −2.3 ppm for Couper's compound (I) leaves no doubt of its identity as an *ortho*-substituted phenyl phosphorodichloridate (Ib). This value lies between the figures, −2.6 for the *meta* derivative II and −1.5 and −1.4 for phenyl phosphorodichloridate[12,13] (III) and the *para* derivative IV, respectively. Cyclic structures analogous to Ia are not possible for the *meta* and *para* derivatives. Large positive values would be expected[12] for structure Ia

(1) Based on Ph.D. Dissertation of P. G. W., Baylor University, 1965.

(2) To whom correspondence should be addressed.

(3) A. S. Couper, *Compt. Rend.*, **46**, 1157 (1858); *Ann.*, **109**, 369 (1859).

(4) A. S. Couper, *Edinburgh New Philosophical Journal*, New Series, **8**, 213 (1858); republished in Alembic Club Reprints, No. 21, "On a New Chemical Theory and Researches on Salicylic Acid," Edinburgh, 1933; *Phil. Mag.*, [4] **16**, 104 (1858).

(5) The other two are[4,6-8] cyanuric acid and 1,2-benzoylene phosphorochloridate (Xa).

(6) O. T. Benfey in "Great Chemists," E. Farber, Ed., Interscience Publishers, Inc., New York, N. Y., 1961, pp 705 ff.

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

(8) A. G. Pinkus, P. G. Waldrep, and W. J. Collier, *J. Org. Chem.*, **26**, 682 (1961).

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

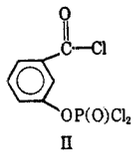
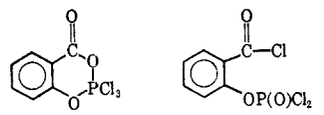
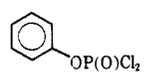
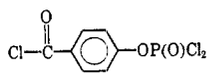
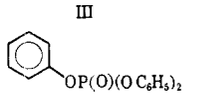
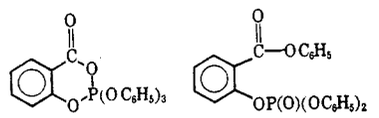
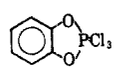
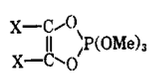
(10) R. Anschütz and W. O. Emery, *ibid.*, **239**, 301 (1887).

(11) R. Anschütz, *ibid.*, **346**, 286 (1906).

(12) R. A. Y. Jones and A. R. Katritzky, *Angew. Chem. Intern. Ed. Engl.*, **1**, 32 (1962).

(13) E. Schwarzmann and J. R. Van Wazer, *J. Am. Chem. Soc.*, **81**, 6366 (1959).

TABLE I
P^{31} NMR SPECTRA

Structure	Solvent or state	Chemical shift, ppm
 II	Neat	−2.6
 Ia Ib	Neat	−2.3
 IV	...	−1.5
 III	Neat	−1.4
	...	+17
 VIIa VIIb	Benzene	+18.5
 V	...	+26
 VI, X = -C_6H_5, -Me	...	+53

analogous to the values obtained for cyclic compounds in which phosphorus is pentacovalent and forms part of the ring: +26 for compound V[12] and +53 for structure VI.[14] Such large positive shifts have been attributed to the involvement of the d orbitals of phosphorus in the bonding. Since only one sharp peak was obtained for Couper's compound, this indicates that either there is no equilibrium between Ia and Ib or that any possibility of an equilibrium between Ia and Ib would have to be extremely rapid, with Ia present in only very small concentration; the possibility of an equilibrium was considered by Anschütz during his series of investigations. In passing, it is of interest to point out the relative order of the P^{31} resonances for the series as *para* > H > *ortho* > *meta*. No other such data of the P^{31} shifts on a disubstituted benzene series have been reported for a comparison and assessment of electrical and steric effects in the present system.

The infrared spectrum can be interpreted in terms of the phosphorodichloridate structure Ib. A strong carbonyl absorption band occurs at 5.63 μ (1776 cm^{-1}) with a shoulder at *ca.* 5.76 μ (1736 cm^{-1}); the corresponding bands[15] for benzoyl chloride are at 5.64 (1773 cm^{-1}) and 5.76 μ (1736 cm^{-1}) (sh). The P=O band occurs at 7.76 μ (1289 cm^{-1}) with a shoulder at 7.87 μ (1271 cm^{-1}). The P–O–C (aromatic) absorption bands[15-17] occur at 8.27 (1209 cm^{-1}) (C–O portion) and 10.57 μ (946 cm^{-1}) (pentavalent P–O portion).

Chemical Studies.—Chemical studies were carried out to obtain further support for the open-chain structure Ib for Couper's compound. The reaction of Couper's compound with excess phenol was studied. Structure VIIa might be expected to form from Ia, whereas structure VIIb would be expected from Ib (Chart I), assuming that no rearrangements occurred during reaction. Structure VIIa is analogous to the cyclic phosphoranes obtained by Ramirez and coworkers as exemplified by structure VI,[14] whereas VIIb is a previously described[18] compound, having been formed by the reaction of compound VIII with 2 equiv of sodium phenoxide (Chart I).

Couper's compound (I) reacted smoothly with 3 equiv each of phenol and triethylamine. The product (VII) obtained in 91% yield, mp 75.5–76.3°, was identical with the compound obtained from the reaction of the phosphorodichloridate VIII with phenol (90% yield, mp 75.6–76.2°, lit.[18] mp 76–77°) as evidenced by mixture melting point and comparison of infrared curves. The structure of VIIb follows from its straightforward synthesis from compound VIII (a compound of unambiguous structure)[19] and its infrared and P^{31} nmr spectra. The infrared spectrum (cyclohexane solvent) shows carbonyl ester stretching absorption[15a] at 5.68 μ (1761 cm^{-1}); the corresponding band for VIII is at 5.74 μ. The P=O stretching absorption[15b,16] occurs at 7.77 μ (1287 cm^{-1}) compared with 7.78 μ (1285 cm^{-1}) for compound VIII. The P–O–C (aromatic band) (C–O absorption)[15c,16,17] appears at 8.38 μ (1193 cm^{-1}) with a shoulder at 8.31 μ (1203 cm^{-1}), compared with the corresponding band at 8.39 μ (1192 cm^{-1}) in the phosphorodichloridate VIII. The shoulder may be explained on the basis of two different types of P–O–C (aromatic) bonds, one involving the aromatic rings of the phenyl groups and the other the *ortho*-substituted aromatic ring. Phenyl–O–P (pentavalent) absorptoni[16,17] is found at 10.40 μ (961 cm^{-1}) compared with absorption at 10.60 μ (943 cm^{-1}) for the phosphorodichloridate VIII.

The P^{31} nmr spectrum confirms structure VIIb as correct. The chemical shift of +18.5 ppm is in accord with its structure as a triphenyl phosphate, since this value is close to the value of +17 ppm reported[12,20] for triphenyl phosphate. A much larger positive value would be expected for structure VIIa comparable to the value of +53 for structure VI.[14]

In another chemical approach to the structure determination of Couper's compound, an independent straightforward synthesis of structure Ib was made. Salicylic acid was converted to salicyloyl chloride

(14) F. Ramirez and N. B. Desai, *J. Am. Chem. Soc.*, **82**, 2652 (1960).

(15) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958; (a) pp 179 ff; (b) pp 312 ff; (c) pp 315 ff; (d) p 162. (e) Bellamy (p 312) lists the free P=O vibration as generally at 1250–1350 cm^{-1}; Thomas and Chittenden[16] list 1160–1350 cm^{-1}.

(16) L. C. Thomas and R. A. Chittenden, *Chem. Ind.* (London), 1913 (1961).

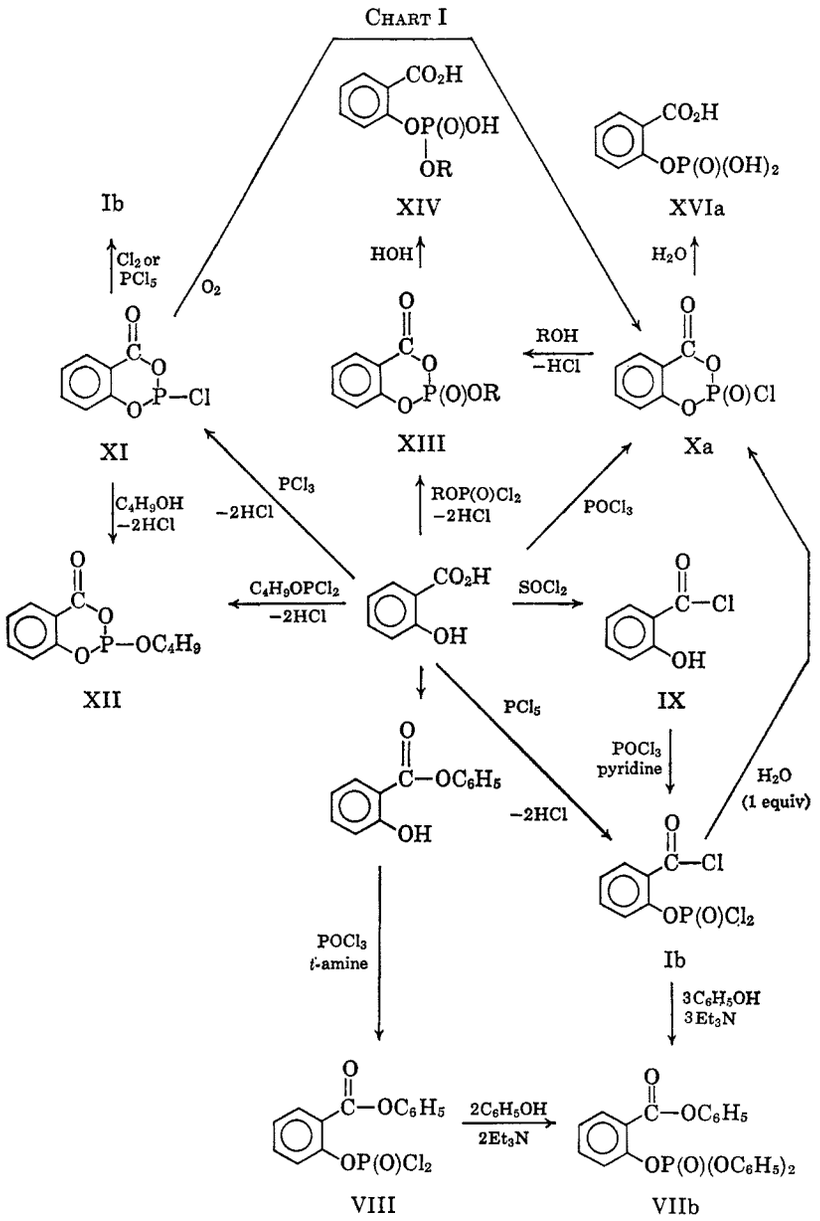
(17) R. A. Nyquist, *Appl. Spectry.*, **4**, 161 (1957); A. C. Chapman and R. Harper, *Chem. Ind.* (London), 985 (1962).

(18) A. Michaelis and W. Kerkhof, *Ber.*, **31**, 2172 (1898).

(19) A. G. Pinkus and P. G. Waldrep, *Chem. Ind.* (London), 302 (1962).

(20) N. Muller, P. C. Lauterbur, and J. Goldenson, *J. Am. Chem. Soc.*, **78**, 3557 (1956).

CHART I



(IX) (Chart I) by reaction with thionyl chloride. Salicyloyl chloride was then reacted with phosphorus oxychloride, using an equivalent amount of pyridine to form in 18.9% yield[21] a compound (Ib) identical with Couper's compound. The reaction between salicyloyl chloride and phosphorus oxychloride to form the phosphorodichloridate (Ib) is entirely analogous to the reactions of phosphorus oxychloride with phenol or phenyl salicylate to form the corresponding phosphorodichloridates as described elsewhere in this paper. Since the compound was isolated by distillation, a P^{31} nmr determination was also carried out on the reaction mixture *before* heating to obviate the possibility that a rearrangement of some sort might have occurred on heating. The determination on a reaction mixture diluted with benzene also showed the presence of structure Ib.

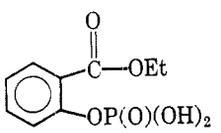
Discussion

Chart I summarizes the various interrelationships among the compounds involved and is an attempt to clarify the situation relating to Couper's compound and related compounds that has been in a state of confusion for a period of over 100 years. It is evident that the confusion has resulted from the presence of both cyclic and acyclic structures and unusual reactions resulting in cyclization or ring opening. An attempt will be made to rationalize these unusual reactions. The present work establishes the structure of Couper's compound as the open-chain structure, Ib, on the basis of chemical evidence substantiated by P^{31} nmr spectra. The chemical evidence consists of the following. (1) The reaction of Couper's compound with phenol formed compound VIIb, which was also obtained in unambiguous fashion from compound VIII by reaction with phenol; these reactions are the normal functional group reactions of an acid chloride to form a phenyl ester and a phosphoryl chloride to form a phenyl phosphate grouping. (2) Couper's compound was independently synthesized by a known route from the reaction of salicyloyl chloride (IX) with phosphorus oxychloride; the reaction is analogous to the

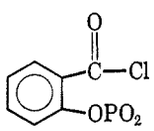
(21) The reason for the low yield is the self-condensation of salicyloyl chloride by loss of hydrogen chloride to form the polyester. In several other attempted reactions using pyridine and redistilled salicyloyl chloride, the polymer was the main product.

well-known reaction of phenols with phosphorus oxychloride to form phenyl phosphorodichloridates as exemplified by the preparation of compound VIII from phenyl salicylate.

The partial hydrolysis of Couper's compound (using 1 equiv of water) to form 1,2-benzoylene phosphorochloridate[22] (Xa) involves a novel ring closure. The cyclic structure for compound X has been established by the following evidence: (1) independent syntheses (a) by the reaction of salicylic acid and phosphorus oxychloride[7,23,24] and (b) by the oxidation[7,8] of 1,2-benzoylene phosphorochloridite[22] (XI), the cyclic nature of which has been established[25] by its reaction with butanol to form compound XII which was also obtained by the reaction of salicylic acid and butyl phosphorodichloridite; (2) by the reaction of compound X with alcohols or phenols to form the cyclic esters (XIII)[7,23,26] which were also obtained[26] by salicylic acid reacting with aryl phosphorodichloridates; and (3) by the formation from the ethyl derivative of XIII, on mild hydrolysis, of the monoethyl ester of *o*-carboxyphenyl dihydrogen phosphate (XIV) which was not identical with the isomeric known *o*-ethoxycarboxylphenyl dihydrogen phosphate (XV).[7]



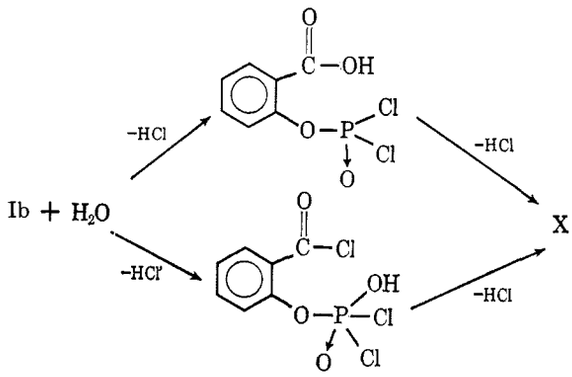
XV



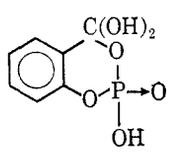
Xb

Historically, the cyclic structure, Xa, was first proposed by Couper.[4] Anschütz first proposed[9] an open structure, Xb, and later considered[10] also structure Xa, which he proposed independently, not being aware of Couper's work until 1906.[11] He favored structure Xb in his final paper[11] on the subject, since this structure appeared to explain better its formation from partial hydrolysis of the open structure (Ib) of Couper's compound and further hydrolysis of salicyl phosphate, an open structure (XVIa) (see below). The structure Xb is the only one mentioned in the book by Kosolapoff[27] and in the more recent treatise by Rodd.[28]

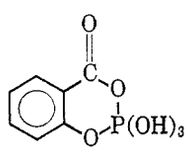
Reasonable mechanisms can be written to explain the hydrolytic ring closure. Nucleophilic attack by water can be considered to occur initially either on the carbonyl carbon or phosphorus as shown. This is followed by elimination of hydrogen chloride and the final cyclization step. A decision as to the initial step might be made in a comparison of the experimental rates of hydrolysis of benzoyl chloride and phenyl phosphorodichloridate.



More extensive hydrolysis of Couper's compound forms[9,29] salicyl phosphate. It is clear from the above discussion that the cyclic phosphorochloridate, Xa, is an intermediate in this hydrolysis. The generally accepted structure for salicyl phosphate is XVIa, which necessitates a ring opening in the hydrolysis. This structure was also first proposed by Couper.[4] In order to establish structure XVIa with more certainty, an infrared study was made in order to eliminate two other possibilities, XVIb and c.



XVIb



XVIc

The infrared spectrum[30] of salicyl phosphate showed a carbonyl stretching band at 5.91 μ (1692 cm^{-1}) which is in the region between 1650–1700 cm^{-1} generally given[15d] for arylcarboxylic acids. The carbonyl absorption clearly eliminates structure XVIb from consideration. The position of the band also tends to eliminate the cyclic structure XVIc, since the infrared spectrum of the cyclic phosphorochloridate Xa having this type of ring system shows carbonyl absorption at 5.62 μ (1779 cm^{-1}). Furthermore, the spectrum shows a P=O absorption band[15e] at 7.71 μ (1297 cm^{-1}) (with a shoulder at 7.83 μ); this also would tend to eliminate structure XVIc. The hydrolytic ring opening can be rationalized on the basis that the -C(=O)-O-P grouping in the cyclic phosphorochloridate can be considered to be a mixed anhydride of a carboxylate group and a phosphoric acid grouping and would therefore have acylating properties.

Since the phosphorochloridite XI is established[25] as a cyclic structure, it is clear that chlorination or phosphorus pentachloride treatment results in ring opening, Couper's compound (Ib) being the sole product.[8] A reasonable mechanism for the ring opening involves the cyclic structure Ia as an intermediate.

Support for this proposed mechanism is available in the literature. The addition of chlorine to phosphites

(22) This nomenclature is used for brevity according to the usage adopted by Atherton;[7] the *Chemical Abstracts* names for compounds Xa and XI are, respectively, 1-chloro-4,5-benzo-2,6-dioxaphosphorinan-3-one 1-oxide and 2-chloro-5,6-benzo-1,3,2-dioxaphosphorin-4-one.

(23) H. A. C. Montgomery, J. H. Turnbull, and W. Wilson, *J. Chem. Soc.*, 4603 (1956).

(24) A. G. Pinkus and S. S. Barnes, unpublished work.

(25) J. A. Cade and W. Gerrard, *Chem. Ind.* (London), 402 (1954); for earlier evidence, see R. W. Young, *J. Am. Chem. Soc.*, **74**, 1672 (1952).

(26) F. R. Atherton, British Patent 793,722 (April 23, 1958); *Chem. Abstr.*, **52**, 20063 (1958).

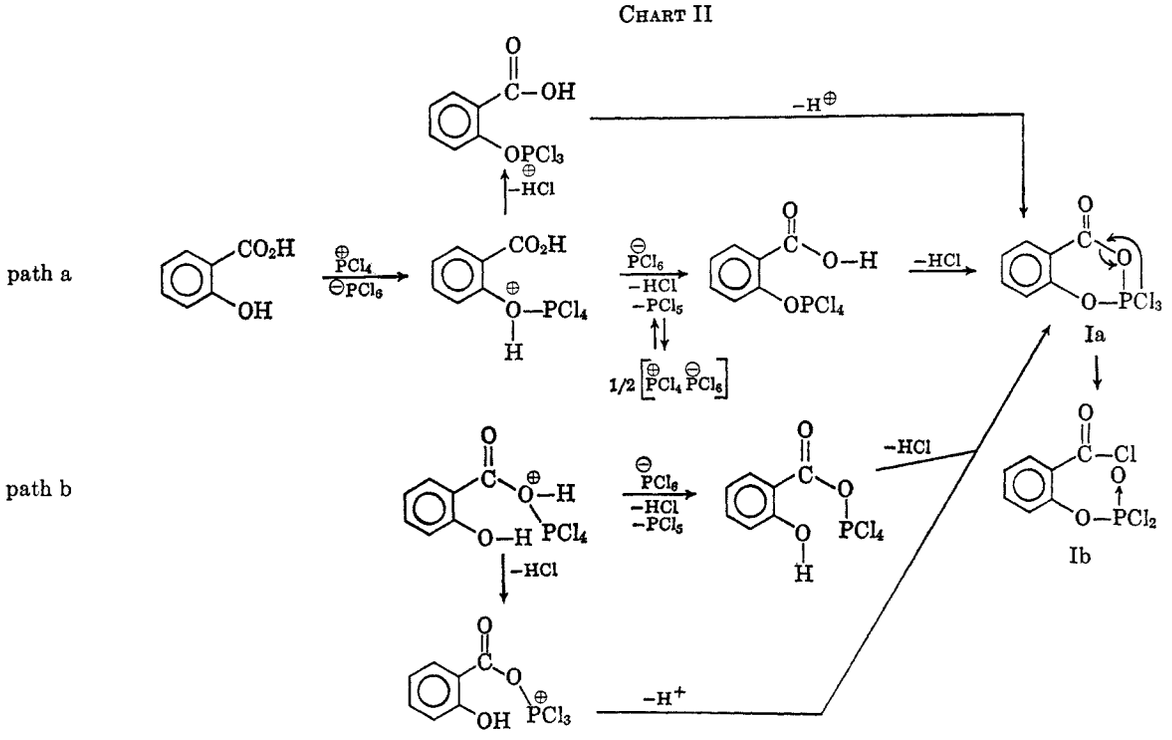
(27) G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, p 352.

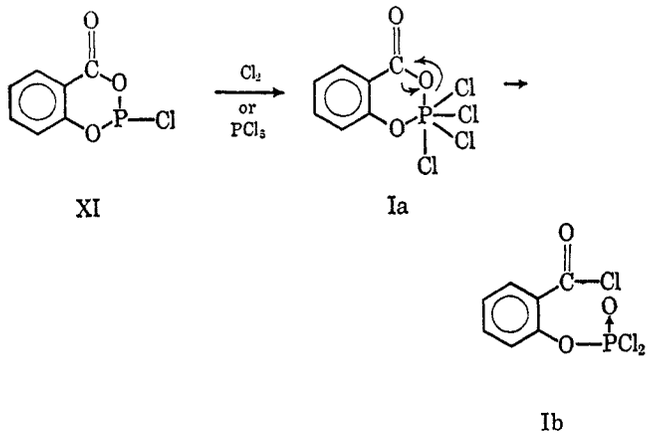
(28) E. H. Rodd, Ed., "Chemistry of Carbon Compounds," Vol. III, Part B, Elsevier Publishing Co., New York, N. Y., 1956, p 763.

(29) J. D. Chanley, E. M. Gindler, and H. Sobotka, *J. Am. Chem. Soc.*, **74**, 4347 (1952).

(30) Because of insolubility in the usual solvents, the spectrum of salicyl phosphate was obtained as a Nujol mull and a potassium bromide pellet. The two spectra did not differ appreciably; the values reported are for the pellet.

CHART II



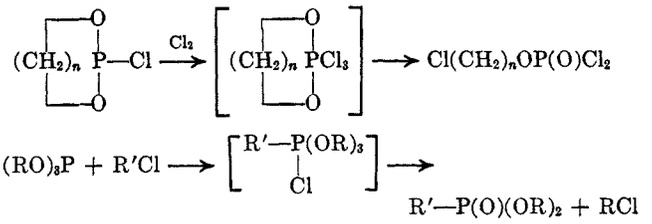


is well known; thus, for example, Zmurova and Kirsanov[31] reported the reaction of triaryl phosphites with phosphorus pentachloride and Grosse–Ruyken and Uhlig[32] reported the reaction of chlorodialkyl phosphites with chlorine to form the trichlorophosphates, which were hydrolyzed to the corresponding phosphoric acids.

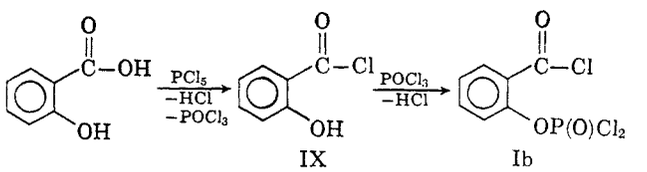
$$(ArO)_3P + PCl_5 \longrightarrow (ArO)_3PCl_2 + PCl_3$$

$$(RO)_2PCl + Cl_2 \longrightarrow [(RO)_2PCl_3] \xrightarrow[NaOH]{HOH} (RO)_2POOH$$

The ring cleavage would be analogous to the chlorination of cyclic phosphite esters reported by Rossiskaya and Kabachnik[33] and Keay and Crook,[34] which also resulted in ring cleavage to chloroalkyl phosphorodichloridates, presumably occurring through the cyclic trichloro intermediates. The formal analogy of the ring cleavage to the Michaelis–Arbuzov type of reaction was pointed out;[33] this analogy can be extended to the ring opening of Ia also.



Possible mechanisms for the reaction of salicylic acid with phosphorus pentachloride will now be considered. Anschütz, in his first[9] and also his final[11] papers on this subject, considered that phosphorus pentachloride reacted first with the carboxyl group to form salicyloyl chloride (IX), hydrogen chloride, and phosphorus oxychloride. Salicyloyl chloride then reacted with phosphorus oxychloride in a second step to produce hydrogen chloride and Couper's compound (Ib). A strong argument in favor of this interpretation was the preparation of the *meta* (II) and *para* (IV) analogs of structure Ib by Anschütz and Moore.[35] However, Anschütz,[36] on attempted reaction between salicyloyl chloride (IX) and phosphorus oxychloride, obtained only unreacted phosphorus oxychloride and self-condensation products (polysalicylides) of salicyloyl chloride; he, therefore, suggested a preliminary reaction at the phenolic hydroxyl but gave no further details concerning a mechanism for conversion to Ib.



(31) I. N. Zmurova and A. V. Kirsanov, *J. Gen. Chem. USSR*, **29**, 1664 (1959).

(32) H. Grosse-Ruyken and K. Uhlig, *J. Prakt. Chem.*, [4] **18**, 287 (1962).

(33) (a) P. A. Rossiskaya and M. I. Kabachnik, *Bull. Acad. Sci. URSS, Classe Sci. Chim.*, 509 (1947); *Chem. Abstr.*, **42**, 2924 (1948). (b) The referee has pointed out that the rearrangement of Ia to Ib need not be intramolecular as shown since the subsequent analogies do not demand this.

(34) L. Keay and E. M. Crook, *J. Chem. Soc.*, 710 (1961).

(35) R. Anschütz and G. D. Moore, *Ann.*, **239**, 333 (1887).

(36) L. Anschütz, *ibid.*, **439**, 265 (1924).

Some possible mechanisms beginning with reaction at the phenolic hydroxyl group appear in Chart II (path a). A similar mechanism with initial reaction at the carboxyl group can also be written (path b). It should be noted that both these proposed mechanisms involve the cyclic structure for Couper's compound (Ia) as an intermediate. The present experimental evidence does not permit a decision among the various proposed mechanisms. It would seem that an experiment in which phosphorus oxychloride with radioactively labeled phosphorus or isotopic oxygen was introduced into the reaction of salicylic acid and phosphorus pentachloride would permit a decision between the Anschütz mechanism[11] and the others.

Experimental Section[37]

Reaction of Couper's Compound (I) and Phenol.—A solution of phenol (11.3 g, 0.120 mole) and dry triethylamine (12.8 g, 0.126 mole) in 175 ml of dry benzene was added dropwise over a 4-hr period to a solution of Couper's compound[38] (I, 10.9 g, 0.0400 mole) in 150 ml of dry benzene in a flask protected from moisture by drying tubes. Triethylamine hydrochloride precipitated during the reaction. After standing overnight, the triethylamine hydrochloride was collected by filtration in a drybox, washed with benzene, dried, and weighed: 15.6 g (94.0% based on 3 equiv). The solvent was removed *in vacuo;* 16.3 g (91.1%) of crude product (compound VII) was obtained. Crystals, mp 75.5–76.3° (lit.[18] mp 76–77°), were obtained on recrystallization from 95% ethanol.

Salicyloyl Chloride (IX).—The procedure is a modification of the method of Kirpal.[39] Salicylic acid (47.2 g, 0.341 mole), thionyl chloride (98.3 g, 0.826 mole), and a catalytic quantity of aluminum chloride (*ca.* 0.1 g) were mixed in a Claisen flask protected from moisture with drying tubes and equipped for distillation. The flask was heated by an oil bath at 40–45° for 3 hr and agitated occasionally to facilitate the reaction. During the reaction sulfur dioxide and hydrogen chloride were evolved. Excess unreacted thionyl chloride was removed *in vacuo* with gentle heating by a water bath. The material was used directly without further purification.[40]

Reaction of Salicyloyl Chloride (IX) and Phosphorus Oxychloride.—The salicyloyl chloride (IX) from the above preparation was dissolved in 150 ml of dry benzene and added dropwise with stirring over a period of 2.5 hr to a solution of phosphorus oxychloride (78.2 g, 0.510 mole) and pyridine (40.2 g, 0.509 mole) in 175 ml of dry benzene in a three-necked flask protected from moisture. Pyridine hydrochloride precipitated during the exothermic reaction which was cooled by an ice bath. The precipitate was filtered in a drybox and solvent was removed *in vacuo* from the filtrate; the residue was vacuum distilled at 11 mm. A white solid (1.1 g) sublimed out of the mixture; the nature of this material was not investigated. The following liquid fractions were obtained: 7.4 g, bp 175–178°; 9.1 g, 178–179° (16.5 g, 18.9%). The identity of these fractions with Couper's compound (I) (from salicylic acid and phosphorus pentachloride) was established by comparison of infrared spectra.

Preparation of Salicyl Phosphate (XVIa).—Salicyl phosphate was obtained by hydrolysis of Couper's compound (I) in moist air according to a modification of the method of Chanley, *et al.*[29] Couper's compound (I, 6.15 g, 0.0225 mole) in a beaker was placed in a desiccator with a beaker containing an aqueous solution of sodium hydroxide. The hydrolysis was followed by weighing the beaker containing the sample. In 100 hr, the sample weighed 5.07 g (4.91 g calcd for hydrolysis to salicyl phosphate). The material, after drying over calcium chloride, weighed 4.89 g. The material was recrystallized by dissolving in acetone to which *ca.* 0.6% water was added, filtering off undissolved solid, and adding an approximately equal quantity of benzene. The crystals which formed on cooling were again recrystallized: mp 162–163° (lit.[29] mp 162.5–163°).

***m*-Chloroformylphenyl Phosphorodichloridate (II).**—The method of preparation was a modification of that used by Anschütz and Moore.[35] Phosphorus pentachloride (29.7 g, 0.142 mole) and *m*-hydroxybenzoic acid (19.7 g, 0.142 mole) were mixed together in a Claisen distilling flask protected from moisture by a calcium chloride drying tube. The flask was shaken during the reaction. Cooling was required to moderate the vigorous exothermic reaction. After the reaction mixture was nearly all liquefied, it was heated to 100° to complete the evolution of hydrogen chloride. The following fractions were obtained on distillation: 13.5 g, bp 169–171° (6.5–8.0 mm), $n^{20.0}$D 1.5570; 1.3 g, bp 173° (6.5 mm), $n^{20.0}$D 1.5577; total distillate, 14.8 g (38.1%).

***p*-Chloroformylphenyl Phosphorodichloridate (III).**—The method was a modification of that used by Anschütz and Moore;[35] the procedure was similar to that used for compound II. From phosphorus pentachloride (53.4 g, 0.256 mole) and *p*-hydroxybenzoic acid (35.4 g, 0.256 mole), the following fractions were obtained on distillation: 6.7 g, bp 170–175° (7 mm), $n^{19.9}$D 1.5570; 19.2 g, bp 167–173° (6–7 mm), $n^{19.9}$D 1.5574; 17.7 g, bp 171–178° (6 mm), $n^{20.0}$D 1.5573; total distillate, 43.6 g (62.5%).

Phenyl Phosphorodichloridate (IV).[42]—Phenol (9.0 g, 0.096 mole) dissolved in a minimum amount of dry carbon tetrachloride was added dropwise to a stirred mixture of phosphorus oxychloride (15 g, 0.098 mole) and pyridine (7.5 g, 0.095 mole) in a three-necked flask protected from moisture. The mixture was stirred for 2 hr and allowed to stand overnight. The precipitated pyridine hydrochloride was filtered in a drybox and carbon tetrachloride was removed from the filtrate by distillation. The residue was distilled: bp 130–134° (<1 mm), yield 15 g (75%).

Compound VIII.—A solution of dry pyridine (15.8 g, 0.200 mole) and phenyl salicylate (42.8 g, 0.200 mole) in 75 ml of dry benzene was added dropwise over a 1-hr period to a stirred solution of phosphorus oxychloride (30.7 g, 0.200 mole) dissolved in 25 ml of benzene in a three-necked flask protected from moisture. The precipitated pyridine hydrochloride was removed by filtration in a drybox after standing overnight. A crude yield of 59.2 g (89.4%) of a white solid was obtained on removal of solvent *in vacuo*. Recrystallization from cyclohexane yielded a product with mp 86.8–87.6°.[43] In other preparations, better results were obtained by using triethylamine in place of pyridine, since pyridine hydrochloride tended to precipitate slowly and to be more hygroscopic as compared with triethylamine hydrochloride, thus causing partial hydrolysis of the product.

P^{31} Nmr and Infrared Spectra.—The P^{31} spectra were determined on the pure liquids or solutions sealed in glass tubes. Referencing was by means of a duplicate sealed tube containing a small sealed capillary with 85% aqueous phosphoric acid. The chemical shifts are in parts per million from the 85% phosphoric acid reference.

The infrared spectra were obtained on a KM-1 Baird-Atomic instrument. Matched 0.1-mm sodium chloride cells were used for the solution spectra. Pure liquids were run as thin films between two sodium chloride plates. The preparation of the solutions and filling of the cells for moisture-sensitive compounds were done in a drybox. The spectra were calibrated against the nearest polystyrene bands run on each chart.

Acknowledgments.—The authors express appreciation to the Public Health Service, National Institutes

(37) Melting points were taken with total immersion thermometers; boiling points are uncorrected. Melting points of moisture-sensitive compounds were taken in sealed tubes prepared by a previously described technique: A. G. Pinkus and P. G. Waldrep, *Mikrochim. Acta*, 772 (1959).

(38) Prepared[3] from the reaction of salicylic acid and phosphorus pentachloride.

(39) A. Kirpal, *Ber.*, **63**, 3190 (1930).

(40) In a repetition of Kirpal's exact procedure, only a 14.7% yield of distilled product was obtained. The low yield was due to extensive polymerization through loss of hydrogen chloride during the vacuum distillation which is necessary to separate the product from aluminum chloride. The procedure of Wilson[41] was also used in other preparations in which crystalline salicyloyl chloride, mp 18°, was obtained in agreement with the melting point reported by Kirpal.[39]

(41) E. H. Wilson, U. S. Patent 2,899,458 (Aug 11, 1959); *Chem. Abstr.*, **54**, 428 (1960).

(42) Preparation was carried out by Mr. C. A. Taylor.

(43) The melting point reported by Michaelis and Kerkhof[18] for this compound was 70–71°; however, they did not recrystallize their material and reported no precautions against moisture. The compound hydrolyzes readily in moist air.

of Health, for support of this work under Research Grant No. CY-3753, to Dr. Victor Mark and Dr. John R. Van Wazer, Monsanto Chemical Company, for the P^{31} nmr spectra, and to the referee for his comments concerning the consideration of the equilibrium between structures Ia and Ib and the possibilities of the intra- *vs.* the intermolecular interpretation of the rearrangement of Ia to Ib.

Bridged Polycyclic Compounds. XXXII. The Proton Magnetic Resonance Spectra of Some Dibenzobicyclo[2.2.2]octadienes[1]

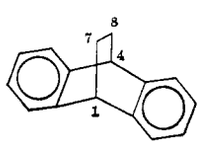
STANLEY J. CRISTOL, THOMAS W. RUSSELL, JERRY R. MOHRIG, AND DONALD E. PLORDE

Department of Chemistry, University of Colorado, Boulder, Colorado 80304

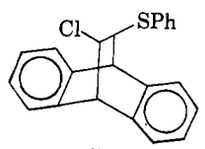
Received August 9, 1965

Proton magnetic resonance spectra for a number of 7- and 8-substituted dibenzobicyclo[2.2.2]octadienes have been measured. Correlations of these data lead to generalizations which permit stereochemical assignments for substituents in this system and permit differentiation of compounds in this system from those in the isomeric dibenzobicyclo[3.2.1]octadiene system.

In the course of elucidating the stereochemical consequences of some carbonium ion reactions in derivatives of dibenzobicyclo[2.2.2]octadiene (I)[2] and dibenzobicyclo[3.2.1]octadiene[2] and of some addition reactions to dibenzobicyclo[2.2.2]octatriene[3] and 7-chlorodibenzobicyclo[2.2.2]octatriene,[3] a large number of mono- and disubstituted dibenzobicyclo[2.2.2]-octadienes with known stereochemistry became available. Examination of the proton magnetic resonance spectra of these compounds led to useful correlations by which compounds in this system can be assigned stereochemical configurations and can also be distinguished from isomeric compounds in the dibenzobicyclo[3.2.1]-octadiene series.[4]



I



II

The structures and configurations of many of the compounds listed in Table I have been proved in this laboratory by chemical[2,3] and dipole moment[5] studies as previously reported. The remaining compounds will be described in detail in later papers.

The spectra discussed herein were obtained using a Varian Associates A-60 n.m.r. spectrometer operating at ambient temperature. Most spectra were taken in carbon tetrachloride solution, except that in a few cases that are noted, chloroform, deuteriochloroform, acetone, or benzene was used as the solvent for solubility reasons and, in some cases, to affect chemical shifts of protons to allow a more precise analysis of the spectrum. In general, saturated or supersaturated solutions of the compounds were used. The spectra were scanned over a range τ 1.7–10.0 using tetramethylsilane (τ 10) as an internal standard.

Since the chemical shifts of the protons were usually different enough to give separate peaks for each proton, it was possible to assign spectral frequencies to each of the four aliphatic protons in most of the 7,8-disubstituted dibenzobicyclo[2.2.2]octadienes and to each of the five aliphatic protons in most of the 7-substituted dibenzobicyclo[2.2.2]octadienes.

The basis for the spectral assignments for the disubstituted compounds may be illustrated by the proton assignments in the p.m.r. spectrum of *trans*-7-chloro-8-phenylthiodibenzobicyclo[2.2.2]octadiene (II). The spectrum of this compound has five absorption peaks, four of which correspond to the four different aliphatic hydrogens bound to carbon and the last of which corresponds to aromatic hydrogens. The absorptions at τ 5.68, 5.87, 6.06, and 6.57 show equal relative areas, while the complex absorption pattern around τ 2.85[6] integrates to 13 times each of the other absorptions.

The two lower-field aliphatic absorptions of II are doublets and the two higher-field absorptions are a triplet and a quartet. This indicates that the absorptions at τ 5.66 and 5.87 are due to the two benzhydrylic bridgehead hydrogens attached to C-1 and C-4. From the correlation of all of the p.m.r. spectra of the dibenzobicyclo[2.2.2]octadiene compounds listed in Table I, the data are consistent with this assignment. Similarly, the aliphatic hydrogens in diphenylmethane are at τ 6.08.[7]

From the data in Table I on the monosubstituted compounds (**14** and **17**), it is seen that the absorption of a benzhydrylic bridgehead hydrogen vicinal to a sulfur atom is at a higher field than is the absorption of a similar hydrogen vicinal to a chlorine atom. It is on this basis that the absorption at τ 5.66 is assigned to the hydrogen on C-1 (adjacent to chlorine) and the

(1) Paper XXXI: S. J. Cristol, R. M. Sequeira, and C. H. DePuy, *J. Am. Chem. Soc.*, **87**, 4007 (1965).

(2) (a) S. J. Cristol and R. K. Bly, *ibid.*, **82**, 6155 (1960); (b) S. J. Cristol, J. R. Mohrig, F. P. Parungo, D. E. Plorde, and K. Schwarzenbach, *ibid.*, **85**, 2675 (1963); (c) S. J. Cristol, Abstracts of the 18th National Organic Symposium of the American Chemical Society, Columbus, Ohio, 1963, p. 12; (d) S. J. Cristol and D. D. Tanner, *J. Am. Chem. Soc.*, **86**, 3122 (1964); (e) S. J. Cristol, F. P. Parungo, and D. E. Plorde, *ibid.*, **87**, 2870 (1965); (f) S. J. Cristol, F. P. Parungo, D. E. Plorde, and K. Schwarzenbach, *ibid.*, **87**, 2879 (1965).

(3) (a) S. J. Cristol and R. P. Arganbright, *ibid.*, **79**, 6039 (1957); (b) S. J. Cristol, R. P. Arganbright, and D. D. Tanner, *J. Org. Chem.*, **28**, 1374 (1963).

(4) For a discussion of the proton magnetic resonance spectra of compounds in the dibenzobicyclo[3.2.1]octadiene series, see S. J. Cristol, J. R. Mohrig, and D. E. Plorde, *ibid.*, **30**, 1956 (1965); A. R. Katritzky and B. Wallis, *Chem. Ind.* (London), 2025 (1964).

(5) D. D. Tanner and T. S. Gilman, *J. Am. Chem. Soc.*, **85**, 2892 (1963).

(6) In all of the spectra, the large complex multiplet around τ 2.5–3.5 was used only for the determination of relative peak areas. The splitting patterns and changes in chemical shifts of these hydrogens were not studied.

(7) G. V. D. Tiers, "Characteristic Nuclear Magnetic Resonance Shielding Values (Spectral Positions) for Hydrogen in Organic Structures," Central Research Department, Minnesota Mining and Manufacturing Co., Inc., St. Paul, Minn., March 28, 1958.