[CONTRIBUTION FROM THE DEPARTMENT OF PHARMACOLOGY OF THE HEBREW UNIVERSITY, HADASSAH MEDICAL SCHOOL]

β-Fluorostyrene

BY FELIX BERGMANN, ABRAHAM KALMUS AND ELI BREUER

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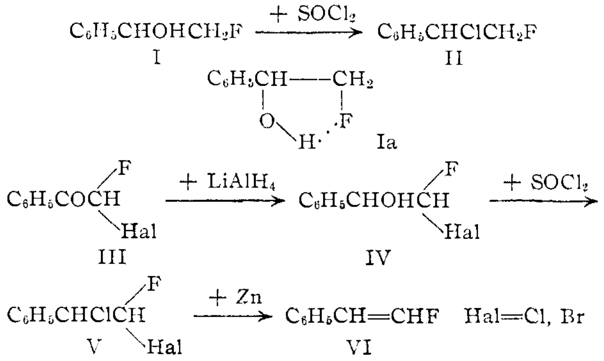
1-Phenyl-2-fluoroethanol or the corresponding chloride cannot be converted into β-fluorostyrene. The latter has been obtained by zinc dehalogenation of 1-phenyl-1,2-dichloro-2-fluoroethane. On the basis of the infrared spectrum, the β-fluorostyrene prepared appears to be the *trans* isomer. This monomer undergoes polymerization under the influence of cationic catalysts, such as stannic chloride.

β-Fluorostyrene (VI) was first described by Swarts,[1] who obtained this olefin by thermal decomposition of α-fluorocinnamic acid and characterized it as the dibromide. From his description it is not clear whether the substance was isolated in pure state and whether it tended to polymerize. In the 40 years since, β-fluorostyrene has been studied only very little, and Truce and Sack[2] did not succeed in preparing a potential starting material for this monomer, *viz.*, α-phenyl-β-fluoroethanol (I) (see below). However, higher fluorinated styrenes have been obtained by a number of authors. Thus, Cohen, Wolosinski and Scheuer[3] prepared α,β,β-trifluorostyrene, α-chloro-β,β-difluorostyrene and β-chloro-α,β-difluorostyrene by zinc dechlorination of the corresponding dichlorides. A somewhat different approach to α,β- and β,β-difluorostyrene and likewise to α,β,β-trifluorostyrene was used by Prober.[4]

α-Phenyl-β-fluoroethanol (I), which has become available recently as a reduction product of α-fluoroacetophenone,[5] was first studied as a source of β-fluorostyrene, but direct dehydration of the alcohol could not be realized. The fluorine present prevents the removal of the adjacent hydroxyl group by acid or base catalysis. This is probably the result of the strong negative inductive effect of fluorine, combined with its tendency to form a hydrogen bridge (as, *e.g.*, in Ia).

The resistance of I to dehydration is shared by derivatives bearing an additional β-halogen (fluorine,[4] chlorine or bromine). The latter two derivatives (IV) were synthesized in good yields by cautious reduction of the ketones III[6] with lithium aluminum hydride, but various dehydration procedures, using either acid or base catalysis, proved unsuccessful. Likewise, the alcohols IV did not form esters with anhydrides or acyl chlorides under a variety of experimental conditions. However, crystalline phenylurethans were isolated after heating the alcohols with phenyl isocyanate.

The alcohol I reacted smoothly with thionyl chloride to give the corresponding chloride II. However, all attempts to eliminate hydrogen chloride from this intermediate failed. The desired end-product VI finally was obtained by the following route: The alcohols IV were converted into the corresponding chlorides V, which were dehalogenated by zinc to VI.



$$\underset{\text{I}}{C_6H_5CHOHCH_2F} \xrightarrow{+\ SOCl_2} \underset{\text{II}}{C_6H_5CHClCH_2F}$$

$$\underset{\text{III}}{C_6H_5COCH(F)(Hal)} \xrightarrow{+\ LiAlH_4} \underset{\text{IV}}{C_6H_5CHOHCH(F)(Hal)} \xrightarrow{+\ SOCl_2}$$

$$\underset{\text{V}}{C_6H_5CHClCH(F)(Hal)} \xrightarrow{+\ Zn} \underset{\text{VI}}{C_6H_5CH{=}CHF} \quad Hal{=}Cl,\ Br$$

β-Fluorostyrene is a mobile liquid, with an ultraviolet spectrum very close to that of styrene. It can be kept in a deep-freezer for several weeks before decomposition becomes measurable. However, at room temperature it turns green within a few days, liberating HF. When an ethanolic solution of VI is stored in the refrigerator, slow polymerization takes place. This process can be accelerated by ionic catalysts, such as $SnCl_4$, so that it is complete within a fraction of a minute. Peroxidic catalysts, on the other hand, proved ineffective.[7] The polymer is soluble in benzene and can be precipitated from this solution by methanol.

In an analogous way, *p*,β-difluorostyrene was synthesized. Its properties are very similar to those of VI, and the ultraviolet spectra of the two styrene derivatives are practically indistinguishable. Some of the physical properties of β-halogenostyrenes are compared in Table I.

TABLE I

PHYSICAL PROPERTIES OF β-HALOGENOSTYRENES, $C_6H_5CH{=}CH{-}R$, FOR WHICH *trans*-STRUCTURE HAS BEEN ASSUMED

R	n^t_D	t, °C.	d^t_4	t, °C.	λ_{max}, mμ	ϵ_{max}
H	1.5441	25	0.9061	20	248	13350
	1.5469	20	0.9012	25		
F	1.5284	20	1.0098	19.5	242	13700
Cl	1.5762	25	1.1046	25	254	18900
Br	1.6072	25	....		258	18050
I	1.6598	25	....		264	19900

The alcohols IV and the corresponding chlorides V contain two centers of asymmetry. If both possible racemates are present in the synthetic products, dehalogenation by zinc should give rise to a mixture of *cis*- and *trans*-β-fluorostyrene, because in this reaction *trans* elimination has been shown to take place preferentially.[8a,b] However,

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[1] F. Swarts, *Bull. soc. chim.*, [4] **25**, 145 (1919).

[2] W. E. Truce and B. H. Sack, THIS JOURNAL, **70**, 3959 (1948).

[3] S. G. Cohen, H. T. Wolosinski and P. J. Scheuer, *ibid.*, **71**, 3439 (1949); **72**, 3952 (1950).

[4] M. Prober, *ibid.*, **75**, 968 (1953).

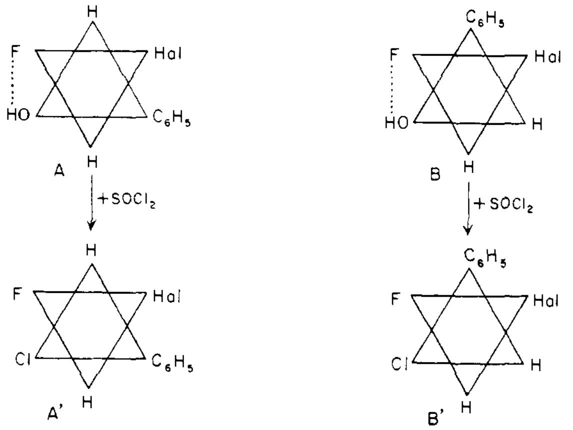
[5] F. Bergmann and A. Kalmus, *ibid.*, **76**, 4137 (1954).

[6] F. Bergmann, A. Kalmus and S. Vromen, *ibid.*, **77**, 2494 (1955).

[7] We have not yet studied the possibility of emulsion polymerization with free radical catalysts.

[8] (a) W. G. Young, Z. Jasaitis and L. Levanas, THIS JOURNAL, **59**, 403 (1937); (b) W. G. Young, S. J. Cristol and T. Skei, *ibid.*, **65**, 2099 (1943).

the presence of a fluorine atom may influence the conformation of a given structure in a decisive manner. Thus, the metal complex of IV, formed primarily during hydride reduction of a ketone III, will contain a coördinative bond to fluorine, and the free alcohols IV form an intramolecular hydrogen bridge, similar to Ia. Therefore, the two possible racemic forms of IV can be represented by A and B, respectively, B showing a less favorable distribution of mutually repelling substituents, because the phenyl is placed between the two halogens of the neighboring carbon.



The stereochemistry of the reaction of an alcohol with thionyl chloride, *in the absence of base*, has been studied by many investigators. Although this substitution in general produces Walden inversion, the opposite effect for carbinols bearing a phenyl group has been claimed by Kenyon and coworkers.[9,10] However, Gerrard later showed that phenylmethylcarbinol reacts with thionyl chloride partly with inversion and partly with retention of configuration.[11,12] In carbinols in which the neighboring carbon bears a halogen atom, reaction with thionyl chloride again proceeds preferentially with retention of configuration.[13] It is assumed that in this case a cyclic chloronium ion forms the intermediate and that the reaction is accompanied by an even number of inversions. Since both structural features, the neighboring phenyl and halogen groups, are present in the alcohols IV, one would expect retention of configuration to prevail so that A would give rise to the chloride A′ and B to B′; A′, upon reaction with zinc, will produce *trans*-β-fluorostyrene, and B′ the *cis* form.

In order to test the steric homogeneity of the intermediate V, we made use of the observation that zinc dehalogenation proceeds only to about 65%. If the chloride V represents a diastereomeric mixture—it was argued—then each racemate should react at a different rate and the residue should therefore be enriched in the more resistant form. The portion of V which could be recovered from the dehalogenation therefore was purified by fractionation. However, boiling point, refractive index and infrared spectrum of this material were indistinguishable from those of the original V. Moreover, the recovered chloride when exposed to the action of zinc again underwent dehalogenation to about 65%. This test, therefore, gave no indication for the presence of a mixture of diastereomers of V.

Direct information about the geometrical structure of β-fluorostyrene was sought from its infrared spectrum (Fig. 1a). *trans*-Olefins show a strong band at 10.1–10.4 μ, whereas *cis*-ethylenic derivatives are characterized by medium or weak absorption at 14–15 μ.[14] In vinyl halogenides, however, these out-of-the-plane hydrogen deformations are shifted; *e.g.*, Haszeldine[15] reported a band at 10.7 μ for *sym*-trifluoromethylvinyl halogenides. The spectrum of β-fluorostyrene reveals strong bands both at 10.85 and at 14.5 μ. Therefore, on this basis alone no definite conclusion about the configuration of VI can be drawn.

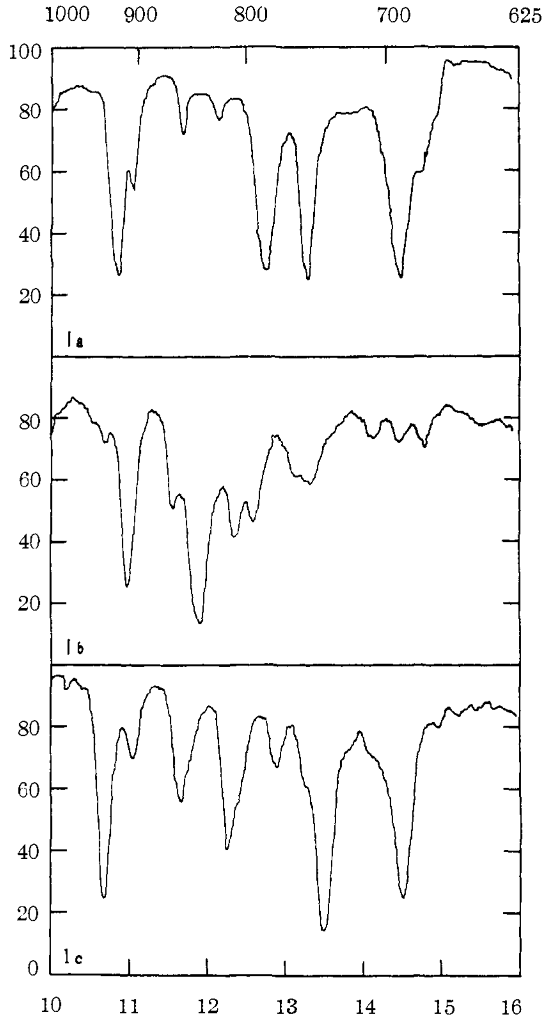


Fig. 1.—Infrared absorption spectra: a, β-fluorostyrene (VI); b, *p*,β-difluorostyrene; c, β-chlorostyrene.

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[9] J. Kenyon, A. G. Lipscomb and H. Philipps, *J. Chem. Soc.*, 415 (1930).

[10] J. Kenyon, H. Philipps and F. M. H. Taylor, *ibid.*, 382 (1931).

[11] W. Gerrard, *ibid.*, 85 (1944).

[12] W. Gerrard, *ibid.*, 741 (1946).

[13] H. J. Lucas and C. W. Gould, Jr., This Journal, **63**, 2541 (1941).

[14] N. Sheppard and D. M. Simpson, *Quart. Revs.*, **6**, 1 (1952).

[15] R. N. Haszeldine, *Nature*, **168**, 1028 (1951).

The problem could be clarified, however, by considering the infrared spectrum of p,β-difluorostyrene (Fig. 1b). Here again, strong absorption is exhibited near 11 μ, whereas the band between 14 and 15 μ has been replaced by a number of weak absorptions. A new, strong band at 11.9 μ is found instead (which is missing in Fig. 1a). The latter region is characteristic for p-disubstituted benzenes.[16]

The characteristic difference between the two spectra can thus be related to the transformation of the monosubstituted benzene VI into the p-disubstituted derivative, p,β-difluorostyrene. Indeed, it is well known that monosubstituted benzenes absorb strongly near 14.5 μ.[16] Therefore, β-fluorostyrene is characterized by the band at 10.85 μ predominantly as *trans*-olefin and the same conclusion can be applied with great probability to its p-fluoro derivative.

Infrared spectra have been used previously for the assignment of structures to geometrical isomers of β-halogenostyrenes. Thus, Grovenstein and Lee[17] reported for *trans*-β-bromostyrene strong absorption bands at 10.7 and 13.7 μ, whereas for the *cis* form they found the values 12 and 13μ. Cope and Burg,[18] on the other hand, ascribed the *cis* structure to a β-chlorostyrene showing strong bands at 10.7, 12.3 and 13.6 μ, and less pronounced absorption at 11.7 and 14.6 μ. In the light of the foregoing discussion, it appears probable that the material of Cope and Burg was predominantly *trans*-β-chlorostyrene, and that all *trans*-β-halogenostyrenes exhibit a characteristic strong band at 10.7–11 μ.

We have tried to obtain additional information on this question by preparing β-chlorostyrene from α,α-dichloroacetophenone in a reaction sequence analogous to III–VI. The infrared spectrum of β-chlorostyrene, represented in Fig. 1c, shows two strong bands at 10.7 and 14.5 μ and thus behaves again like VI and the material prepared by Cope and Burg by rearrangement of chlorocyclooctatetraene. Comparison of Fig. 1a and 1c reveals also certain characteristic differences. Whereas the C–Cl band appears in the latter at 13.5 μ, this is shifted for the C–F bond to 13.3 μ, as seen in Fig. 1a. The latter band is also present in Fig. 1b, but shows here only low intensity.

The stability of VI toward irradiation with ultraviolet light was tested in the hope to observe spectral changes, the direction of which would give some indication about the geometrical configuration of the compound. β-Fluorostyrene proved to be rather stable when irradiated for two hours, all characteristic bands of Fig. 1a remaining in their original position. However, the band at 10.9 μ decreased and the one at 14.5 μ *increased* in intensity. This may be interpreted as partial *trans*→*cis* conversion, since an additional band at 14.5 μ, characteristic for *cis*-α,β-disubstituted olefins, would become superimposed on the already existing band representing monosubstituted benzenes.

Experimental Part[19]

1-Phenyl-1-chloro-2-fluoroethane (II).—A mixture of 1-phenyl-2-fluoroethanol (11 g.) and thionyl chloride (20 g.) was refluxed for one hour, then decomposed with ice and extracted with benzene. After washing and drying, the solution was fractionated *in vacuo*. The chloride II distilled at 89–90° (15 mm.) as a mobile, colorless liquid of a pleasant, fragrant odor; yield 8.3 g., 67%, $n^{17}\text{D}$ 1.5182.

Anal. Calcd. for C_8H_8ClF: C, 60.8; H, 5.1. Found: C, 60.6; H, 5.2.

The chloride II was found resistant to a variety of dehydrohalogenating or dehalogenating agents, such as activated zinc dust, ethanolic potassium hydroxide or pyridine–acetic anhydride.

Reduction of α-Fluoro-α-chloroacetophenone.—A suspension of lithium aluminum hydride (1.2 g.) in absolute ether (60 ml.) was cooled to 0° and stirred vigorously. A solution of the above ketone (10 g.) in ether (40 ml.) was added dropwise during 30 min. A few minutes later the reaction mixture was decomposed with ice and sulfuric acid. The organic layer, after separation and washing, was fractionated to yield 8 g. (80%) of IV (Hal = Cl) as a colorless oil of b.p. 98° (2 mm.), $n^{20}\text{D}$ 1.5285.

Anal. Calcd. for C_8H_8ClFO: C, 55.0; H, 4.6. Found: C, 54.5; H, 4.6.

The carbinol IV (Hal = Cl) was heated on the water-bath for 2 hours with 2 equivalents of phenyl isocyanate. Upon trituration with petroleum ether, the reaction mixture crystallized. From ligroin, the N-phenylcarbamate of IV (Hal = Cl) was obtained in the form of long needles, m.p. 113–114°.

Anal. Calcd. for $C_{15}H_{13}ClFNO_2$: C, 61.3; H, 4.4; N, 4.8. Found: C, 61.0; H, 4.4; N, 4.6.

1-Phenyl-1,2-dichloro-2-fluoroethane (V, Hal = Cl).—The above carbinol (17 g.) and thionyl chloride (15 g.) were warmed in a bath at 50° for 30 min. The mixture was worked up as before to yield 15 g. (80%) of V (Hal = Cl) as a limpid, colorless oil of b.p. 81–83° (5 mm.), $n^{17}\text{D}$ 1.5275.

Anal. Calcd. for $C_8H_7Cl_2F$: C, 49.7; H, 3.6. Found: C, 49.9; H, 3.8.

β-Fluorostyrene (VI).—A suspension of activated zinc dust (24 g.) was covered with absolute ether (100 ml.) and refluxed under vigorous stirring. Freshly fused zinc chloride (10 g.) was added first and then dropwise a solution of 1-phenyl-1,2-dichloro-2-fluoroethane (24 g.) in ether (100 ml.). After a 3-hour reflux, the unreacted zinc was filtered off and the ethereal solution washed with 3% hydrochloric acid, then with water and finally dried over sodium sulfate. Fractionation through a short Vigreux column gave 10 g. (65%) of β-fluorostyrene as a colorless liquid of b.p. 24.5–25° (2 mm.), $n^{20}\text{D}$ 1.5284, $d^{19.5}$ 1.0098. The molar refraction, *MR*D, of β-fluorostyrene is 37.23, *i.e.*, 0.88 higher than the value for styrene (*MR*D 36.35).[20]

Anal. Calcd. for C_8H_7F: C, 78.7; H, 5.7. Found: C, 79.1; H, 5.9.

The dibromide of VI was prepared by adding dropwise a solution of bromine (1.4 g.) in carbon tetrachloride (10 ml.) at room temperature to a solution of VI (1 g.) in the same solvent. After standing overnight, air was passed through to remove the excess bromine, and the residue was redissolved in a small volume of petroleum ether. Upon cooling in acetone–Dry Ice, the dibromide was obtained as white crystals of m.p. 52–53°.[1] Recrystallization was effected in the same manner; yield of pure product 1.5 g. (64%).

Anal. Calcd. for $C_8H_7Br_2F$: C, 34.0; H, 2.5. Found: C, 34.4; H, 2.7.

1-Phenyl-2-bromo-2-fluoroethanol (IV, Hal = Br).—This carbinol was prepared in 72% yield from α-bromo-α-fluoroacetophenone[6] in the manner described for the corresponding chloro derivative. It forms a viscous oil of b.p. 102° (2 mm.), which is difficult to obtain analytically pure.

Anal. Calcd. for C_8H_8BrFO: C, 43.8; H, 3.65; F, 8.7. Found: C, 45.5; H, 3.9; F, 8.3.

The N-phenylcarbamate of this carbinol crystallized from ligroin in rods of m.p. 110–111°.

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(16) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 65.

(17) E. Grovenstein, Jr., and D. E. Lee, THIS JOURNAL, **75**, 2639 (1953).

(18) A. C. Cope and M. Burg, *ibid.*, **74**, 168 (1952).

(19) All m.p.'s are uncorrected.

(20) Landolt-Börnstein, "Physikalisch-Chemische Tabellen," Dritter Ergänzungsband, Julius Springer, Berlin, 1935, p. 1686.

Anal. Calcd. for $C_{15}H_{13}BrFNO_2$: C, 53.3; H, 3.85; N, 4.1. Found: C, 53.6; H, 3.7; N, 3.7.

1-Phenyl-1-chloro-2-bromo-2-fluoroethane (V, Hal = Br) was obtained from the above carbinol by reaction with thionyl chloride in 71% yield. The compound, b.p. 96–97° (3 mm.), could not be prepared analytically pure and retained a faint pink color even after repeated distillation.

Anal. Calcd. for C_8H_7BrClF: C, 40.4; H, 2.95. Found: C, 41.5; H, 3.15.

Dehalogenation of this chloride with zinc dust gave a 60% yield of β-fluorostyrene (VI).

Polymerization of β-Fluorostyrene.—To a solution of β-fluorostyrene (5 g.) in petroleum ether (25 ml.), cooled to 0°, was added dropwise a solution of $SnCl_4$ (2 ml.) in the same solvent (10 ml.). Each drop produced a strong exothermic reaction and formation of a precipitate. The mixture was left overnight, then the polymer was centrifuged and washed with petroleum ether. For purification it was dissolved in benzene and precipitated by addition of methanol. The white, granular material softened at 240–260°.

No polymerization occurred when β-fluorostyrene—in bulk or in benzene solution—was treated with benzoyl peroxide or *t*-butyl hydroperoxide. Likewise, β-fluorostyrene was not attacked by ethanolic potassium hydroxide at temperatures up to 60°.

***p*,β-Difluorostyrene.**—*p*,α-Difluoro-α-chloroacetophenone[21] was reduced by lithium aluminum hydride to 1-(*p*-fluorophenyl)-2-chloro-2-fluoroethanol, b.p. 68–70° (2 mm.), in 74% yield.

Anal. Calcd. for $C_8H_7ClF_2O$: C, 49.9; H, 3.6. Found: C, 50.2; H, 3.9.

This carbinol was converted by thionyl chloride in 70% yield into 1-(*p*-fluorophenyl)-1,2-dichloro-2-fluoroethane, b.p. 55–56° (2 mm.), n^{20}D 1.5102.

Anal. Calcd. for $C_8H_6Cl_2F_2$: C, 45.5; H, 2.8. Found: C, 46.0; H, 3.2.

Dehalogenation with zinc dust gave a 55% yield of *p*,β-difluorostyrene, b.p. 33° (2 mm.), n^{19}D 1.5040, $d^{19.5}$ 1.0345, *MR*D 40.06.

Anal. Calcd. for $C_8H_6F_2$: C, 68.6; H, 4.3. Found: C, 68.9; H, 4.3.

The polymer of *p*,β-difluorostyrene was prepared as described above.

Conversion of α,α-Dichloroacetophenone into β-Chlorostyrene.—Reduction of the above ketone with lithium aluminum hydride gave 85% of 1-phenyl-2,2-dichloroethanol, b.p. 170° (16 mm.) or 117° (4 mm.), m.p. 56°.[22] This carbinol was converted by thionyl chloride into 1-phenyl-1,2,2-trichloroethane, b.p. 130° (17 mm.).[23] Dehalogenation with zinc gave β-chlorostyrene in 60% yield, b.p. 89–92° (15 mm.), n^{13}D 1.5781.

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[21] F. Bergmann, A. Kalmus and E. Breuer, THIS JOURNAL, **79**, 4178 (1957).

[22] M. O. Forster and W. B. Saville, *J. Chem. Soc.*, **121**, 2595 (1922).

[23] H. Biltz, *Ann.*, **296**, 219 (1897).

JERUSALEM, ISRAEL

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF COLUMBIA UNIVERSITY]

The Reaction of Olefins with Oxygen and Phosphorus[1]

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The reaction of white phosphorus and oxygen with olefins, first described by Willstätter, has been found to be a radical chain process, accelerated by azobisisobutyronitrile and inhibited by hydroquinone. The slower oxidation of benzene solutions of phosphorus alone shows similar properties. The initial products have an approximate composition olefin·P_2O_4 and are proposed as having a polymeric anhydride structure containing one P per unit as a phosphonic anhydride, and one P as a phosphite anhydride. When these initial products are benzene-soluble further oxidation occurs to olefin·P_2O_5.

In 1681, Robert Boyle reported that the glow accompanying the oxidation of phosphorus in air was not observed with solutions of phosphorus in turpentine,[2] an observation which may be considered the first on the effect of olefins on the oxidation of phosphorus. The similar effect of ethylene on the slow combustion of solid white phosphorus was studied by Graham, in 1829,[3] and the subject continued to excite interest well into this century, providing one of the important bases for the theory of chain reactions developed by Semenoff.[4] In 1914, Willstätter and Sonnenfeld[5] published a short paper on the products obtained on exposure of benzene or cyclohexane solutions of phosphorus and olefins (chiefly cyclohexene) to oxygen, but the only subsequent work[6] we know of is the report by Montingnie[7] of the formation of an organophosphorus derivative from phosphorus and oxygen in the presence of an unsaturated steroid.

Willstätter[5] reported that phosphorus–cyclohexene mixtures in benzene rather rapidly took up oxygen on shaking to yield initially a product $C_6H_{10}P_2O_3$. Further oxygen absorption was "slower," giving finally a product $C_6H_{10}P_2O_4$. This "phosphorate" was a white or pale yellow, benzene-insoluble, hygroscopic solid which reacts vigorously with water, dissolving with evolution of heat. The only product identification involved treating the phosphorate with 40% HNO_3. Under these conditions the phosphorus was further oxidized and approximately half was liberated as phosphoric acid, precipitable by magnesium ion. The lead salt of an organophosphorus acid was precipitated from the filtrate with a lead analysis corresponding to $C_6H_9PO_3Pb$. These observations were rationalized by the formula scheme shown, although an intermediate β-hydroxyphosphonic acid was also postulated.

This and the following paper[8] describe some fur-

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[1] Work supported by the Chemical Corps, U. S. Army.

[2] R. Boyle, "New Experiments and Observations Made upon the Icy Noctiluca," London, 1681/2.

[3] T. Graham, *Quart. J. Science*, 83 (1829).

[4] For further bibliography and discussion see K. C. Bailey, "The Retardation of Chemical Reactions," Edward Arnold & Co., London, 1937, Chapters 3 and 6.

[5] R. Willstätter and E. Sonnenfeld, *Ber.*, **47**, 2801 (1914).

[6] Willstätter explains his rather incomplete results as follows: "Durch den Eintritt meines Mitarbeiters in den Militardienst bin ich gezwungen worden, die Arbeit abzubrechen. . . ." Apparently the investigation was never resumed.

[7] Montingnie, *Bull. soc. chim.*, **49**, 73 (1931).

[8] C. Walling, F. R. Stacey, S. E. Jamison and E. S. Huyser, THIS JOURNAL, **80**, 4546 (1958).