[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

The Acid-catalyzed Rearrangement of Phenylethynylcarbinols

BY EDWARD E. SMISSMAN,[1] RUSSELL H. JOHNSEN, ARTHUR W. CARLSON AND BEN F. AYCOCK

RECEIVED DECEMBER 5, 1955

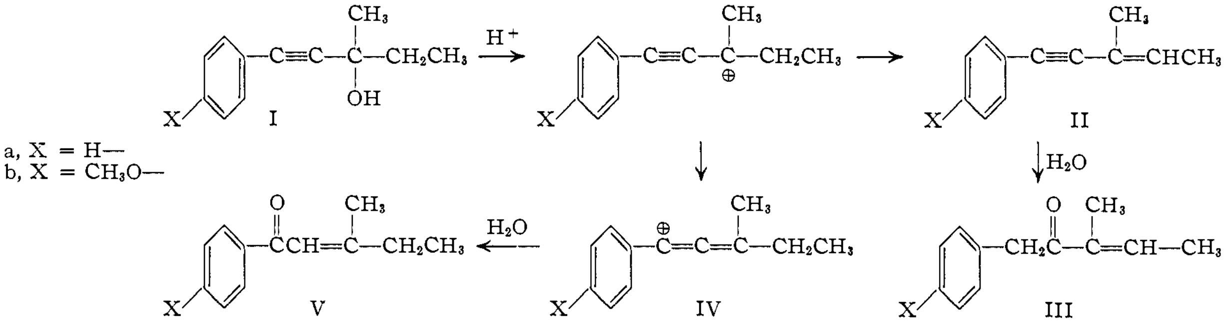
The acid-catalyzed rearrangements of five phenylethynylcarbinols, which are capable of rearranging by either the Rupe or Meyer–Schuster mechanisms, have been investigated. The course of rearrangement and structure of the products have been determined. It has been demonstrated that a methoxyl group in the *para* position of a phenylethynylcarbinol is capable of changing the course of hydration of the Rupe rearrangement intermediate.

Acetylenic carbinols, $R_1—C\equiv C—C(OH)R_2R_3$, have been reported to undergo at least two different types of rearrangement on treatment with acidic reagents. These reactions are now well known as the Meyer–Schuster and Rupe rearrangements.[2-7] The Meyer–Schuster rearrangement has been postulated to proceed through the formation of an allenic carbonium ion intermediate, while the Rupe reaction has been shown to form a vinylacetylene intermediate.[7]

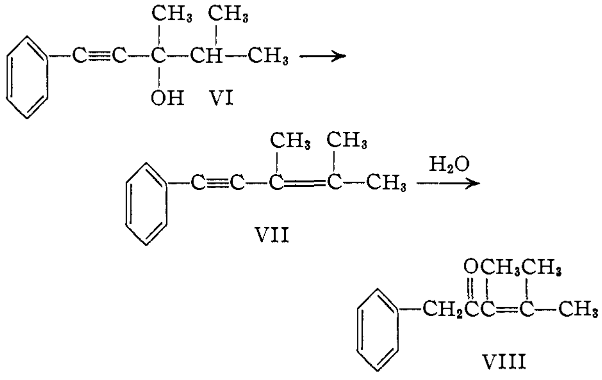
The purpose of this work was to investigate the course of rearrangement in molecules which were capable of both the Meyer–Schuster type reaction (formation of an allenic intermediate) and the Rupe type reaction (formation of a vinyl acetylene intermediate).

The compounds utilized in this study were methylethyl-(phenylethynyl)-carbinol (Ia), methylisopropyl-(phenylethynyl)-carbinol (VI), *t*-butyl-(phenylethynyl)-carbinol (IXa), methylethyl-(*p*-methoxyphenylethynyl)-carbinol (Ib), and *t*-butyl-(*p*-methoxyphenylethynyl)-carbinol (IXb).

Methylethyl-(phenylethynyl)-carbinol (Ia), on treatment with 88% formic acid, rearranged to yield an unsaturated ketone. Ozonolysis of this ketone yielded acetaldehyde and phenylacetic acid, the latter arising from a cleavage of benzyl methyl glyoxal. This demonstrated the rearrangement product to be 1-phenyl-3-methyl-3-pentene-2-one (IIIa)



The rearrangement of methylisopropyl-(phenylethynyl)-carbinol (VI) under similar conditions afforded an α,β-unsaturated ketone in 75% yield. On degradation by means of ozonolysis, acetone and phenylacetic acid were produced. Thus it is apparent that the ketone produced is 1-phenyl-3,4-dimethyl-3-pentene-2-one (phenylacetyltrimethylethylene) (VIII). Reverse aldolization of this rearrangement product yielded ethyl benzyl ketone and acetone.



The rearrangement of *t*-butyl-(phenylethynyl)-carbinol (IXa) was conducted by refluxing with a large excess of 88% formic acid under a nitrogen atmosphere for a period of 8 hr. A mixture of isomeric ketones was obtained in about 75% yield.

The first evidence of the identity of the components of the mixture was obtained from the ultraviolet absorption spectra. Two poorly defined maxima were evident at 243 and 250 mμ in isoöctane. These maxima are near the absorption maxima exhibited by phenylacetyltrimethylethylene (VIII) (245 mμ) and pivalacetophenone (XIIa) (250 mμ), respectively (see next set of formulas).

The mixture of unsaturated ketones was hydrogenated to the saturated ketones over 5% palladium-on-strontium carbonate. The ultraviolet absorption spectrum of the hydrogenated material (λ_{max} 238 mμ) was similar to the spectrum of γ,γ-dimethylvalerophenone, the hydrogenation product of pivalacetophenone (XIIIa). The hydrogenation product of phenylacetyltrimethylethylene (VIII) would not be expected to exhibit intense

---

(1) College of Pharmacy, University of Wisconsin, Madison, Wisconsin.

(2) K. H. Meyer and K. Schuster, *Ber.*, **55**, 819 (1926).

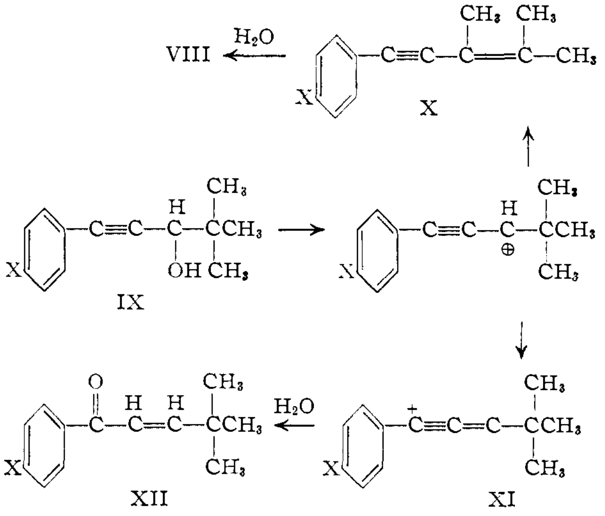
(3) H. Rupe, *et al.*, *Helv. Chim. Acta*, **11**, 965 (1928); **12**, 193 (1929); **14**, 687 (1931); **16**, 685 (1933).

(4) F. G. Fischer and K. Lowenberg, *Ann.*, **475**, 203 (1929).

(5) C. D. Hurd and R. E. Christ, THIS JOURNAL, **59**, 118 (1937).

(6) J. D. Chanley, *ibid.*, **70**, 244 (1948).

(7) G. F. Hennion, *et al.*, *ibid.*, **71**, 2813 (1949); **77**, 3253 (1955).



a, X = H—
b, X = CH_3O—

absorption in this region, since the carbonyl group is not conjugated with the benzene ring.

The infrared analysis indicated pivalacetophenone phenylacetyltrimethylethylene and ethyl benzyl ketone to be present in the reaction mixture in mole percentages of 24, 59 and 7, respectively. These concentrations of the products in the rearrangement mixture, in conjunction with the yield, indicate that the isomeric unsaturated ketones, XIIa and VIII, were originally formed in yields of 24 and 47%, respectively. The formation of phenylacetyltrimethylethylene is explained by a Wagner–Meerwein shift of a methyl group prior to formation of the vinylacetylene intermediate. The allenic type intermediate must occur if the alkyl migration does not take place. The latter would give rise to pivalacetophenone.

t - Butyl - (*p* - methoxyphenylethynyl) - carbinol (IXb) in the presence of 88% formic acid rearranged to form *p*-methoxypivalacetophenone (XIIb) in 85% yield. The structure of the ketone was established on the basis of the ozonolysis products anisic acid and pivalic aldehyde. The rearrangement product was also synthesized by an aldol condensation of pivalic aldehyde and *p*-methoxyacetophenone.

On treating methylethyl-(*p*-methoxyphenylethynyl)-carbinol (Ib) with 88% formic acid, the principal product was a tar. A more dilute acid (44%) gave the vinyl acetylenic material, IIb, as the chief product. The structure of the dehydrated carbinol was established by the formation of anisic acid and acetaldehyde on ozonolysis and by its characteristic ultraviolet absorption.[8] In the presence of glacial acetic acid containing about 1% concentrated sulfuric acid at 70–80° for 20 minutes, methylethyl-(*p*-methoxyphenylethynyl)-carbinol (Ib) rearranged to 1-*p*-methoxyphenyl-3-methyl-2-pentene-1-one (Vb) in 45% yield. The ketone was accompanied by varying amounts of the enyne, IIb, depending upon the period of reaction. When the reaction was allowed to proceed for 15 hr., there was 5–6% *p*-methoxyacetophenone present in the reaction mixture. This material was formed through a reverse aldol condensation of the unsaturated ketone, Vb.

The structure of the product of rearrangement was indicated by ozonolysis to be Vb in that the products were anisic acid and methyl ethyl ketone. The compound absorbed one mole of hydrogen to produce a saturated ketone which was identical with the ketone synthesized from β-methylvaleroyl chloride and anisole by the method of Wilds and Biggerstaff.[9]

Discussion

The results of the experiments involving *t*-butyl-(*p*-methoxyphenylethynyl)-carbinol (IXa) are to be contrasted with those obtained for *t*-butyl-(phenylethynyl)-carbinol (IXb). For the latter compound it was shown that the primary reaction product resulted from the initial migration of a product which would be expected if the Rupe type mechanism had been involved. In the case of the methoxy compound the rearrangement product can be explained by assuming that the methoxy group suppresses the tendency of the carbonium ion formed to stabilize itself by the migration of a methyl group. The ketone which then results is that which would be predicted if the Meyer–Schuster rearrangement were to take place.

In the case of methylethyl-(*p*-methoxyphenylethynyl)-carbinol (Ib), the situation is more complicated. The product obtained is that which would result from an allenic type intermediate, *i.e.*, a Meyer–Schuster rearrangement. However, the compound devoid of the *para*-methoxyl group underwent only the Rupe rearrangement.

The postulated intermediate in the Rupe rearrangement is the enyne arising by dehydration of the carbinol. The ketonic product results from the hydration of the triple bond of this intermediate. The vinyl acetylenic compound, IIb, isolated in the present work, could be converted to the unsaturated ketone, Vb, by further treatment with acid, but the resulting ketone has the structure anticipated on the basis of a Meyer–Schuster rearrangement rather than that associated with the Rupe for which such an intermediate is postulated. This leads to the conclusion that the *para*-methoxyl group causes a polarization of the acetylenic bond in the enyne intermediate so as to allow hydration to occur at the carbon atom adjacent to the ring.

Experimental

Preparation of Methylethyl-(phenylethynyl)-carbinol (Ia).—Thirty grams (0.294 mole) of phenylacetylene and 22.0 g. (0.305 mole) methyl ethyl ketone were added to 100 ml. of absolute ether. The flask was cooled to 0°, while 20 g. of potassium hydroxide pellets were being powdered under ether. The powdered potassium hydroxide was added to the flask. The reaction mixture was stirred mechanically for 11 hr. and allowed to stand overnight at 0°.

The mixture was transferred to a large beaker and mixed well with powdered, solid carbon dioxide, after which the solution was filtered from the precipitated potassium carbonate. The ether was removed and the residue was distilled *in vacuo*. The fraction boiling at 151–154° (30 mm.) was collected, 38.29 g. (74.4%) of a clear viscous liquid (lit. b.p. 138–140° (15 mm.)).[10]

---

(8) I. Heilbron, *et al.*, *J. Chem. Soc.*, 1583 (1947).

(9) A. L. Wilds and W. R. Biggerstaff, THIS JOURNAL, **67**, 789 (1945).

(10) Bork, *J. Russ. P. C. Soc.*, **37**, (1905); *Brit. Chem. Abs.*, **I**, 774, (1905).

Preparation of Methylisopropyl-(phenylethynyl)-carbinol (VI).—Twelve grams (0.5 mole) of magnesium and 73 g. (0.7 mole) of ethyl bromide were allowed to react in 100 ml. of anhydrous ether. After the reaction had subsided, 61 g. (0.6 mole) of phenylacetylene was added and allowed to reflux for 6 hr. After cooling the reaction mixture, 34 g. (0.4 mole) of methyl isopropyl ketone was added dropwise with stirring. The mixture was then refluxed for 2 hr. The Grignard complex was decomposed with ice and sufficient acetic acid to form the soluble magnesium salt. The excess acid was neutralized with 10% sodium bicarbonate and the neutral organic material extracted with two 100-ml. portions of ether. The combined extracts were washed with water and dried over anhydrous sodium sulfate. After removal of ether, the residue was distilled. Twelve grams of unchanged phenylacetylene, b.p. 30–40° (10 mm.), was collected. The impure product was collected, 120–135° (10 mm.) and a residue of 14 g. of tarry material remained. The impure product was redistilled through a 10-in. Vigreux column under reduced pressure yielding 60.3 g. (80%) of carbinol, b.p. 128–132° (8 mm.), $n^{25}\text{D}$ 1.5378. The liquid readily crystallized to give a white solid mass, m.p. 42–43° (lit. b.p. 136–137° (12 mm.), m.p. 41°), $\lambda_{\max}$ 240 mμ, $\lambda_{\max}^{\text{EtOH}}$ 19,600; $\lambda_{\max}$ 251 mμ, $\lambda_{\max}^{\text{EtOH}}$ 17,700.

Preparation of *t*-Butyl-(phenylethynyl)-carbinol (IXa). (A) From Phenylacetylene and Pivaldehyde.—Two and four tenths grams (0.1 mole) of magnesium and 15 g. (0.14 mole) of ethyl bromide were allowed to react in 25 ml. of anhydrous ether. After the initial reaction had subsided, 11.0 g. (0.108 mole) of phenylacetylene was added and allowed to reflux for 5 hr. The reaction mixture was cooled and 19.0 g. (0.22 mole) of pivaldehyde was added dropwise with stirring. The mixture was allowed to reflux for 1 hr. The complex was decomposed by pouring the cooled mixture over crushed ice and acetic acid. The aqueous solution was extracted with ether and the extracts washed with dilute potassium bicarbonate, followed by water. The ether extracts were dried over anhydrous potassium carbonate. The ether was removed and the residue distilled under reduced pressure. The carbinol, b.p. 133–135° (8 mm.), was obtained in 42% yield (7.9 g.) as a viscous, light yellow liquid $n^{25}\text{D}$ 1.5340. *Anal.* Calcd. for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 82.52; H, 8.56.

The 3,5-dinitrobenzoate was prepared by the procedure of Shriner and Fuson[11] and recrystallized from ethanol, m.p. 137.0–137.5°. *Anal.* Calcd. for $C_{20}H_{18}O_6N_2$: C, 62.82; H, 4.74; N, 7.33. Found: C, 62.74; H, 4.91.

(B) From Phenylpropargyl Aldehyde and *t*-Butyl Chloride.—The Grignard reagent of *t*-butyl chloride was prepared by the procedure of Whitmore and Houk.[12] To 30.4 g. (0.26 mole) of magnesium turnings was added a crystal of iodine and 5 ml. of a solution containing 117 g. (1.25 mole) of *t*-butyl chloride in 158 ml. of dry ether. As soon as the reaction began, 65 ml. of dry ether was added and then 158 ml. of the solution was added dropwise with stirring at a rate sufficient to maintain gentle refluxing. The remaining solution was diluted with 95 ml. of dry ether and the addition continued in the same manner. After all the halide had been added, the mixture was refluxed for 1 hr. and then 130 g. (1.0 mole) of phenylpropargyl aldehyde, b.p. 118–120° (18 mm.), in 150 ml. of dry ether was added at a rate which maintained gentle refluxing. Reflux was continued for 1 hr. after addition was complete and the reaction mixture then allowed to cool. The complex was decomposed by the use of saturated ammonium chloride solution. The layers were separated. After removal of ether from the non-aqueous layer, the residual oil was fractionated under reduced pressure. Sixty-five and one tenth grams (50% yield) of the desired carbinol, b.p. 138–139° (11 mm.), was collected. Upon cooling the carbinol solidified and was recrystallized from petroleum ether (b.p. 60–68°) to give small colorless prisms, m.p. 45–46°, $\lambda_{\max}$ 241 mμ, $E_{\max}^{\text{EtOH}}$ 19,500, $\lambda_{\max}$ 251 mμ, $E_{\max}^{\text{EtOH}}$ 16,800. *Anal.* Calcd. for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 83.32; H, 8.59.

Preparation of Methylethyl-(*p*-methoxyphenylethynyl)-carbinol (Ib).—To a solution of 13 g. of potassium in 300 ml. of anhydrous *t*-butyl alcohol was added 42.0 g. (0.296 mole) of *p*-methoxyphenylacetylene and the solution allowed to stand at room temperature for 30 minutes. In the meantime a solution of 48.0 g. (0.666 mole) of redistilled methyl ethyl ketone (b.p. 78–80°) in 250 ml. of anhydrous ether was cooled to −10°. The solution of potassium acetylide was then added dropwise, with stirring, over a period of 3 hr. and the mixture stirred for an additional 9 hr. with the bath temperature rising during this period to 15°. At the end of this interval, 20 g. of ammonium chloride in 500 ml. of water was added, the aqueous phase was saturated with sodium chloride, separated from the ethereal layer and re-extracted with two 50-ml. portions of ether. The extracts were combined and dried over anhydrous sodium sulfate. The ether and *t*-butyl alcohol were removed by distillation at atmospheric pressure and the higher boiling residue distilled under reduced pressure. The fraction boiling at 165–170° (10 mm.) was collected as carbinol, 44.0 g. (75% based on phenylacetylene). Redistillation afforded a product boiling at 175–176° (13 mm.), $n^{25}\text{D}$ 1.5538; $\lambda_{\max}$ 254 mμ $E_{\max}^{\text{EtOH}}$ 24,000. *Anal.* Calcd. for $C_{13}H_{16}O_2$: C, 76.40; H, 7.8. Found: C, 76.09; H, 7.9.

Preparation of *p*-Methoxyphenylacetylene.—To a solution of 13.0 g. of potassium in 600 ml. of *t*-butyl alcohol (which had been distilled from sodium) was added 61.0 g. (0.286) of distilled *p*-methoxy-ω-bromostyrene and the mixture heated on the steam-bath for 3 hr. At the end of this period about 300 ml. of the alcohol was removed by distillation and 400 ml. of distilled water added to dissolve the potassium bromide which had precipitated. The resulting solution was extracted three times with 75-ml. portions of ether and the combined extracts dried over anhydrous sodium sulfate. After the ether and remaining *t*-butyl alcohol were removed at atmospheric pressure, the residue was distilled under reduced pressure and the fraction boiling 90–95° (10 mm.) was collected, giving 27.0 g. (72%) (lit. b.p. 89–94° (15 mm.)).

***p*-Methoxy-ω-bromostyrene** was prepared in 80% yield by the action of bromine and sodium carbonate on *p*-methoxycinnamic acid.[13]

p-Methoxycinnamic acid was prepared in 74% yield from anisaldehyde and malonic acid by the procedure of Robinson and Shinoda.[14]

Preparation of *p*-Methoxyphenylethynyl-*t*-butylcarbinol (IXb).—This carbinol was prepared by a procedure analogous to that employed for methylethyl-(*p*-methoxyphenylethynyl)-carbinol. The fraction boiling 179–180° (15 mm.) gave 21.0 g. of (49%) the carbinol, $\lambda_{\max}$ 253 mμ, $E_{\max}^{\text{EtOH}}$ 24,000. *Anal.* Calcd. for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 76.67; H, 8.08.

Rearrangement of Methylethyl-(phenylethynyl)-carbinol.—Thirty-eight g. (0.218 mole) of methylethyl-(phenylethynyl)-carbinol and 300 ml. of 88% formic acid were refluxed vigorously for 3 hr. The reaction mixture became cloudy and a clear, red oil rose to the surface. After cooling, the mixture was transferred to a beaker and neutralized with solid sodium bicarbonate. Benzene was added to the reaction mixture, and the layers were separated; the aqueous solution was extracted three times with 50-ml. portions of benzene and the extracts combined with the original benzene solution. The benzene was removed by distillation, and the residue was fractionated under reduced pressure using a modified Claisen flask; yield 16.1 g. (42%) of a pale-yellow viscous liquid, b.p. 154–157° (24 mm.), $n^{20}\text{D}$ 1.5418, $d^{20}{}_4$ 1.005. *Anal.* Calcd. for $C_{12}H_{14}O$: C, 82.7; H, 8.1. Found: C, 82.49; H, 8.47.

Hydrogenation of Rearrangement Product of Methylethyl-(phenylethynyl)-carbinol.—Five grams (0.029 mole) of rearrangement ketone in 100 ml. of methanol was refluxed for 10 minutes with Raney nickel. The solution was centrifuged and the methanol solution decanted from the Raney nickel and this solution placed in a narrow-mouth, heavy-wall hydrogenation bottle. One gram of 5% palladium suspended on strontium carbonate was added. The theoretical amount of hydrogen was consumed during a period of 30 minutes. The solution was filtered, the methanol removed *in vacuo* and the residue distilled; yield 3.84 g. (75.4%) of clear, colorless liquid, b.p. 127–128 (17 mm.), $n^{20}\text{D}$ 1.5019, $d^{20}{}_4$ 0.964. *Anal.* Calcd. for $C_{12}H_{16}O$: C, 81.8; H, 9.2. Found: C, 81.77; H, 9.37.

Ozonolysis of the Rearrangement Product of Methylethyl-(phenylethynyl)-carbinol. (A).—One gram of ketone and

---

[11] R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1946.

[12] F. C. Whitmore and A. L. Houk, THIS JOURNAL, **54**, 3716 (1932).

[13] W. Manchot, *Ann.*, 387 (1912).

[14] R. Robinson and J. Shinoda, *J. Chem. Soc.*, **127**, 1977 (1925).

30 ml. of methylene chloride were placed in a gas wash bottle. Ozone was passed through the solution at −30° until escaping gas caused acidified 5% potassium iodide to turn red instantly.

Decomposition of Ozonide.—One gram of powdered zinc and 20 ml. of water were placed in a 150-ml. erlenmeyer flask, which was fitted with a 50-ml. dropping funnel and a glass delivery tube. The delivery tube extended through a rubber stopper to the bottom of a 7-inch test-tube. The flask was placed on a steam-bath and the test-tube was filled $^3/_4$ full with 2,4-dinitrophenylhydrazine reagent, (2,4-DNPH).[11] The methylene chloride solution of the ozonide was placed in the dropping funnel and added dropwise to the flask. Escaping gases passed into 2,4-DNPH, turning the solution cloudy. After 10 ml. of the ozonide solution had been added to the flask, heat was applied gently and methylene chloride was distilled. The 2,4-dinitrophenylhydrazone dissolved in the methylene chloride as it formed, and the acidified 2,4-DNPH remained in the aqueous upper layer. When the upper layer of reagent would no longer give an immediate test with acetone, it was replaced by fresh 2,4-DNPH solution. This procedure was carried out until all reaction mixture had been added and no more methylene chloride remained on the bottom of the flask. The methylene chloride solution was separated from the aqueous solution and evaporated under a stream of nitrogen. A yellow 2,4-dinitrophenylhydrazone remained. Upon recrystallization from alcohol, a yellow crystalline solid was obtained, m.p. 162–163.5° (lit. 168°). No depression was obtained when admixed with an authentic sample of acetaldehyde-2,4-DNPH. *Anal.* Calcd. for $C_8H_8O_4N_4$: C, 42.9; H, 3.6. Found: C, 43.36; H, 3.41.

(**B**).—One gram of rearrangement ketone and 30 ml. of ethyl acetate were placed in a gas wash bottle and ozone was passed through as in procedure A.

The ethyl acetate was evaporated under reduced pressure and replaced by 5 ml. of water and 2 ml. of hydrogen peroxide. The ozonide was allowed to stand overnight and was then refluxed for 1 hr. and was allowed to cool. Clear, colorless plates crystallized out of the water solution on standing, m.p. 76.5–77.5°. A mixed melting point determination with an equal portion of phenylacetic acid and crystals from the decomposition of the ozonide gave no depression of melting point.

Rearrangement of Methylisopropyl-(phenylethynyl)-carbinol.—The rearrangement was carried out by refluxing 9.4 g. (0.05 mole) of the carbinol, m.p. 42–43°, in 100 ml. 88% formic acid for 2 hr. An oily layer rapidly formed on the surface of the liquid, but most of it appeared to redissolve during the first hour. The solution was transferred to a separatory funnel containing 50 ml. of saturated sodium chloride solution and extracted twice with benzene. The combined benzene extracts were washed with water, dilute sodium bicarbonate solution, again with water and then dried over anhydrous potassium carbonate. After removal of solvent the residual oil was distilled under reduced pressure. The fraction boiling 128–135° (7 mm.) was collected, 7.16 g. (76%), n^{25}_{D} 1.5278, $\lambda_{\max}$ 251 mμ, $E^{\mathrm{EtOH}}_{\max}$ 5,550. *Anal.* Calcd. for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 83.13; H, 8.66. 2,4-Dinitrophenylhydrazone, m.p. 147–148°, $\lambda_{\max}$ 367 mμ, $E^{\mathrm{CHCl_3}}_{\max}$ 25,000. *Anal.* Calcd. for $C_{19}H_{20}O_4N_4$: C, 61.94; H, 5.47; N, 15.21. Found: C, 62.10; H, 5.42; N, 14.68. Semicarbazone, m.p. 116.5–118°, $\lambda_{\max}$ 230 mμ, $E^{\mathrm{EtOH}}_{\max}$ 14,000. *Anal.* Calcd. for $C_{14}H_{19}N_3$: C, 68.45; H, 7.81; N, 17.13. Found: C, 68.32; H, 7.55.

Ozonization of Rearrangement Product of Methylisopropyl-(phenylethynyl)-carbinol.—Ozone was passed through a solution of 2 g. of rearrangement product in 30 ml. ethyl acetate until the escaping gases liberated iodine from a solution of acidified 5% potassium iodide. The solvent was removed and replaced by 20 ml. of water and allowed to stand overnight. The mixture was refluxed for 1 hr. The volatile components were then passed into 2,4-dinitrophenylhydrazine reagent. The residue was extracted with ether and upon evaporation of the ether left a white solid residue weighing 1.05 g. On recrystallization from water 0.80 g. of white leaflets, m.p. 75–76°, were obtained. A mixed melting point with phenylacetic acid, m.p. 75–76°, showed no depression.

The 2,4-dinitrophenylhydrazone of the volatile material was recrystallized from ethanol, m.p. 124–126°. Admixture with an authentic sample of 2,4-dinitrophenylhydrazone, m.p. 126–127°, showed no depression in melting point.

Reversed Aldolization of Phenylacetyltrimethylethylene (VIII).—A 6.75-g. (0.036 mole) sample of phenylacetyltrimethylethylene and 65 ml. of 88% formic acid were placed in a 200-ml. round-bottom flask fitted with a reflux condenser and a nitrogen inlet tube. The solution was refluxed for 23 hr. During the reflux period, volatile material was collected by passing a tube from the top of the condenser into an 8-inch test-tube immersed in a Dry Ice-bath. The mixture was heated an additional hour without running water in the condenser.

Thirty milliliters of a saturated solution of sodium chloride was added to the reaction mixture, and the mixture was then extracted with benzene. The extracts were washed with water, sodium bicarbonate solution and finally with water. The benzene solution was dried over potassium carbonate. The solvent was removed *in vacuo* and the residue distilled; yield 4.89 g., b.p. 120–123° (22 mm.), n^{25}_{D} 1.5110. This corresponds to 92% yield of ethyl benzyl ketone.

A 2,4-dinitrophenylhydrazone was prepared from the distillate, m.p. 146–147°. This material showed no depression of melting point when mixed with an authentic sample of the 2,4-dinitrophenylhydrazone of ethyl benzyl ketone, m.p. 146–147°.

The 2,4-dinitrophenylhydrazone of the volatile fragment upon recrystallization from ethanol, m.p. 126–126.5°, showed no depression of melting point when mixed with 2,4-dinitrophenylhydrazone of acetone, m.p. 126–127°.

Rearrangement of *t*-Butyl-(phenylethynyl)-carbinol.—A solution of 18.8 g. of *t*-butyl-(phenylethynyl)-carbinol in 200 ml. of 88% formic acid was refluxed under nitrogen for 8 hr. The solution was cooled, mixed with 100 ml. of saturated sodium chloride solution and extracted with two 50-ml. portions of benzene. The benzene extracts were washed with water, dilute sodium bicarbonate and again with water. The resulting non-aqueous solution was dried over anhydrous potassium carbonate. The solvent was removed and the residual oil distilled to give 14.9 g. of crude product, b.p. 60–85° (0.2 mm.). Fractional distillation of the crude product through a 10-in. Vigreux column gave the following fractions: (1) 6.52 g., 70–73° (0.2 mm.), n^{25}_{D} 1.5110; (2) 1.77 g., 73–75° (0.2 mm.), n^{25}_{D} 1.5290; (3) 5.32 g., 75–80° (0.2 mm.), n^{25}_{D} 1.5300. Fractions 2 and 3 exhibited maxima in the ultraviolet at 256 mμ, $E^{\mathrm{EtOH}}_{\max}$ 9,100, 9,050, respectively.

Fraction 1: d^{25}_{4} 0.9822, n^{25}_{D} 1.5110, b.p. 70° (0.2 mm.), 117–119° (18 mm.). Ethyl benzyl ketone reported constants d^{20}_{4} 0.9877, n^{20}_{D} 1.5113, b.p. 121–122° (23 mm.); *MR* calcd. 44.7, *MR* found 45.1.

A 2,4-dinitrophenylhydrazone of fraction 1, m.p. 146–147°, showed no depression when mixed with an authentic sample of ethyl benzyl ketone 2,4-dinitrophenylhydrazone, m.p. 146–147°. Semicarbazone of fraction 1, m.p. 148–150°.

The 2,4-dinitrophenylhydrazone was prepared from 0.210 g. of fraction 3. Recrystallization of the crude precipitate from ethanol–ethyl acetate gave a first crop of 0.105 g. of red needles, m.p. 179–183° and a second crop of 0.177 g. of orange yellow powder, m.p. 129–138°. On recrystallization the first crop gave red needles, m.p. 188–190°, which did not depress the melting point of the 2,4-dinitrophenylhydrazone of pivalacetophenone. The second crop was recrystallized to give 0.065 g. of orange red plates, m.p. 145–147°, which did not depress the melting point of the 2,4-DNPH of the rearrangement product of methylisopropyl-(phenylethynyl)-carbinol, phenylacetyltrimethylethylene.

To 150 ml. of glacial acetic acid and 15.0 g. (0.074 mole) of methylethyl-(*p*-methoxyphenylethynyl)-carbinol was added 0.2–0.3 ml. of concentrated sulfuric acid, immediately after which the solution became dark purple in color. After standing at room temperature for a period of 1.75 hr., the solution was heated on the steam-bath for 20 minutes, then poured into 500 ml. of distilled water and neutralized with sodium carbonate. After cooling, the mixture was extracted with five 50-ml. portions of ether, the ether extracts combined and dried over Drierite. Removal of the ether left a mobile brown liquid weighing 13.95 g. This material was distilled under reduced pressure through a 15 cm. Vigreux column: (1) 4.86 g., b.p. 81.5–86.0° (0.05 mm.), n^{25}_{D} 1.5795; (2) 3.46 g., b.p. 86.0–99.5° (0.05 mm.),

$n^{25}\mathrm{D}$ 1.5802; (3) 1.67 g., b.p. 91–102° (0.09 mm.), $n^{25}\mathrm{D}$ 1.5610; (4) 2.00 g., b.p. 102–112° (0.09 mm.), $n^{25}\mathrm{D}$ 1.5598; (5) 1.6 g. residue.

The 2,4-dinitrophenylhydrazone of fraction 4 was prepared, m.p. 142–145°. This material could not be separated further by chromatographing on an acid-washed alumina column. Ozonolysis of fraction 4 resulted in the formation of anisic acid and methyl ketone (isolated as the 2,4-dinitrophenylhydrazone).

Since fraction no. 2 did not form a 2,4-dinitrophenylhydrazone and had a much higher refractive index, it is considered to consist chiefly of vinyl acetylene. This was further borne out by the following experiment in which the suspected vinyl acetylene was converted to the same ketone as was obtained in the higher boiling fractions of the reaction product. To 10 ml. of glacial acetic acid was added 1.0 g. of fraction no. 2 and one drop of concentrated sulfuric acid. This solution was heated on the steam-bath for 0.5 hr. following which it was poured into 100 ml. of distilled water. The acids were neutralized and the water-insoluble material treated as above. A dark brown oil weighing 1.05 g. was recovered. A sample of this material weighing 0.08 g. was heated with 0.10 g. of 2,4-dinitrophenylhydrazine in 10 ml. of ethanol and 0.5 ml. of concentrated hydrochloric acid on the steam-bath for 0.5 hr. Upon cooling, there was obtained 0.15 g. of a red crystalline solid, m.p. 148–150°, which was found to be the 2,4-DNPH of the rearrangement ketone, Vb.

Preparation of the 2,4-dinitrophenylhydrazone of fraction 1 gave orange red needles after recrystallization from ethyl alcohol–ethyl acetate, m.p. 227.2–228.2°. The mixed melting point with an authentic sample of the 2,4-dinitrophenylhydrazone of *p*-methoxyacetophenone was not depressed; $\lambda_{\max}$ 390 mμ, $E_{\max}^{\mathrm{CHCl_3}}$ 25,000. Authentic *p*-methoxyacetophenone 2,4-dinitrophenylhydrazone; $\lambda_{\max}$ 389 mμ, $E_{\max}^{\mathrm{CHCl_3}}$ 25,000. *Anal.* Calcd. for $C_{15}H_{14}O_5N_4$: C, 54.54; H, 4.27. Found: C, 54.46; H, 4.05.

A portion of fraction 4 was hydrogenated in 20 ml. of 95% ethanol, using pre-reduced 5% palladium-on-carbon (Mozingo-B catalyst). The catalyst was removed by filtration and the solvent distilled, leaving a residue $n^{25}\mathrm{D}$ 1.5264, $\lambda_{\max}$ 214 mμ, $E_{\max}^{\mathrm{EtOH}}$ 8,500 and $\lambda_{\max}$ 274, mμ, $E_{\max}^{\mathrm{EtOH}}$ 15,000. A 2,4-dinitrophenylhydrazone was prepared and upon recrystallization resulted in the 2,4-dinitrophenylhydrazone of *p*-methoxy-β-methylvalerophenone, m.p. 138.6–139.4°. *Anal.* Calcd. for $C_{19}H_{22}O_5N_4$: C, 59.05; H, 5.74. Found: C, 59.23; H, 5.61.

Preparation of *p*-Methoxy-β-methylvalerophenone.—β-Methylvaleric acid was prepared by stirring a mixture of 250 ml. of absolute ethanol, 81 g. of diethyl malonate and 30.0 g. of commercial sodium methoxide at room temperature for 2 hr. after which 69 g. of *sec*-butyl bromide was added dropwise with continued stirring. This solution was refluxed for 3 hr. Then 200 ml. of ethanol was removed by distillation. The resulting slurry of sodium bromide was dissolved in 200 ml. of water, the organic layer removed by extraction with ether and the ether removed on the steam-bath. The resulting ethyl *sec*-butylmalonate was then refluxed for 4 hr. with a solution of 100 ml. of glacial acetic acid in 150 ml. of concentrated hydrochloric acid. The solution was cooled and extracted several times with ether. The ether and acetic acid were removed by distillation. The residue was distilled under reduced pressure giving 20.0 g. (35%) of β-methylvaleric acid, b.p. 127–128°, $n^{25}\mathrm{D}$ 1.4158.[15] The acid chloride was prepared in 15% yield with phosphorus trichloride, b.p. 139–140° (750 mm.).

For the preparation of the ketone a solution of 4.3 g. of β-methylvaleroyl chloride in 50 ml. of anhydrous benzene was treated with 10 g. of anisole followed by 10 ml. of anhydrous stannic chloride. The solution which resulted was allowed to stand at 50° protected from moisture for 24 hr. The reaction product was poured onto a mixture of ice and hydrochloric acid and stirred for 0.5 hr. The organic layer was extracted with ether and the ether solution washed several times with dilute hydrochloric acid, with water, with dilute sodium hydroxide and finally with water. After drying over anhydrous sodium sulfate, the ether was removed on the steam-bath and the residue distilled under reduced pressure. The fraction boiling at 155–160° (14 mm.) was collected, 1.2 g. (20%) ($d^{25}\mathrm{D}$ 1.5263). The 2,4-dinitrophenylhydrazone was prepared in 85% yield, m.p. 138–139°. A mixed melting point with the 2,4-DNPH of the product of hydrogenation was undepressed.

Dehydration of Methylethyl-(*p*-methoxyphenylethynyl)-carbinol.—The method employed for this dehydration was essentially that of Favorsky.[16]

A sample of the carbinol weighing 1.5 g. (0.0074 mole) was steam distilled from 50 ml. of a 5% sulfuric acid solution. The distillate was extracted with ether, the extracts dried and the ether removed on the steam-bath. The residue was distilled under reduced pressure. The fraction boiling at 124–125° (1.0 mm.) was the vinylacetylene, 0.35 g. (26%). *Anal.* Calcd. for $C_{13}H_{14}O$: C, 83.83; H, 7.50. Found: C, 83.10; H, 7.50. $\lambda_{\max}$ 278 mμ, $E_{\max}^{\mathrm{EtOH}}$ 37,000.

Rearrangement of *t*-Butyl-(*p*-methoxyphenylethynyl)-carbinol. Using 88% Formic Acid.—In this experiment 10.0 g. (0.051 mole) of *t*-butyl-(*p*-methoxyphenylethynyl)-carbinol (b.p. 179–180° (15 mm.)) was added to 125 ml. of 88% formic acid and allowed to stand at room temperature for a period of 9 hr., after which the solution was heated on the steam-bath for 20 minutes. At the end of this period, the solution, which was opaque and showed a strong green fluorescence, was cooled, extracted five times with petroleum ether (30–68°), the combined extracts washed with 10% sodium carbonate solution and dried over anhydrous sodium sulfate. The petroleum ether was removed by distillation and the residue distilled under reduced pressure, 5.10 g., b.p. 140–141° (2.0 mm.), $n^{25}\mathrm{D}$ 1.5498. Redistillation gave *p*-methoxypivalalacetophenone with the constant refractive index $n^{25}\mathrm{D}$ 1.5506, $\lambda_{\max}$ 296 mμ, $E_{\max}^{\mathrm{EtOH}}$ 17,380. The 2,4-dinitrophenylhydrazone derivative was made and on recrystallization melted at 225.4–225.6°. The mixed melting point of this derivative with the 2,4-dinitrophenylhydrazone of an authentic sample of *p*-methoxypivalalacetophenone (see below) showed no depression. *Anal.* Calcd. for $C_{20}H_{21}O_5N_4$: C, 60.29; H, 5.5. Found: C, 60.43; H, 5.4. The total yield of ketonic material obtained in this rearrangement was 74%.

A portion of the product of this rearrangement ($n^{25}\mathrm{D}$ 1.5506) was subjected to ozonolysis. Volatile products of the decomposition of the ozonide were trapped in an ethanolic solution of 2,4-dinitrophenylhydrazone. The resulting solid was recrystallized from 95% ethanol, affording a product, m.p. 211.5–212.0°. A mixed melting point with an authentic sample of the 2,4-dinitrophenylhydrazone of pivalaldehyde (m.p. 209°) showed no melting point depression. The non-volatile residue from the decomposition of the ozonide on purification was found to be anisic acid, m.p. 180–183°, and a mixed m.p. with an authentic sample of anisic acid (m.p. 182–183°) showed no depression.

Preparation of *p*-Methoxypivalacetophenone.—This compound was prepared in the usual manner from *p*-methoxyacetophenone and pivalaldehyde using sodium hydroxide as the condensing agent. In a 250-ml. wide-mouthed bottle were placed 17.0 g. of pivalaldehyde, 30.0 g. of *p*-methoxyacetophenone, 100 ml. of water, 50 ml. of 95% ethanol and 10.0 g. of sodium hydroxide pellets. The reaction mixture was shaken in a mechanical shaker at room temperature for 25 hr., after which it was extracted with ether, the ether extracts dried and distilled. The fraction boiling at 120–121° (0.20 mm.) was collected (5.14 g., 11%), $\lambda_{\max}$ 294 mμ $E_{\max}^{\mathrm{EtOH}}$ 17,380. This is identical with the absorption data obtained for the rearrangement product.

The 2,4-dinitrophenylhydrazone was prepared, m.p. 200–203°; after recrystallization from ethanol, m.p. 225.2–225.4°. A mixed melting point of this material with the derivative of the rearrangement product showed no depression.

Preparation of Pivalaldehyde.—The procedure employed was that of R. A. Myren.[17] *t*-Butylmagnesium chloride was prepared in the usual manner,[12] following which the reaction mixture was allowed to cool to room temperature and 45 g. of N-methylformanilide added as rapidly as possible. The solution was refluxed for 2 hr., after which it was stirred at room temperature for an additional 3 hr. At the end of this period the Grignard complex was decomposed by pouring on 500 g. of washed, crushed ice and 20 ml. of concentrated sulfuric acid. The ether layer was separated

---

[15] R. R. Levene and L. A. Mikeska, *J. Biol. Chem.*, **84**, 571 (1929).

[16] A. E. Favorsky, *Bull. soc. chim.*, **28**, 34 (1902).

[17] R. A. Myren, University of Wisconsin, B.S. thesis, 1948.

and the aqueous phase extracted three times with 50-ml. portions of ether. The ether extracts were dried over "Drierite" and the ether solution then very slowly distilled through a 75-cm. Vigreux column. The fraction boiling at 73–75° (750 mm.) amounted to 13.6–15.2 g. (53–58%) in four different runs based on N-methylformanilide (lit. b.p. 74–75°).

MADISON 6, WISCONSIN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUQUESNE UNIVERSITY]

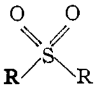
Concerning the Variable Character of the Sulfone Group

BY H. HARRY SZMANT AND GEORGE SULD

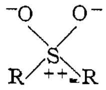
RECEIVED JULY 29, 1955

The apparent acidity constants of a series of benzoic acids and phenols containing sulfur substituents in the *para* positions were determined. By application of the Hammett equation, it is shown that the arylsulfonyl group has a variable effect on the ionization equilibrium depending on the nature of the substituents present in the aryl group and on the particular equilibrium under consideration.

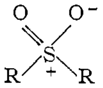
The advent of the octet theory[1] caused a revision of the traditional structure of sulfones (I) and the preferred structure became that showing coordinate covalent sulfur–oxygen bonds (II).



I



II



III

With time, however, as it was recognized that the second-row element sulfur may well expand its outer shell of electrons beyond the octet, there began a discussion as to the relative merits of structures I and II, and physical and chemical data were cited[2] in support of either structure I, II or III.[3] The general question of the expansion of the octet involved in the sulfur–oxygen bonds of sulfones (as well as those of sulfoxides, sulfates, etc.) has been closely associated with the question of resonance interactions between the sulfone function and adjacent free electron systems.

In an attempt to explain the results of a cryoscopic study of sulfones in sulfuric acid,[4] the hypothesis was advanced that the presence of electron-withdrawing substituents in phenyl sulfones favors sulfone structure I while electron-donating substituents favor sulfone structure II. The rather unexpected finding that the introduction of a *p'*-nitro group *increases* the basicity of *p*-(phenylsulfonyl)-aniline and the report that a *p'*-amino group has the opposite effect,[5] suggested the study of a series of suitably *p*-substituted benzoic acids and phenols. The assumption that the electronic character of the sulfone group varies with the nature of the substituents (contrary to the conclusions of Koch and Moffitt)[2c] would predict the acidity of these compounds to be directly affected by the relative positive charge at the sulfur atom. It is noteworthy that while one may be uncertain about the exact effect on physical and chemical properties caused by the participation of d-orbitals of sulfur in bond formation, the obvious difference between the structures I, II and III lies in the magnitude of the positive charge localized at the sulfur atom.

Experimental and Results

Materials.—*p*-Nitrobenzoic acid, *p*-nitrophenol and *m*-nitrophenol were Eastman Kodak Co. white label products which were purified before use by crystallization. Benzoic acid, U. S. Bureau of Standards sample 39F, was dried before use, and *p*-thiocyanophenol was supplied generously by Professor F. G. Bordwell. The following compounds were available in this Laboratory: *p*-phenylmercaptobenzoic acid,[6] m.p. 176–177°; *p*-phenylsulfinylbenzoic acid,[7] m.p. 201–202°; *p*-phenylsulfonylbenzoic acid,[8] m.p. 276–278°; *p*-(4-nitrophenylmercapto)-benzoic acid,[7] m.p. 236–238°; *p*-(4-nitrophenylsulfonyl)-benzoic acid,[7] m.p. 298–300°; *p*-(4-carboxyphenylsulfonyl)-benzoic acid,[8] m.p. 370–371°; *p*-(4-aminophenylsulfonyl)-benzoic acid,[7] m.p. 263–264°; these materials were recrystallized and dried before use.

***p*-Methylmercaptobenzoic Acid.**—A mixture of 20 g. of *p*-carboxyphenyl disulfide, 10 g. of sodium sulfide and 300 cc. of water was refluxed with mechanical stirring for 6 hr. To the cooled reaction mixture there was added 9 cc. of dimethyl sulfate and the resulting solution was stirred for 1 hr. The desired acid was precipitated by addition of hydrochloric acid, and after drying it was extracted with carbon disulfide to remove sulfur. The crude acid was extracted in a Soxhlet apparatus with *n*-heptane and further recrystallized from the same solvent to a constant m.p. 192–193° (lit.[9] m.p. 192°).

***p*-Methylsulfonylbenzoic Acid.**—The above acid upon oxidation with chromic acid in glacial acetic acid gave the desired sulfone, m.p. 266–267.5° after two crystallizations from ethanol.

***p*-(4-Nitrophenylsulfinyl)-benzoic Acid.**—A solution of 5 g. of the corresponding sulfide and 7.5 g. of phenyliodosoacetate in 150 cc. of glacial acetic acid was refluxed for 24 hr., cooled and poured on crushed ice. The precipitate, 4.9 g., m.p. 230–235° after several crystallizations from ethanol gave a constant m.p. 239–239.5°.

Anal.[10] Calcd. for $C_{13}H_9NO_5S$: C, 53.60; H, 3.12. Found: C, 53.37; H, 3.15.

---

[1] G. N. Lewis, THIS JOURNAL, **38**, 762 (1916).

[2] For references consult the following publications: (a) C. M. Suter, "The Organic Chemistry of Sulfur," John Wiley and Sons, Inc., New York, N. Y., 1944, pp. 658–660; (b) H. P. Koch, *J. Chem. Soc.*, 408 (1949); (c) H. P. Koch and W. E. Moffitt, *Trans. Faraday Soc.*, **47**, 7 (1951); (d) E. A. Fehnel and M. Carmack, THIS JOURNAL, **71**, 231 (1949); (e) C. C. Price and H. Morita, *ibid.*, **75**, 4747 (1953); (f) E. Rothstein, *J. Chem. Soc.*, 815 (1953); (g) W. von E. Doering and L. K. Levy, THIS JOURNAL, **77**, 509 (1955).

[3] E. D. Amstutz, I. M. Hunsberger and J. J. Chessick, *ibid.*, **73**, 1220 (1951).

[4] H. H. Szmant and G. A. Brost, *ibid.*, **73**, 4175 (1951), H. H. Szmant and R. L. Lapinski, *ibid.*, **74**, 4395 (1952).

[5] (a) J. J. McIntosh, M.S. Thesis, Duquesne University, 1951; (b) K. A. Allen, J. Cymerman-Craig and H. H. Diamantis, *J. Chem. Soc.*, 234 (1954).

[6] H. H. Szmant, M. J. Segedi and J. Dudek, *J. Org. Chem.*, **18**, 745 (1953).

[7] H. H. Szmant and G. Levitt, THIS JOURNAL, **76**, 5459 (1954).

[8] H. H. Szmant and F. P. Palopoli, *ibid.*, **72**, 1757 (1950).

[9] J. W. Baker, G. F. C. Barrett and W. T. Tweed, *J. Chem. Soc.*, 2831 (1952).

[10] All microanalyses by Drs. Strauss and Weiler, Oxford, England.