Except for one instance the crystalline material was a single, white compound which was purified by recrystallization from methanol and from petroleum ether, m.p. 165–166°.

Anal. Calcd. for $(C_9H_8O)_3$: C, 81.79; H, 6.10; OCH_3, 23.48; mol. wt., 396.5. Found: C, 82.40; H, 6.47; OCH_3, 23.4; mol. wt. (Rast), 360.

On one occasion after the first crop of crystals had been separated as usual, evaporation of the methanol gave a new material which was purified by recrystallization from methanol, m.p. 134–135°.

Anal. Calcd. for $(C_9H_8O)_2$: C, 81.79; H, 6.10; mol. wt., 264.3. Found: C, 81.64; H, 5.79; mol. wt. (Rast), 240.

Phenylethoxyacetylene.—Using the directions for phenylmethoxyacetylene, 25- to 30-g. samples of bromoethoxystyrene[13] were treated with powdered potassium hydroxide to give 30–35% yields of crude material, b.p. 60–70° (1 mm.). Analysis of this distillate by hydrogenation over Raney nickel and quantitative saponification of the saturated solution gave 93–96% acetylenic ether and 24–25% ester (total 117–121%) which suggests that hydrogenolysis occurred even under these mild conditions. Purification of the acetylenic ether was attempted as for the methyl ether; a 5.5-g. sample was isolated, b.p. 49–50° (0.5 mm.), $n^{25}D$ 1.5421.

Anal. Calcd. for $C_{10}H_{10}O$: C, 82.16; H, 6.90; for $C_{10}H_{12}O_2$ (ethyl phenylacetate): C, 73.15; H, 7.36. Found: C, 80.64; H, 7.79.

Analysis of this purified sample as above showed 11% ester; the hydrogen uptake corresponded to 100% acetylenic ether.

The residues from the distillation or from allowing the impure phenylethoxyacetylene to stand closely resembled those from phenylmethoxyacetylene. White crystals were isolated, m.p. 170–170.5°, from methanol.

Anal. Calcd. for $(C_{10}H_{10}O)_3$: C, 82.16; H, 6.90; mol. wt., 438.5. Found: C, 82.03; H, 6.95; mol. wt. (Rast), 430.

The Reaction of Bromobutoxystyrene with Sodamide.—To 0.1 mole of sodamide[16] in 80 ml. of liquid ammonia was added dropwise with stirring 9.5 g. (0.037 mole) of bromobutoxystyrene.[13] After 15 minutes of stirring, 5 g. of ammonium nitrate and then 50 ml. of water were added (slowly at first). The reaction mixture was extracted with ether, the ether solution dried over anhydrous potassium carbonate, filtered, and the ether removed under reduced pressure. The red oil which remained was distilled from a Claisen flask into a receiver cooled in Dry Ice. Redistillation through a small column gave 1.6 g., b.p. 100° (12 mm.), $n^{25}D$ 1.5210. Known benzyl cyanide gave the same b.p. through the column and the same refractive index.

Anal. Calcd. for C_8H_7N: C, 82.02; H, 6.02. Found: C, 82.15; H, 5.95.

Hydrolysis with sulfuric acid gave phenylacetic acid in 86% yield, m.p. crude 74–76°.

The Dry Ice trap in the distillation yielded a little butyl alcohol identified as its phenylurethan, m.p. and mixed m.p. 61–62°.

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[16] T. H. Vaughn, R. R. Vogt and J. A. Nieuwland, THIS JOURNAL, **56**, 2120 (1934).

LOS ANGELES 24, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, LOS ANGELES]

Bromoalkoxystyrenes[1]

BY THOMAS L. JACOBS AND WILLARD R. SCOTT, JR.

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Dehydrobromination of alkoxystyrene dibromides by several methods gave bromoalkoxystyrenes. These were shown to have the structure $C_6H_5CBr{=}CHOR$, but small amounts of the isomeric compounds, $C_6H_5CH{=}CBrOR$, were also present. These structures were established by acid hydrolysis and ozonization. Methoxystyrene dibromide was also converted to α-bromophenylacetaldehyde and to the corresponding acetal.

Haloalkoxystyrenes of the type $C_6H_5CX{=}CHOR$ or $C_6H_5CH{=}CXOR$ were needed for the synthesis of acetylenic ethers.[2] Compounds of the first sort were unknown when the present investigation began, but a brief report of the preparation of α-bromo-β-methoxystyrene by distillation of α-bromophenylacetaldehyde dimethyl acetal has since appeared.[3] The formation of β-chloro-β-ethoxystyrene, a compound of the second type, by the action of alcoholic potassium hydroxide on chlorophenylacetylene also has been reported.[4] The only product obtained from bromophenylacetylene under the same conditions was phenylacetic acid.[4,5]

The synthetic method investigated in the present work is summarized in equation 1. It was chosen because the starting materials are readily available and the first two steps proceed easily in excellent yield. Removal of hydrogen bromide from II to yield bromoalkoxystyrenes was attempted by several methods, but no completely satisfactory procedure was found. The products, which had the expected composition but broad boiling points, could have been mixtures of four different compounds: *cis*- and *trans*-α-bromo-β-alkoxystyrenes (III) and β-bromo-β-alkoxystyrenes (IV). Evidence was obtained which indicated that compounds of structure III were the principal components, but compounds of structure IV were also present in some of the products. It would be desirable to obtain a pure stereoisomer of structure III in which the hydrogen and bromide atoms were *trans* because this should yield the acetylenic ether readily, but no progress has yet been made toward a stereospecific synthesis or the separation of the isomers.

$$C_6H_5C{\equiv}CH + ROH \xrightarrow{NaOR} \underset{I}{C_6H_5CH{=}CHOR} \xrightarrow{Br_2} \underset{II}{C_6H_5CHBrCHBrOR} \longrightarrow \underset{III}{C_6H_5CBr{=}CHOR} \text{ or } \underset{IV}{C_6H_5CH{=}CBrOR} \quad (1)$$

Alkoxystyrenes I were prepared with R = methyl, ethyl and butyl. All were converted to bromoalkoxystyrenes, but most of the work was done on the methoxy compound. The best results in the dehydrohalogenation of dibromide

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[1] Taken in part from a dissertation presented by Willard R. Scott, Jr., in partial satisfaction of the requirements for the degree Doctor of Philosophy, July, 1950.

[2] T. L. Jacobs and W. R. Scott, Jr., THIS JOURNAL, **75**, 5497 (1953).

[3] S. M. McElvain and M. J. Curry, *ibid.*, **70**, 3781 (1948).

[4] J. U. Nef, *Ann.*, **308**, 264 (1899).

[5] V. Grignard and H. Perrichon, *Ann. chim.*, [10] **5**, 5 (1926).

II (R = CH_3) were realized with potassium *t*-butoxide in *t*-butyl alcohol at room temperature which gave quantitative removal of one bromine and 60–75% yields of bromomethoxystyrene. Equally good yields were obtained with powdered potassium hydroxide or sodium hydroxide in ether, but the product gave less satisfactory results in the acetylenic ether synthesis, possibly because larger amounts of IV were present.

Pyrolysis of II (R = CH_3) at reduced pressure resulted in the elimination of hydrogen bromide and gave a product of approximately the composition of bromomethoxystyrene. However, methyl bromide was also eliminated and the product almost certainly contained some α-bromophenylacetaldehyde. The erratic nature of the results of attempts to prepare methoxyphenylacetylene[2] from different samples of this material suggests that the ratio of these reactions varies depending on undetermined factors. Small-scale, semiquantitative experiments indicated that elimination of methyl bromide was often the principal reaction and the procedure was abandoned as a synthetic method for the methoxy compound. However, bromobutoxystyrene is more readily separated from α-bromophenylacetaldehyde and was prepared in pure condition and in satisfactory yield by pyrolysis.

Several other dehydrohalogenation methods were tried with limited success. Only tars resulted from the action of dry powdered potassium hydroxide on III (R = CH_3). Diethylaniline, which has been used successfully to convert aliphatic α,β-dibromoethers to β-bromovinylethers,[6] gave a 30% yield of bromomethoxystyrene and 40% of methoxystyrene. The elimination of adjacent bromine atoms by amines is relatively common with dibromides of compounds like stilbene and cinnamic acid.[7] Pyridine reacted rapidly with the dibromide II (R = CH_3) to give a crystalline salt which failed to yield III or IV on pyrolysis or under other conditions. Reaction of the same dibromide with trimethylamine followed by a suspension of silver oxide in water gave a low yield of α-bromophenylacetaldehyde as the only pure product; there was no evidence that unsaturated compounds such as III or IV were produced.

When dehydrobromination of II (R = CH_3 or C_2H_5) was attempted in methanol or ethanol, the principal reaction was solvolysis to the corresponding acetal of α-bromophenylacetaldehyde even when concentrated solutions of sodium alkoxide or potassium hydroxide were used at various temperatures. Excellent yields of the acetals were realized by solvolysis of II in the pure alcohols or better in the presence of potassium carbonate. In our hands this procedure was superior to that of Bedoukian[8] for the synthesis of these acetals. A 70% yield of the methyl acetal was also obtained by treating methoxystyrene, I (R = CH_3), in dry methanol with N-bromosuccinimide.

As reported by McElvain and Curry[3] it was possible to prepare bromomethoxystyrene, III (R = CH_3), by pyrolytic distillation of the methyl acetal, but the reaction appeared to depend on traces of catalysts and it was difficult to get reproducible results. The product even under the most favorable conditions darkened more rapidly than the material obtained from II (R = CH_3) by the action of potassium *t*-butoxide, and separation from unchanged acetal was difficult because the boiling points are close together. Addition of 1% of *p*-toluenesulfonic acid resulted in extensive decomposition during distillation even at 2 mm.; a low yield of material boiling over a wide range was obtained. The ethyl acetal has not yet been tried in this reaction.

Several reactions of the bromoalkoxystyrenes obtained by the various methods were examined to determine whether compounds of both structures III and IV were present. Acid-catalyzed hydrolysis or hydration of III would be expected to give α-bromophenylacetaldehyde readily; IV should yield phenylacetic acid. Unfortunately this reaction proceeded slowly under mild conditions and was accompanied by extensive polymerization to tarry products. More polymerization occurred under more vigorous conditions. Low yields of α-bromophenylacetaldehyde were obtained from bromoalkoxystyrenes prepared by all the methods. The best yield (15% with 50% recovery of starting material) was attained in aqueous dioxane with *p*-toluenesulfonic acid as the catalyst. Under other conditions, small amounts of benzoylcarbinol, phenylacetic acid and benzoic acid were isolated as well. The yield of phenylacetic acid was never more than 3%; this acid was usually obtained in experiments with bromomethoxystyrene prepared using potassium hydroxide in ether, but only once from a sample prepared using potassium *t*-butoxide. Its presence among the hydrolysis products is not conclusive evidence for compounds of structure IV because small amounts of phenylalkoxyacetylenes may have been formed in the dehydrohalogenation step, incompletely removed, and hydrolyzed to this acid. Benzoic acid may have arisen by air oxidation. Benzoylcarbinol was probably formed by hydrolysis of α-bromophenylacetaldehyde to hydroxyphenylacetaldehyde and rearrangement of the latter.[9,10] It was shown that the bromoaldehyde gave a little benzoylcarbinol and a great deal of tar when heated with dilute mineral acid.

The difficulty of hydrolyzing the bromoalkoxystyrenes made it desirable to have a simple method of identifying α-bromophenylacetaldehyde when it was formed. This compound has been prepared by bromination of phenylacetaldehyde[9,11,12] and by hydrolysis of its methyl acetal with citric acid (25% yield).[8] In our hands the bromination gave 34% of a rather crude product and the acetal hydrolysis gave even less than 25% yields. Hydrolysis of methoxystyrene dibromide with cold

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[6] A. E. Favorskiĭ and M. N. Shchukina, *Zhur. Obshcheĭ Khim.*, **15**, 385 (1945); *C. A.*, **40**, 4347 (1946).

[7] T. L. Jacobs, "Organic Reactions," Vol. V, John Wiley and Sons, Inc., New York, N. Y., 1949, pp. 17–18.

[8] P. Z. Bedoukian, THIS JOURNAL, **66**, 1325 (1944).

[9] J. U. Nef, *Ann.*, **335**, 247 (1904).

[10] W. G. Dauben, W. L. Evans and R. I. Meltzer, THIS JOURNAL, **63**, 1883 (1941).

[11] E. Fischer, *Ber.*, **29**, 213 (1896).

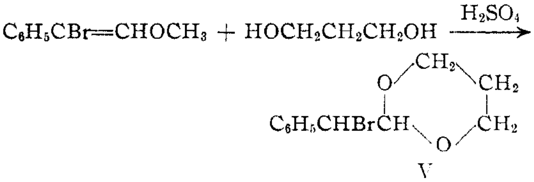
[12] H. Erlenmeyer, C. Becker, E. Sorkin, H. Bloch and E. Suter, *Helv. Chim. Acta*, **30**, 2058 (1947).

sodium bicarbonate solution was the best synthesis and gave the pure aldehyde in 48% yield. Somewhat different physical properties from those reported earlier were observed.

Even when the pure aldehyde was obtained it was difficult to prepare a satisfactory derivative in good yield. The oxazole[11] and thiazole[12] reported earlier were not suitable, and standard procedures for oximes, semicarbazones or dimethone derivatives gave only gums. A 2,4-dinitrophenylhydrazone, m.p. 139°, has been reported, but we found that the usual procedure[13] employing hydrochloric acid gave mainly the 2,4-dinitrophenylosazone of phenylglyoxal, while reaction with 2,4-dinitrophenylhydrazine in cold methanolic or ethanolic solution gave 2,4-dinitrophenylhydrazones corresponding in composition to derivatives of methoxy- or ethoxyphenylacetaldehyde. An attempt to prepare α-ethoxyphenylacetaldehyde was unsuccessful so the structures of these derivatives were not proved. However, they were different from the corresponding ω-alkoxyacetophenone 2,4-dinitrophenylhydrazones. The ethoxy derivative melted at 135–136° which is not far from the melting point (139°) reported[3] for the 2,4-dinitrophenylhydrazone of α-bromophenylacetaldehyde. The loss of halogen in similar reactions has been observed before.[14–16] The bromoaldehyde reacted with 2,4-dinitrophenylhydrazine in chloroform in the absence of acid to give a derivative, m.p. 115–117°, which had approximately the composition of the hydrazone desired; further purification was unsuccessful.

When bromomethoxystyrene was treated with 2,4-dinitrophenylhydrazine under the usual conditions for forming 2,4-dinitrophenylhydrazones,[13] it gave a moderate yield of phenylglyoxal 2,4-dinitrophenylosazone. Under the conditions used to convert β-bromovinyl ethyl ethers to α-ethoxyaldehyde 2,4-dinitrophenylhydrazones[16] a new substance was obtained. This compound differed in melting point and composition from any expected product; its structure has not yet been determined.

The most conclusive evidence that III constituted the principal component in the bromomethoxystyrene mixture was the isolation in 47% yield of 2-(α-bromobenzyl)-1,3-dioxolane (V) from reaction with trimethylene glycol and sulfuric acid (equation 2).

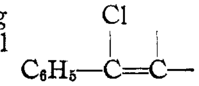


$$C_6H_5CBr{=}CHOCH_3 + HOCH_2CH_2CH_2OH \xrightarrow{H_2SO_4} C_6H_5CHBrCH\langle O\text{-}CH_2CH_2CH_2\text{-}O\rangle \quad (2)$$

V

This compound was first obtained from bromophenylacetaldehyde dimethyl acetal.[3] No evidence for 2-benzyl-2-methoxy-1,3-dioxolane or any other derivative of phenylacetic acid, which might have arisen from IV, was obtained. Higher yields of V could not be realized. It was also possible to convert bromomethoxystyrene to the dimethylacetal of bromophenylacetaldehyde in comparable yield by dissolving it in methanol containing a little perchloric acid.

Ozonization is rarely useful to establish the relative amounts of compounds of different structures in a mixture because yields of products are usually rather low. With compounds such as III and IV oxidative rearrangements[17] may occur during ozonization and the possibility of even semi-quantitative work seems remote. However, Straus[18] ozonized two compounds containing the grouping and obtained evidence for benzoyl chloride among the products.



$C_6H_5\text{—}\overset{Cl}{C}{=}C\text{—}$

Bromomethoxystyrene prepared by the action of potassium *t*-butoxide was ozonized and the product treated with aniline; a 5% yield of benzanilide was obtained along with 10% of benzoic acid and 50% of aniline hydrobromide. In a second experiment in which the ozonide was decomposed with water a very low yield of benzaldehyde was isolated as the 2,4-dinitrophenylhydrazone. This evidence indicated that compounds with both structures III and IV were present in the starting material.

Other experiments on bromomethoxystyrene were relatively unfruitful. Bromine added at low temperature but the product was an unstable oil that lost hydrogen bromide readily. Attempts to form a Grignard reagent under conditions which had been successful with α-bromostyrene led to a stable amorphous solid which contained magnesium. Attempts at basic hydrolysis led to intractable oils from which a very low yield of benzoic acid was obtained as the only pure product.

Although the exact composition of the bromoalkoxystyrene mixture obtained in the work has not been elucidated, it has been possible to demonstrate that compounds of structure III were the main components and that small amounts of compounds of structure IV were present. This product could be used for the synthesis of methoxyphenylacetylene as reported in the next paper.[2]

Experimental Part

β-Alkoxystyrenes, I, were prepared from phenylacetylene[19] and sodium alkoxides[20,21] or potassium hydroxide[4,22] in the corresponding alcohol in yields of 70–80%. β-Butoxystyrene, a new compound, was obtained using sodium butoxide in 74% yield, b.p. 139–139.5° (19 mm.), $n^{20}D$ 1.5381, d^{20}_4 0.940.

Anal. Calcd. for $C_{12}H_{16}O$: C, 81.83; H, 9.09. Found: C, 81.58; H, 8.87.

A small amount of phenylacetaldehyde dibutyl acetal, b.p. 107–108° (1.5 mm.), $n^{20}D$ 1.4763, d^{20}_4 0.929, was isolated from the distillation residue from the above synthesis, and identified by hydrolysis to phenylacetaldehyde (semicarbazone, m.p. 156–157°).

Anal. Calcd. for $C_{16}H_{26}O_2$: C, 76.76; H, 10.47. Found: C, 77.10; H, 10.29.

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[13] R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," Second Edition, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 143.

[14] F. Fleck, A. Rossi and H. Schinz, *Helv. Chim. Acta*, **32**, 998 (1949).

[15] F. D. Chattaway and H. Irving, THIS JOURNAL, **54**, 263 (1932).

[16] M. N. Shchukina, *Zhur. Obshchei Khim.*, **18**, 1350 (1948); *C. A.*, **43**, 2158 (1949).

[17] H. Biltz, *Ber.*, **46**, 143 (1913).

[18] F. Straus, *Ann.*, **393**, 278 (1912).

[19] "Organic Syntheses," Coll. Vol. I, second ed., John Wiley and Sons, Inc., New York, N. Y., 1946, p. 438.

[20] C. Moureu, *Bull. soc. chim.*, [3] **31**, 526 (1904).

[21] C. Dufraisse and R. Chaux, *ibid.*, [4] **39**, 905 (1926).

[22] K. Auwers, *Ber.*, **44**, 3514 (1911).

Bromoalkoxystyrenes, III and IV.—Alkoxystyrene dibromides were prepared by adding the theoretical amount of purified bromine dropwise to the alkoxystyrene in twice its volume of anhydrous ether at −25 to −15°. It was not possible to purify these dibromides because they tended to darken and lose hydrogen bromide even below room temperature. The ether solutions were used directly in the experiments described below.

To an approximately 0.5 *M* solution of potassium *t*-butoxide in *t*-butyl alcohol at 25° was added quite rapidly with vigorous stirring 5% less than the theoretical amount of a freshly prepared ether solution of alkoxystyrene dibromide, maintaining the temperature below 35° by cooling in ice. The maximum yield of bromoalkoxystyrene was obtained by stirring at room temperature for 4 hr. The yield was not improved by increasing the excess of alkali to 40%. The reaction mixture was poured into double its volume of water, the layers separated, the aqueous portion extracted with ether and the combined organic layers washed several times with water, dried over sodium sulfate, the ether and *t*-butyl alcohol removed under reduced pressure and the residue distilled rapidly at 2 mm. or below. Redistillation was usually carried out rapidly at 1 mm. or below because attempts at careful fractionation led to extensive decomposition.

Bromomethoxystyrene was thus obtained with a maximum yield of 75%, b.p. 89–97°, $n^{25}\text{D}$ 1.585–1.590 (several fractions).

Anal. of a center cut. Calcd. for C_9H_9OBr: C, 50.67; H, 4.25; Br, 37.5. Found: C, 51.09; H, 4.37; Br, 38.4.

In one run potassium bromide was centrifuged from the reaction mixture before it was added to water, and found to amount to about 2% more than theoretical for one molecular equivalent.

Bromoethoxystyrene, 63% yield, b.p. 85–95° (1 mm.), $n^{25}\text{D}$ 1.568.

Anal. Calcd. for $C_{10}H_{11}OBr$: C, 52.88; H, 4.88. Found: C, 53.00; H, 5.24.

A forerun, b.p. 60–65° (0.5 mm.), proved to be mainly α-bromophenylacetaldehyde (about 3% yield).

Bromomethoxystyrene was also prepared by adding the ether solution of the dibromide to a fourfold excess of powdered potassium hydroxide or sodium hydroxide suspended in anhydrous ether (1 liter per mole of base) with vigorous stirring and without cooling (heat evolved to reflux the ether). The reaction mixture was worked up about as described above and gave 60–72% yields of material, b.p. 85–95° (1 mm.) after two distillations, $n^{25}\text{D}$ 1.579–1.589 (different runs).

Anal. Found: C, 48.14; H, 4.11; Br, 36.7.

Bromobutoxystyrene was synthesized by the pyrolysis method only. Butoxystyrene dibromide was prepared in carbon disulfide solution below −20°, the solvent removed under reduced pressure and the dibromide pyrolyzed under nitrogen in a Claisen flask, maintaining a low pressure by a pump protected with Dry Ice trap and Ascarite tower. As the flask was slowly heated in an oil-bath under a pressure of 2 mm., gas evolution increased and became vigorous around 90°. The pressure in the system increased (a manometer recorded 7 to 25 mm. maximum) and then dropped to the original value. A clear liquid distilled at 138–147°, bath 175–185°. Redistillation from a Claisen flask followed by fractionation through a short column gave a 63% yield of bromobutoxystyrene, b.p. 114.5–115.5° (1.5 mm.), $n^{20}\text{D}$ 1.5612, d^{20}_4 1.274.

Anal. Calcd. for $C_{12}H_{15}OBr$: C, 56.48; H, 5.92. Found: C, 56.08; H, 6.03.

The pyrolysis of methoxystyrene dibromide under similar conditions gave 75–86% yields of material boiling at 99–106° (2 mm.). Fractionation was unsuccessful, resulting in much decomposition and no constant boiling fractions. A small fraction taken at 105° showed $n^{20}\text{D}$ 1.5953.

Anal. Calcd. for C_9H_9OBr: Br, 37.51; Calcd. for α-bromophenylacetaldehyde, C_8H_7OBr: Br, 40.15. Found: 38.69, 38.25.

This sample gave a Schiff test and silver mirror test almost instantaneously. Methoxystyrene gave a Schiff test slowly and no silver mirror test.

These data suggest that α-bromophenylacetaldehyde was a major contaminant in the bromomethoxystyrene prepared by this method. This was confirmed by carrying out the pyrolysis of methoxystyrene dibromide on a small scale with provision for absorbing hydrogen bromide in Ascarite and condensing methyl bromide. The relative amounts of hydrogen bromide and methyl bromide varied widely, but in these small scale experiments the yield of hydrogen bromide never surpassed 25% although methyl bromide was isolated in 24 to 68% yields. The methyl bromide was identified by conversion to methylmercuric bromide.[23] Higher yields of methyl bromide were obtained at lower pyrolysis pressures.

Attempts to convert bromomethoxystyrene prepared by this method to methoxyphenylacetylene gave very erratic results[2] which suggests that the proportion of bromophenylacetaldehyde varied widely and was dependent on undetermined factors.

α-Bromophenylacetaldehyde Dimethyl Acetal.—An ether solution of 0.11 mole of methoxystyrene dibromide was poured into 200 ml. of anhydrous methanol containing 15 g. (0.11 mole) of finely powdered, anhydrous potassium carbonate, and the mixture allowed to stand overnight at room temperature. Dilution with water and ether extraction gave 18.5 g. (75%) of the acetal, b.p. 89–91° (1 mm.), $n^{25}\text{D}$ 1.5409.

Anal. Calcd. for $C_{10}H_{13}O_2Br$: C, 49.02; H, 5.31. Found: C, 49.26; H, 5.59.

A similar experiment without the potassium carbonate gave a 57% yield of the acetal after the reaction mixture stood 3 days.

α-Bromophenylacetaldehyde.—To 10 g. of methoxystyrene in 50 ml. of anhydrous ether at −20° was added the theoretical amount of purified bromine with stirring, and the solution poured at once into a stirred solution of 10 g. of sodium bicarbonate in 100 ml. of water at 0°. After stirring for 2 hr. at 0° the layers were separated, the ether solution washed with water and dried, and the ether removed at reduced pressure. Careful distillation gave 7.2 g. (48%) of the bromoaldehyde, b.p. 82–85° (2 mm.), $n^{25}\text{D}$ 1.5750.

Anal. Calcd. for C_8H_7OBr: C, 48.38; H, 3.53. Found: C, 48.35; H, 3.83.

Bromination of phenylacetaldehyde in[9,11,12] chloroform solution in the presence of calcium carbonate gave a 34% yield of a slightly yellow oil, b.p. 80–90° (2 mm.), $n^{25}\text{D}$ 1.5786; 15% of an oil, b.p. 90–100° (2 mm.) and a dark green tar were the other products of the reaction.

Addition of 0.1 g. of the pure bromoaldehyde to 50 ml. of a cold, saturated solution of 2,4-dinitrophenylhydrazine in ethanol gave an acid solution that slowly deposited an orange solid. Recrystallization from a small volume of ethanol followed by heating with petroleum ether, b.p. 60–70°, gave yellow, felt-like needles, m.p. 135–136°.

Anal. Calcd. for ethoxyphenylacetaldehyde 2,4-dinitrophenylhydrazone, $C_{16}H_{16}O_5N_4$: C, 55.81; H, 4.68; N, 16.28; OC_2H_5, 13.09. Found: C, 55.74; H, 4.82; N, 16.30; OC_2H_5, 12.89.

This compound was not α-ethoxyacetophenone 2,4-dinitrophenylhydrazone which was prepared from α-ethoxyacetophenone[24,25] in glacial acetic acid and found to melt at 195–196°.

The bromoaldehyde was allowed to react with 2,4-dinitrophenylhydrazine in methanol to yield a yellow solid, m.p. 147–148°.

Anal. Calcd. for methoxyphenylacetaldehyde 2,4-dinitrophenylhydrazone, $C_{15}H_{14}O_5N_4$: C, 54.60; H, 4.27. Found: C, 54.76; H, 4.54.

The bromoaldehyde was refluxed with alcoholic 2,4-dinitrophenylhydrazine containing a little concd. hydrochloric acid.[13] The main product was an orange precipitate, m.p. 285–290°, which was recrystallized with difficulty from a relatively large volume of glacial acetic acid to give a bright red powder, m.p. 297–300° (no depression of m.p. when mixed with known phenylglyoxal 2,4-dinitrophenylosazone).

Anal. Calcd. for $C_{20}H_{14}O_8N_8$: C, 48.59; H, 2.85. Found: C, 48.24; H, 2.74.

A small amount of the ethoxy 2,4-dinitrophenylhydrazine was isolated from the filtrate from the reaction mixture.

Bromomethoxystyrene gave very similar results when

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[23] C. S. Marvel, C. G. Gauerke and E. L. Hill, THIS JOURNAL, **47**, 3009 (1925).

[24] M. Sommelet, *Ann. chim.*, [8] **9**, 521 (1906); *Bull. soc. chim.*, [4] **1**, 389 (1907).

[25] C. Dufraisse and R. Chaux, *ibid.*, [4] **39**, 450 (1926).

treated with alcoholic 2,4-dinitrophenylhydrazine in the presence of concd. hydrochloric acid as described above.

2-(α-Bromobenzyl)-1,3-dioxolane.[3]—A solution containing 5 g. (0.023 mole) of bromomethoxystyrene, 10 g. (0.11 mole) of trimethylene glycol, 10 ml. of purified dioxane and 3 drops of concd. sulfuric acid was left at room temperature for 10 days. An excess of dilute sodium bicarbonate solution was added, water and dioxane removed under reduced pressure on the steam-bath and the residue taken up in ether, dried and distilled, b.p. 120–125° (1 mm.). The distillate solidified on standing, yield 2.8 g. (47%), m.p. 47–48° after one recrystallization from 50% ethanol.

LOS ANGELES 4, CALIFORNIA

[CONTRIBUTION FROM THE SCHOOL OF SCIENCE, BRANDEIS UNIVERSITY]

The Effects of Structure on the Kinetics of Decomposition of Substituted Phenyl-azo-triphenylmethanes

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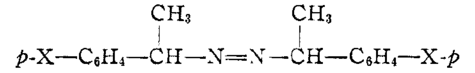
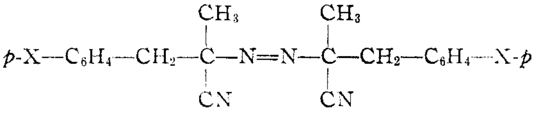
In a study of the effects of substituents on the formation of substituted phenyl radicals, a series of *p*-substituted-phenyl-azo-triphenylmethanes was prepared and decomposed, $p\text{-X-C}_6\text{H}_4\text{—N=N—C(C}_6\text{H}_5)_3$, X = H, CH_3, Br, NO_2, HO, CH_3O, CH_3CONH. The decompositions showed first-order kinetics. The rates were determined for each compound at two temperatures (at about 43 and 53° or 53 and 64°) in toluene and for two of the compounds, X = H, HO, in acetic acid and in pyridine. Energies of activation were in the range of 27–30 kcal. mole^{-1}, except for one compound, X = CH_3, E_A 24 kcal.; entropies of activation were not constant. All substituents (except methyl) decreased the rates of decomposition as compared with the unsubstituted compound, which decomposed about four times as fast as the slowest (X = *p*-NO_2). The results were compared with those of the decomposition of similarly substituted peroxy compounds and of other azo compounds, and discussed in terms of the conjugation of the phenyl and azo groups and the effects of the substituents on the phenyl radicals.

Examination of the effects of substituents in the benzene ring on the rates of decomposition of certain azo compounds has been of interest to us as an aspect of the relation of structure and reactivity in the chemistry of free radicals. In the decomposition of 1-azo-bis-1-phenylethanes[1]



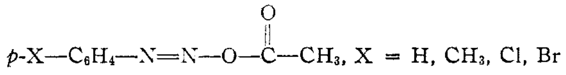
$$p\text{-X—C}_6\text{H}_4\text{—}\overset{\mathrm{CH_3}}{\mathrm{CH}}\text{—N=N—}\overset{\mathrm{CH_3}}{\mathrm{CH}}\text{—C}_6\text{H}_4\text{—X-}p$$

the substituents methyl and methoxyl led to small (about 8 and 30%) increases in rate, while the substituents chlorine and nitro led to small decreases (about 24 and 14%) in the rates of decomposition of azo compounds of structure[2]



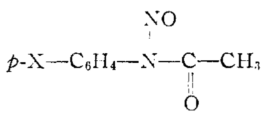
$$p\text{-X—C}_6\text{H}_4\text{—CH}_2\text{—}\underset{\mathrm{CN}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\text{—N=N—}\underset{\mathrm{CN}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\text{—CH}_2\text{—C}_6\text{H}_4\text{—X-}p$$

Still smaller effects (a total range of ±10% in the rate constants) were observed in the decomposition of the benzene diazoacetates[3]



$$p\text{-X—C}_6\text{H}_4\text{—N=N—O—}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\text{—CH}_3\text{, X = H, CH}_3\text{, Cl, Br}$$

but it is not clear whether the decompositions of the diazoacetates or the rearrangements of the nitrosoacetanilides



$$p\text{-X—C}_6\text{H}_4\text{—}\overset{\mathrm{NO}}{\mathrm{N}}\text{—}\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}\text{—CH}_3$$

were actually being measured.[4]

We are reporting a study of the effects of substituents on the rates of decomposition of phenyl-azo-triphenylmethanes

$p\text{-X—C}_6\text{H}_4\text{—N=N—(C}_6\text{H}_5)_3$, X = H,[5] CH_3,[5] Br, NO_2,[5] HO, CH_3O,[6] CH_3CONH

reactions which lead to a substituted phenyl radical, a nitrogen molecule and a triphenylmethyl radical by the dissociation of two carbon–nitrogen bonds.[7] While the decomposition of symmetrical azo compounds like azomethane[8] or azo-bis-isobutyronitrile[9] and the unsymmetrical methyl-azo-2-propane[8c] may proceed by simultaneous symmetrical dissociation of the two carbon–nitrogen bonds, the decomposition of the phenyl-azo-triphenylmethanes need not. The triphenylmethyl–nitrogen bond is probably much weaker than the phenyl–nitrogen bond and might be almost completely broken when the phenyl–nitrogen bond is only in small part dissociated. In an extreme case, the weaker bond might break first in a rate-determining process, leading to an unstable intermediate radical of type R—N=N·, and the nature of the group R and the R-N bond would have no effect on the observed rate. However, the apparent differences in the ease of decomposition of aryl-azo-triphenylmethanes, acyl-azo-triphenylmethanes[6] and azo-bis-triphenylmethanes[10] indicate that such decompositions are affected by the strength of both carbon–nitrogen bonds or by the ease of formation of both radicals, and that substituents in the phenyl group of the phenyl-azo-triphenylmethanes would influence the kinetics of the decompositions, the effects possibly being damped by the dominant ease of formation of the triphenylmethyl radicals.

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(1) S. G. Cohen, S. J. Groszos and D. B. Sparrow, THIS JOURNAL, **72**, 3947 (1950).

(2) C. Overberger and H. Biletch, *ibid.*, **73**, 4880 (1951).

(3) S. M. Grieve and D. H. Hey, *J. Chem. Soc.*, 689 (1935).

(4) D. F. DeTar, THIS JOURNAL, **73**, 1446 (1951).

(5) M. Gomberg and A. Campbell, *ibid.*, **20**, 780 (1898).

(6) H. Wieland, A. Hintermaier and J. Dennstedt, *Ann.*, **452**, 1 (1927).

(7) *Cf.* W. A. Waters, "The Chemistry of Free Radicals," 2nd Ed., Oxford University Press, New York, N. Y., 1948, p. 147–148.

(8) (a) H. C. Ramsperger, THIS JOURNAL, **49**, 912 (1917); (b) **50**, 714 (1928); (c) **51**, 2134 (1929).

(9) F. M. Lewis and M. Matheson, *ibid.*, **71**, 747 (1949).

(10) H. Wieland, H. vom Hove and K. Borner, *Ann.*, **456**, 31 (1926). Azo-bis-triphenylmethane was too unstable to be isolated, and attempts to prepare it by oxidation of the hydrazine led to the decomposition products.