Notes

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Triphenylethylene Derivatives. III

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Received November 19, 1956

In a previous paper[1] we dealt with a novel synthesis of triphenylethylenes, adopting the Friedel-Crafts reaction instead of the Grignard synthesis.

With a view to preparing tris(alkoxyphenyl)-ethylenes, some further work has been performed. A *p,p'*-dialkoxydesoxybenzoin was prepared by the Friedel-Crafts condensation between a *p*-alkoxyphenylacetyl chloride and the corresponding phenyl ether. Desoxyanisoin and desoxyphenetoin (I) thus obtained were converted to the corresponding chlorostilbenes, which were treated with anisole and phenetole to afford the desired triphenylethylenes. The chlorination of these triphenylethylenes was carried out in satisfactory yields by the action of sulfuryl chloride in carbon tetrachloride.

Although the action of an equimolar amount of bromine on I gave α-bromodesoxyphenetoin (II), I was oxidized by 2 equivalents of bromine to phenetil ($EtOC_6H_4COCOC_6H_4OEt$).

The action of sodium ethoxide on II did not yield an ether, but only phenetoin. It has been confirmed by the other investigator[2] that the principal product obtained by the reaction of α-bromodesoxyanisoin with anisole in the presence of aluminum chloride was trianisylethanone, identified by comparison with the product obtained by hydrolysis of trianisylbromoethylene.

EXPERIMENTAL

p-Ethoxyphenylacetic acid. (III). This compound was prepared in 53% yield from *p*-ethoxyacetophenone by a procedure analogous to that used for *p*-methoxyphenylacetic acid.[3] The intermediate thiomorpholide could be crystallized from ethanol as almost colorless needles, m.p. 92–93°, but subsequent hydrolysis was carried out without further purification.

Desoxyphenetoin. (I). A solution of the acid chloride prepared from III (9 g., 0.05 mole) in carbon disulfide (25 ml.) was added dropwise with stirring to a well-cooled mixture (−5°) of phenetol (7.3 g.; 0.06 mole), aluminum chloride (14.7 g.; 0.11 mole) and carbon disulfide (100 ml.) so that vigorous reaction might not occur. After the reaction mixture had stood for 20 hr. below 10° the carbon disulfide layer was removed by decantation, and the residue was treated with ice and concentrated hydrochloric acid. The separated crystals of I were collected and air-dried; weight 10 g. (70.4%), m.p. 105–107°. Two recrystallizations from hot ethanol afforded colorless plates, m.p. 107.5°, reported m.p. 102°.[4]

Anal. Calcd. for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09. Found: C, 75.98; H, 6.92.

The oxidation of I with selenium dioxide in glacial acetic acid gave colorless needles, m.p. 151–153°, which showed no depression on admixture with authentic samples of phenetil prepared by Lewis' method.[4]

Similarly, desoxyanisoin was made from *p*-methoxyphenylacetic acid and anisole in 75% yield.

p,p'-Diethoxy-α-chlorostilbene. (IV). A mixture of I (7.1 g.; 0.025 mole), phosphorus pentachloride (5.4 g.; 0.026 mole), and dry benzene (20 ml.) was allowed to stand at room temperature over a period of 15 hr., and then refluxed on a water bath for 1 hr. The resulting red solution was poured into ice water and the products were extracted with an additional 100 ml. of benzene. When the dried extract was evaporated to dryness, and the crystalline residue was treated with a moderate amount of ethanol to remove the noncrystalline part, there remained colorless plates, 4.5 g. (60%), m.p. 103–105°. After two recrystallizations from absolute ethanol, the m.p. reached 105–106°.

Anal. Calcd. for $C_{18}H_{19}O_2Cl$: C, 71.39; H, 6.32. Found: C, 71.36; H, 6.08.

Similarly, *p,p'*-dimethoxy-α-chlorostilbene was obtained from desoxyanisoin as colorless plates (from absolute ethanol); m.p. 117–118°.

Anal. Calcd. for $C_{16}H_{15}O_2Cl$: C, 69.94; H, 5.50. Found: C, 69.98; H, 5.55.

Tris(p-ethoxyphenyl)ethylene. (V). To a cooled mixture of phenetole (0.5 g.; 0.0041 mole), aluminum chloride (0.5 g.; 0.0038 mole), and carbon disulfide (20 ml.) was added IV (1 g.; 0 0.0034 mole) in small portions with stirring. After standing at room temperature for 3 hr., the reaction mixture was treated as usual. The crude product was recrystallized from hot ethanol (20 ml.), giving colorless prisms, m.p. 100–101°. Yield: 0.8 g. (60%). For analysis, small samples were thrice recrystallized from absolute ethanol to give the m.p. of 103–104°, reported m.p. 102°.[5]

Anal. Calcd. for $C_{26}H_{28}O_3$: C, 80.38; H, 7.27. Found: C, 80.58; H, 7.31.

The bromination of V with bromine in carbon tetrachloride afforded *tris(p-ethoxyphenyl)bromoethylene*, which melted at 96–98° after several recrystallizations from absolute ethanol, reported[6] m.p. 81–82°.

Anal. Calcd. for $C_{26}H_{27}O_3Br$: Br: 17.10. Found: Br. 16.83.

Tris(p-ethoxyphenyl)chloroethylene. To a cold solution of V (0.39 g.; 0.0010 mole) in carbon tetrachloride (3 ml.) was added sulfuryl chloride (0.2 g.; 0.0013 mole) drop by drop. The reaction mixture was allowed to stand overnight at room temperature, and then evaporated to dryness on gently warming. The resulting red-colored residue, when treated with a small amount of ethanol, gave a crystalline product (0.40 g.), m.p. 96–98°. On several recrystallizations from ethanol, it gave colorless prisms which melted at 103–104°.

Anal. Calcd. for $C_{26}H_{27}O_3Cl$: C, 73.83; H, 6.43; Cl, 8.38. Found: C, 73.59; H, 6.55; Cl, 8.17.

Action of bromine on I. (A) To a solution of I (0.7 g.; 0.0025 mole) in carbon tetrachloride (15 ml.) was added dropwise a solution of bromine (0.4 g.; 0.0025 mole) in carbon tetrachloride (6 ml.) with vigorous stirring for 30 min. After most

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(1) Nagano, *J. Am. Chem. Soc.*, **77**, 1691 (1955).

(2) Oki, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **72**, 1046 (1951) [*Chem. Abstr.*, **47**, 3284 (1953)].

(3) Wiechell, *Ann.*, **279**, 337 (1894).

(4) Lewis, Cramer, and Bly, *J. Am. Chem. Soc.*, **46**, 2063 (1924).

(5) Hey and Carter, Brit. Patent 586,493 (1941).

(6) Carter and Hey, *J. Chem. Soc.*, 154 (1948).

of the solvent was removed under reduced pressure without heating, the residue, after being treated with petroleum ether (20 ml.), gave crystals weighing 0.6 g. Further recrystallization from carbon tetrachloride petroleum ether gave colorless prisms, m.p. 100–102°. The analysis indicated that this material was α-bromodesoxyphenetoin (II).

Anal. Calcd. for $C_{18}H_{19}O_3Br$: Br, 22.00. Found: Br, 21.87.

(B) A mixture of I (0.3 g.) and bromine (0.2 g.) in carbon tetrachloride (3 ml.) was warmed on a water bath until the solvent had evaporated. The residue was crystallized from ethanol (3 ml.), yielding halogen-free compound (0.2 g.). Repeated recrystallization from ethanol gave colorless needles, m.p. 151–153°, which failed to depress the melting point of authentic phenetil.

Phenetoin. A mixture of II (0.4 g.; 0.001 mole) and sodium ethoxide [sodium (0.07 g.; 0.003 mole) in 3 ml. of absolute ethanol] was allowed to stand overnight at room temperature. Then it was poured into water and neutralized with cold 10% hydrochloric acid. Resulting precipitates were collected, washed with water, and dried (0.3 g.). Twice recrystallized from ethanol, the compound had m.p. 88–89°, reported m.p. 86–87°.

Anal. Calcd. for $C_{18}H_{20}O_4$: C, 71.98; H, 6.71. Found: C, 72.04; H, 6.58.

1,2,2-Trianisylethanone. (A) Trianisylbromoethylene (0.6 g.) was heated with 20 ml. of 50% ethanol in a sealed tube at 100° for 24 hr. After the supernatant fluid was removed, the oily residue was treated with 10 ml. of absolute ethanol denatured with 1% anisole, giving colorless prisms (0.4 g.), which melted at 74–76° to a cloudy liquid and became clear at 79°. Reported[8] m.p. for *1,2,2-trianisylethanone anisolate,* 77–79°.

(B) To a cooled solution of α-bromodesoxyanisoin (1.1 g.) and anisole (1.1 g.) in carbon disulfide (30 ml.), pulverized aluminum chloride (2 g.) was added in small portions with stirring (30 min.), and the mixture was allowed to stand at room temperature for 20 hr. Upon decomposition of the complex in ice and concentrated hydrochloric acid, a viscous yellow liquid was obtained from the organic layer. This could be crystallized from the same solvent as employed in the former case, the crystals thus obtained (0.6 g.) showing no depression of melting point when mixed with the material described under A.

The reduction of the anisolate with sodium borohydride in methanol gave 1,2,2-trianisylethanol, m.p. 107–108°; reported[9] m.p. 107–108°.

Acknowledgment. The author wishes to thank Mr. Konomu Matsumura for advice and encouragement in this work.

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(7) Weisberger, *et al., Ann.,* **478,** 126 (1930).

(8) Sumrell and Goheen, *J. Am. Chem. Soc.,* **77,** 3806 (1955).

(9) Sisido, *et al., J. Am. Chem. Soc.,* **77,** 6582 (1955).

The Color Produced in Acetone Solutions of Nitroaromatics and Sodium Iodide

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Received November 26, 1956

It was recently reported by Blatt and Gross[2] that aromatic nitro compounds and alkali iodides in acetone solution develop colors in the visible region which can be used as a qualitative test for aromatic nitro compounds and the number of nitro groups they contain: Acetone solutions approximately 0.1M with respect to both the aromatic nitro compound and sodium iodide are very pale yellow if the aromatic nitro compound contains one nitro group; deeper yellow, comparable with the color of 0.3M aqueous iron (III) chloride, if the aromatic nitro compound contains two nitro groups; and red-brown, comparable with the color of 3.0M aqueous iron (III) chloride, if the aromatic nitro compound contains three nitro groups.

The only earlier report of the color reaction in question is that of Tronow, D'yakonova-Schultz, and Zonova,[3] who examined three trinitro- and two dinitroaromatics, varied the solvent and inorganic iodide widely, and concluded from indirect evidence that the acetone complexes had the probable composition, one aromatic nitro compound: one alkali iodide: three acetone.

EXPERIMENTAL

Reagents and apparatus. 1,3-Dinitrobenzene (DNB) was recrystallized from ethanol until a product with a constant melting point of 90.5–91.5° (uncorr.) was obtained. As a test for water-soluble impurities, a small amount of the product was shaken with distilled water and then filtered. The water was unchanged in *p*H, and tests for nitrate and nitrite were negative. 2,4,6-Trinitrotoluene (TNT) was recrystallized from ethanol until a constant melting point of 80.5–81.5° (uncorr.) was obtained. An earlier observation[4] that TNT when exposed to light develops a red impurity was confirmed. The red color (corresponding to an absorption centered at about 510 mμ) develops more quickly in solutions of TNT in acetone than it does in the dry solid. Solid TNT in a brown bottle can be kept for several weeks without appreciable decomposition; when the red color does develop, it can be removed by one or two recrystallizations. 4,4'-Dinitrobiphenyl, recrystallized from acetone, had a melting point of 241–242° (uncorr.). Mallinckrodt Analytical Reagent acetone was used as solvent without further purification. Mallinckrodt Analytical Reagent sodium iodide was dried at 110° overnight and weighed from a weighing bottle. (Sodium iodide was selected rather than potassium iodide because of its higher solubility in acetone.)

Spectrophotometric measurements were made on a Beckman model DK-1 recording spectrophotometer.

1,3-Dinitrobenzene. 1,3-Dinitrobenzene absorbs strongly in the ultraviolet region of the spectrum. Since this absorption is centered at wave lengths at which acetone is opaque, the measurements in acetone solution were made along the side of the absorption curve. Addition of sodium iodide moves the absorption toward longer wave lengths corresponding to the appearance of the yellow color, and the cut-off becomes much less sharp. (See Figure 1.) The region between about 420 mμ and 550 mμ appeared to be the most fruitful region for study, for at these wave lengths the mixture solutions absorb strongly whereas the solutions of either reactant alone are transparent or nearly so.

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(2) Reported by A. H. Blatt and Norma Gross, at The Office of Ordnance Research Conference on High Nitrogen Compounds, Duke University, March 28–29, 1956.

(3) B. V. Tronow, L. N. D'yakonova-Schultz, and E. Zonova, *J. Russ. Phys.-Chem. Soc.,* **59,** 333 (1927); *Chem. Abstr.,* **22,** 2555 (1928).

(4) G. Schultz and K. L. Ganguly, *Ber.,* **58B,** 702 (1925).