

only single products it seemed of interest to examine *trans*-1,2-diphenyl-1-propene. We have found only one product, 1,2-diphenyl-1-chloromercuripropanol-2, by hydroxymercuration in 1,2-dimethoxyethane. Methoxymercuration gives only 1,2-diphenyl-1-chloromercuri-2-methoxypropane. These structures have been defined by hydrazine hydrate reduction to 1,2-diphenylpropanol-2 and 1,2-diphenyl-2-methoxypropane.

Experimental²

1,2-Diphenyl-1-chloromercuripropanol-2.—To a suspension of 3.0 g. (0.0155 mole) of *trans*- α -methylstilbene³ (m.p. 80.5–81.5°, diffraction [20] 4.88; [16] 6.96, 6.48; [12] 4.52, 3.86; [10] 4.68; [8] 3.79; [6] 3.71; [4] 11.78, 3.25; [2] 5.86; [1] 7.52, 4.35, 4.02) and 9.6 g. (0.031 mole) of mercuric acetate in 125 ml. of 50% aqueous 1,2-dimethoxyethane was added 1.00 g. (0.004 mole) of benzoyl peroxide. After 6 days agitation at 20–25° the system was filtered into 200 ml. of 3% aqueous sodium chloride. The precipitate was filtered off, washed with methanol (50 ml.) and ether (50 ml.), 1.85 g. (28%), m.p. 131–134°. Crystallization from acetone (15 ml./g.) raised the m.p. to 133.5–135.0°.

Anal. Calcd. for C₁₅H₁₅ClHgO: Hg, 45.0. Found: Hg, 44.4.

1,2-Diphenyl-1-chloromercuri-2-methoxypropane.—To a solution of 6.00 g. (0.031 mole) of α -methylstilbene and 19.1 g. (0.06 mole) of mercuric acetate in 200 ml. of anhydrous methanol was added 1.85 g. (0.0076 mole) of benzoyl peroxide. After 7 days agitation at 20–25° the system was filtered into 350 ml. of 4% aqueous sodium chloride. The precipitate was filtered off and washed with 100 ml. of diethyl ether, 7.8 g. (74%), m.p. 81.5–82.5°. Crystallization from absolute ethanol (8 ml./g.) raised the m.p. to 84.3–85.0°. Diffraction is [20] 8.93; [16] 12.27, 3.18; [14] 7.82, 6.96; [10] 4.16; [8] 6.06, 4.79; [4] 4.44, 4.11, 3.82; [2] 4.37, 3.52, 2.94, 2.79, 2.73, 2.66, 2.45, 2.33, 2.23, 2.17; [1] 3.66, 3.42, 2.54, 2.26.

Anal. Calcd. for C₁₆H₁₇ClHgO: Hg, 43.5. Found: Hg, 43.0.

The etherous extract contained 0.80 g. of unchanged α -methylstilbene.

1,2-Diphenylpropanol-2.—To a solution of 1.45 g. (0.0033 mole) of 1,2-diphenyl-1-chloromercuripropanol-2 in 10 ml. of methanol was added a solution of 1.27 g. (0.0066 mole) of sodium hydroxide in 2.0 ml. of water, then 2.00 ml. (0.035 mole) of 85% hydrazine hydrate. After 7 hours reflux, the system was filtered to remove 0.62 g. (95%) of mercury. The filtrate was diluted with 60 ml. of water and extracted with a total of 30 ml. of diethyl ether. A colorless oil (0.58 g.) obtained from this extract was distilled, b.p. 145–148° (3 mm.), 0.42 g. (60%), m.p. 49.5–51.0°. Mixture melting point with authentic 1,2-diphenylpropanol-2 was not lowered.

A mixture melting point with the alcohol prepared according to the method of Hell⁴ was not lowered. We have never been able to reproduce the melting point of 71–72° quoted by Tuot and Guyard.⁵

1,2-Diphenyl-2-methoxypropane.—To 9.2 g. (0.02 mole) of 1,2-diphenyl-1-chloromercuri-2-methoxypropane in 40 ml. of methanol was added a solution of 1.60 g. (0.004 mole) of sodium hydroxide in 4 ml. of water, then 2.9 ml. (0.05 mole) of 85% aqueous hydrazine hydrate. After 450 minutes reflux the system was filtered to remove 3.65 g. (91%) of mercury. The filtrate was diluted to 150 ml. with water and extracted with a total of 140 ml. of ether. Evaporation of this extract left an oil which was distilled, b.p. 110–112° (13 mm.), 1.33 g. (29%).

Anal. Calcd. for C₁₆H₁₈O: C, 83.9; H, 8.04. Found: C, 83.9; H, 8.50.

When this ether (1.13 g., 0.005 mole) was heated at 70–75° for 150 minutes with 3.3 ml. (0.025 mole) of 47% hydro-

bromic acid in 6.5 ml. of glacial acetic acid, a yield of 0.90 g. (90%) of 1,2-diphenylpropanol-2, m.p. 50.5–51.5°, was obtained. A mixture melting point was not lowered.

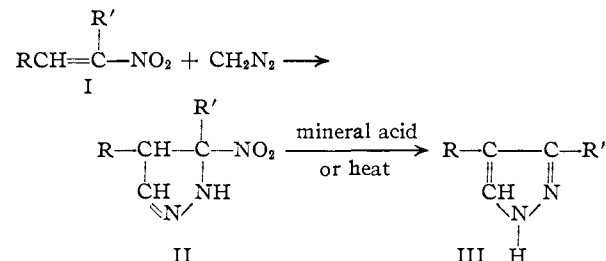
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Action of 9-Diazofluorene on ω -Nitrostyrenes and its Substituted Derivatives

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Recently, Parham and Bleasdale¹ have shown that the condensation of nitroolefins (I) which contain no hydrogen atom alpha to the nitro group with diazomethane results in the formation of products (presumably nitropyrazolines (II)) which yield 3,4-disubstituted pyrazoles (III) in good yields when treated with mineral acids or heat. In two cases the intermediate nitropyrazolines were obtained as crystalline solids. When diazomethane was allowed to react with ω -nitrostyrene (Ia) at room temperature, a quantitative yield of additive product was obtained. However, the product appeared to be polymeric and had no properties commensurate with those of the expected nitropyrazolines (II).



We have now investigated the action of 9-diazofluorene on the ω -nitrostyrenes (Ia–Ie) listed in Table I and found that they react to give the cyclopropane derivatives V listed in Table II, believed to be formed by way of the intermediate pyrazoline, e.g., IV.²

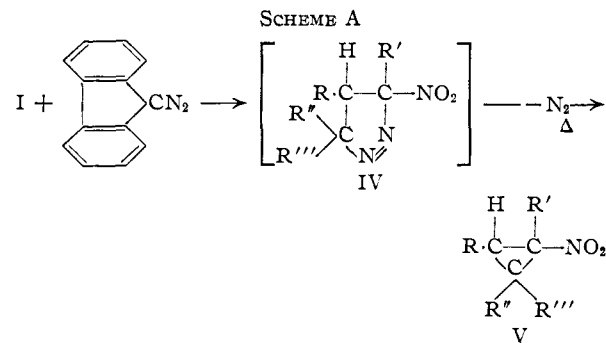


TABLE I

Ia, R = C₆H₅, R' = H; b, R = C₆H₄NO₂-*o*, R' = H; c, R = C₆H₄NO₂-*m*, R' = H; d, R = C₆H₄NO₂-*p*, R' = H; e, R = 3-pyrenyl (C₁₆H₉), R' = H

(1) W. E. Parham and J. L. Bleasdale, *THIS JOURNAL*, **72**, 3843 (1950); **73**, 4664 (1951).

(2) The reaction of 9-diazofluorene with acrylonitrile and methyl vinyl ketone leads directly to the formation of cyclopropane derivatives. Cf. L. Horner and E. Lingnau, *Ann.*, **673**, 30 (1951).

(2) Melting points have been corrected against reliable standards. X-Ray diffraction patterns are expressed at d spacings in Å. with relative intensities [I/I₁] using CuK α radiation.

(3) C. F. Koelsch and R. V. White, *J. Org. Chem.*, **6**, 602 (1941).

(4) C. Hell, *Ber.*, **37**, 453 (1904).

(5) M. Tuot and M. Guyard, *Bull. soc. chim. France*, 1086 (1947).