

Acknowledgment.—The author wishes to express his appreciation for the valuable technical assistance given by Mr. J. B. Campbell.

The Preparation of Diarylcyclopropenones by the Reaction of Phenyl(bromodi- chloromethyl)mercury with Diarylacetylenes¹

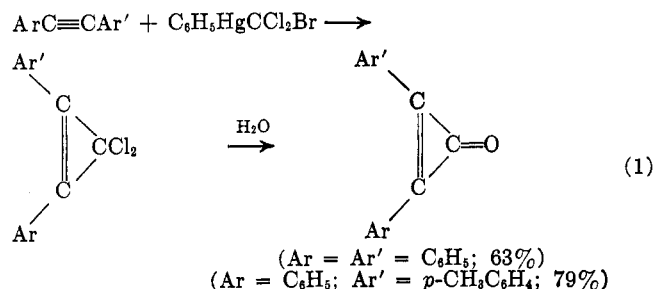
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Received December 16, 1965

Diarylcyclopropenones have been of interest in recent years, and considerable effort has been expended on the development of useful procedures for their preparation. The best route to symmetrically substituted diarylcyclopropenones is Breslow's elimination of HBr from α, α' -dibromobenzyl ketones.⁴ Vol'pin, *et al.*,⁵ have reported that reaction of diphenylacetylene with bromoform and potassium *t*-butoxide produces diphenylcyclopropenone in 20–30% yield. All other routes reported to date appear to be considerably less practical.⁶

In an extension of our study of the reactions of olefins with phenyl(trihalomethyl)mercury compounds,⁷ we have found that diarylacetylenes react with phenyl(bromodichloromethyl)mercury to give, after hydrolysis of the reaction mixture, high yields of diarylcyclopropenones (eq 1). This procedure should find es-



pecially useful application in the preparation of unsymmetrical diarylcyclopropenones and of diarylcyclopropenones containing base-sensitive functional groups. Analogous reactions could not be realized with dialkylacetylenes.

Experimental Section

General Comments.—All reactions were carried out under an atmosphere of prepurified nitrogen. Diphenylacetylene was purchased from Orgmet; phenyl-*p*-tolylacetylene was prepared

by the method of Stephens and Castro⁸ in 83% yield: mp 72.5–74°. The preparation of phenyl(bromodichloromethyl)mercury has been described in a previous paper of this series.⁹

Diphenylcyclopropenone.—A solution of 3.56 g (20 mmoles) of diphenylacetylene and 8.82 g (20 mmoles) of phenyl(bromodichloromethyl)mercury in 50 ml of dry benzene was heated at reflux with stirring under a nitrogen atmosphere for 1 hr. The reaction mixture was cooled and filtered to remove phenylmercuric bromide (6.3 g, 88%). The filtrate was hydrolyzed by heating it at reflux with 25 ml of 95% ethanol for 5 min.¹⁰ The solvents were removed at reduced pressure to leave a hard, yellow solid. The latter was dried at 0.05 mm for 18 hr to give 4.65 g of light yellow crystals. These were sublimed at 82° (0.03 mm), giving 4 g (97%) of slightly yellow crystals which melted over a range of 100–140°. This crude product was recrystallized from dry cyclohexane, being separated from some yellow, cyclohexane-insoluble solid in the process. Slow crystallization from cyclohexane solution at room temperature gave 2.60 g (63.3%) of pure diphenylcyclopropenone, mp 120–122° (cor), lit.⁴ mp 119–121°. The infrared spectrum of the product (CCl₄ and CS₂) was identical with that of an authentic sample prepared by Breslow's method,⁴ as was the ultraviolet spectrum in ethanol solution.

Phenyl-*p*-tolylcyclopropenone.—Essentially the same procedure was used in the reaction of 20 mmoles each of phenyl-*p*-tolylacetylene and phenyl(bromodichloromethyl)mercury. The yield of crude product (light yellow crystals, mp ~116°) was 3.50 g (79.6%). Recrystallization of 1.0 g of this material from benzene gave 0.55 g of solid with mp 128.5–129°. An analytical sample melted at 129.5–131.5°.

Anal. Calcd for C₁₅H₁₂O: C, 87.24; H, 5.49. Found: C, 87.14; H, 5.27.

The infrared spectrum (CCl₄-CS₂ composite, Perkin-Elmer 337) showed bands at 3075 (w), 3060 (w), 3025 (w), 2975 (w), 2915 (w), 1850 (s), 1630(s), 1510 (m), 1485 (m), 1450 (m), 1340 (m), and 788 (s) cm⁻¹. The nmr spectrum (CDCl₃ solution, Varian A-60) showed a singlet (3 H) at 2.44 ppm and a 9 H multiplet at 7.26–8.04 ppm downfield from tetramethylsilane. The ultraviolet spectrum (in ethanol) showed the following bands, m μ (log ϵ): 223 (4.25), 228 (sh) (4.22), 234 (sh) (4.16), 293 (sh) (4.40), 302 (4.47), and 317 (sh) (4.29).

Acknowledgments.—The authors are grateful to the U. S. Air Force Office of Scientific Research for generous support of this work. This investigation was supported in part by Public Health Service Fellowship 5-F1-GM-24,781-02 (to R. D.).

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Determination of the Hammett σ Constants for the Picryl Group

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Received November 3, 1965

In a recent communication from this laboratory¹ the values for the σ constants for *m*- and *p*-picrylbenzoic acids were reported. These values were determined by measuring the rates of reaction of these acids with diphenyldiazomethane (DDM) and are 0.430 and 0.412 for the *meta* and *para* compounds, respectively.

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