The Preparation of Diarylcyclopropenones by the Reaction of Phenyl(bromodichloromethyl)mercury with Diarylacetylenes[1]
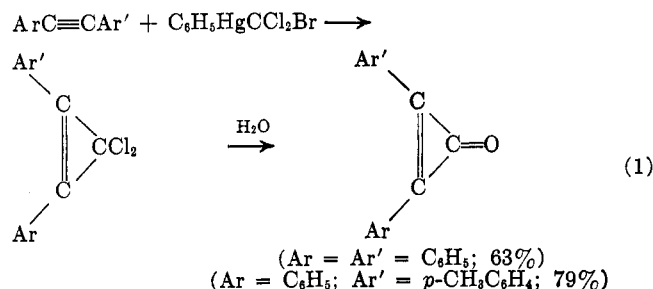
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Diarylcyclopropenones have been of interest in recent years, and considerable effort has been expended on the development of useful procedures for their preparation. The best route to symmetrically substituted diarylcyclopropenones is Breslow's elimination 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 especially useful application in the preparation of unsymmetrical diarylcyclopropenones and of diarylcyclopropenones containing base-sensitive functional groups. Analogous reactions could not be realized with dialkylacetylenes.

$$ArC\equiv CAr' + C_6H_5HgCCl_2Br \longrightarrow$$

$$\begin{array}{c}(Ar = Ar' = C_6H_5; \ 63\%)\\ (Ar = C_6H_5; \ Ar' = p\text{-}CH_3C_6H_4; \ 79\%)\end{array} \tag{1}$$

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 purchase from Orgmet; phenyl-p-tolylacetylene was prepared

by the method of Stephens and Castro[8] 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 (CCl_4 and CS_2) 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 $C_{16}H_{12}O$: C, 87.24; H, 5.49. Found: C, 87.14; H, 5.27.

The infrared spectrum (CCl_4–CS_2 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 ($CDCl_3$ 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, mμ (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).

(1) Part V of the series, Halomethylmetal Compounds. Part IV: D. Seyferth, J. K. Heeren, G. Singh, S. O. Grim, and W. B. Hughes, J. Organometal. Chem. (Amsterdam), 5, 267 (1966).

(2) Alfred P. Sloan Foundation Fellow, 1962–1966.

(3) National Institutes of Health Predoctoral Fellow.

(4) R. Breslow, T. Eicher, A. Krebs, R. A. Peterson, and J. Possner, J. Am. Chem. Soc., 87, 1320 (1965).

(5) (a) M. E. Vol'pin, Yu. D. Koreshkov, and D. N. Kursanov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 560 (1959); (b) D. N. Kursanov, M. E. Vol'pin, and Yu. D. Koreshkov, Zh. Obshch. Khim., 30, 2877 (1959).

(6) These are discussed, with references, in ref 4.

(7) D. Seyferth, J. M. Burlitch, R. J. Minasz, J. Y.-P. Mui, H. D. Simmons, Jr., A. J.-H. Treiber, and S. R. Dowd, J. Am. Chem. Soc., 87, 4259 (1965).

(8) R. D. Stephens and C. E. Castro, J. Org. Chem., 28, 3313 (1963).

(9) D. Seyferth and J. M. Burlitch, J. Organometal. Chem. (Amsterdam) 4, 127 (1965).

(10) Hydrolysis procedure of S. W. Tobey, Ph.D. Thesis, University of Wisconsin, 1965. We are indebted to Dr. Tobey for bringing this procedure to our attention.

Determination of the Hammett σ Constants for the Picryl Group

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In a recent communication from this laboratory[1] 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.

(1) H. E. Ruskie and L. A. Kaplan, J. Org. Chem., 30, 319 (1965).

Because these compounds were readily available, it was decided to determine the σ constants by still another procedure. The ionization constants were determined at 25° in 50 vol % aqueous ethanol and compared with that of benzoic acid determined under like conditions. The value for ρ for this ionization is 1.423.[2] The ionization constants found were 5.32, 5.27, and 5.71[3] for the m- and p-picrylbenzoic and benzoic acids, respectively. σ values calculated from this data are 0.274 for the m-picryl group and 0.309 for the p-picryl group.

Although these σ values are smaller than those reported previously,[1] they are within the range of differences found for other groups.[2] It is to be noted also, that the ordering of these constants are in the reverse of the earlier values and differ by about 13%.

Experimental Section

The preparation of the m- and p-picrylbenzoic acids are described elsewhere.[1]

Determination of pk Values.—Approximately 0.25 mequiv of the acid was dissolved in 10 ml of absolute ethanol, and 8 ml of water was added and mixed. The solution was titrated potentiometrically with standard sodium hydroxide solution, using a Beckman Model G pH meter. For each aliquot of base added, a volume of water was added so that at the calculated half-neutral point the solution would be 50 vol % ethanol. The equivalent point was determined from which the half-neutral point was found. The pH meter reading was taken as the pk value. The pH meter was standardized with aqueous potassium hydrogen phthalate (NBS), and so the actual pH may be different for the organic solvent. However, the σ values were obtained by using the differences in pk between benzoic acid and the desired acid, and these differences are probably correct.

A check on the pk obtained by the above procedure was obtained by preparing a second solution exactly half-neutralized made up in 50 vol % ethanol. These pH meter readings agreed with those reported above within 0.02 pH unit.

(2) H. H. Jaffé, Chem. Rev., 53, 191 (1953).
(3) J. D. Roberts, E. A. McElhill, and R. Armstrong [J. Am. Chem. Soc., 71, 2923 (1949)] reported that the pk for benzoic acid is 5.75 determined by the same procedure.

The Reaction of Triphenylamine with Alkali Metals. Observations on the Mechanism

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Wittenburg and Gilman[3] have shown that triphenyl derivatives of group Vb elements are easily cleaved by alkali metals (M) in tetrahydrofuran (THF), according to the equation

$$Ph_3(Vb) + 2M \longrightarrow Ph_2(Vb)M + MPh$$
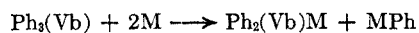
(1) National Science Foundation Fellow 1964–.
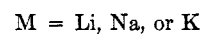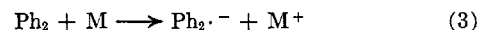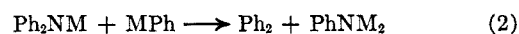(2) To whom inquiries concerning this article should be addressed.
(3) D. Wittenburg and H. Gilman, J. Org. Chem., 23, 1063 (1958).

The connection between this general reaction and subsequent free-radical formation has been described for Ph_3P.[4] We now wish to report the results of similar studies on Ph_3N.

Ph_3N was dissolved in THF and reacted with Li, Na, and K, using the customary high-vacuum procedures. The general reaction given above was observed together with formation of the biphenyl negative ion, identified by its well-known electron spin resonance (esr) spectrum.[5] No free radicals were observed by esr prior to the detection of $Ph_2\cdot^-$.

As the reaction proceeded, aliquots were removed, opened to air, and analyzed by vapor phase chromatography. In every case, biphenyl and aniline were obtained in about equal amounts together with small (and variable) amounts of Ph_2NH. (The metal phenide converted to benzene, which was merged with the THF solvent peak). Relatively large amounts of unreacted Ph_3N were also observed. Biphenyl was present in solution prior to subsequent reduction to the corresponding anion radical.

These observations can be explained by the following reaction sequence.

$$Ph_3N + 2M \longrightarrow Ph_2NM + MPh^3 \qquad (1)$$

$$Ph_2NM + MPh \longrightarrow Ph_2 + PhNM_2 \qquad (2)$$

$$Ph_2 + M \longrightarrow Ph_2\cdot^- + M^+ \qquad (3)$$

$$M = \text{Li, Na, or K}$$

A crucial test of this explanation would be the study of reaction 2, isolated from either reaction 1 or reaction 3. For this test, Ph_2NK was prepared and treated with freshly prepared LiPh. Vapor phase chromatographic analysis showed that biphenyl and aniline were produced in equal amounts, confirming reaction 2, and also indicated the absence of a detectable amount of $PhNH_2$, suggesting that this reaction was quantitative.

If p,p',p''-trideuteriotriphenylamine was used as starting material, the corresponding p,p'-dideuteriobiphenyl anion radical was produced, identified by esr. The formation of biphenyl from Ph_3N therefore appears to involve the successive breaking of two carbon–nitrogen bonds, the first cleavage occurring by the reaction with alkali metals and the second cleavage occurring with alkali metal phenides.[6]

Experimental Section

All compounds were purified by recrystallization until literature melting points were obtained and no impurities were detected by vapor phase chromatography (vpc).

Ph_3N (70–120 mg) was dissolved in ca. 10 ml of THF in the glass apparatus usually used for esr studies[4] to form solutions ranging from 3–5 × 10^{-2} M. After degassing the THF the initial reaction between Ph_3N and either Na or Li was conducted at room temperature; the corresponding reaction with K was usually conducted in the range 0–10°. In the cases of Na or K, after the solutions became yellow-brown due to the initial reaction, they were cooled to −50° and reacted further. The blue color of the biphenyl anion radical was observed at the surface of each metal and confirmed by esr. The reaction of Li with Ph_3N pro-

(4) A. D. Britt and E. T. Kaiser, J. Phys. Chem., 69, 2775 (1965).
(5) A. Carrington and J. dos Santos-Veiga, Mol. Phys., 5, 21 (1962).
(6) The support of the donors of the Petroleum Research Fund is gratefully acknowledged.