Co.) was redistilled before using. 1-Buten-3-yl methyl ether (bp 49–50°) was prepared by reaction of α-methallyl chloride[9] with sodium methoxide in methanol.[10] 1-Buten-3-yl acetate, bp 112° (lit.[11] bp 110°), was prepared by reaction of the alcohol with acetic acid in the presence of pyridine. The infrared and nmr spectra of the three compounds were consistent with their assigned structures.

Determination of k_a/k_{tr} Ratios.—Solutions consisting of compounds I, II, and III and bromotrichloromethane in the amounts shown in Table I were sealed in Pyrex (6 mm by 120 mm) tubes. In the reactions of I, cyclohexene oxide in an amount slightly in excess of the bromotrichloromethane was added. The tubes were wrapped in aluminum foil to protect the contents from light and placed in a constant temperature water bath (40 ± 0.1°). After being allowed to warm to the temperature of the bath, the foil was removed and the tubes were illuminated with a 275-W G.E. sunlamp positioned about 5 in. from the tubes. Illumination was allowed to take place until most of the polyhalomethane had reacted (2–5 hr). The amounts of bromotrichloromethane that had reacted and amounts of chloroform produced were determined by gas chromatographic analysis of a weighed portion of reaction mixtures along with a weighed amount of 3-pentanol which served as an internal standard. The analyses were performed on an F & M Model 5750 Research chromatograph equipped with a Mosely Model 17503A recorder with a disc integrator and employing a thermal conductivity detector. The separations were accomplished on a 0.125-in. by 10-ft column packed with 15% E-600 on 60–80 mesh Chromosorb W.

Registry No.—I, 598-32-3; II, 17351-24-5; III, 6737-11-7; bromotrichloromethane, 75-62-7.

[9] W. G. Young, S. H. Sharman, and S. Winstein, *ibid.*, **82**, 1376 (1960).

[10] A. G. Catchpole and E. O. Huges, *ibid.*, 4 (1948).

[11] D. Semenow, C. H. Shih, and W. G. Young, *ibid.*, **80**, 5472 (1958).

Diphenylketene. Triphenylphosphine Dehalogenation of α-Bromodiphenylacetyl Bromide[1]

S. D. DARLING AND R. L. KIDWELL[2]

Department of Chemistry, Southern Illinois University, Carbondale, Illinois 62901

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The reactions of triphenylphosphine with halogen derivatives of carbonyl compounds have been the subject of intensive study.[3] In view of the proposed mechanisms for the reactions of triphenylphosphine with these compounds, an α-haloacyl halide should offer attack by the nucleophilic phosphine at the α-carbon, carbonyl carbon, or at either halogen. While phosphonium salts at carbon would not be unusual, displacements at halogen might yield a new enol phosphonium salt or a ketene. Attack at the α halogen appears favorable considering that the acyl halide would stabilize a carbanion. Such a reaction might be considered similar to the zinc dehalogenation of α-haloacyl halides.[4] Additional stabilization could be achieved by phenyl substitution on the α carbon.

We wish to report a convenient synthesis of diphenylketene **2** from α-bromodiphenylacetyl bromide **1**.

$$\underset{\mathbf{1}}{Ph_2CBrCOBr} + Ph_3P \longrightarrow \underset{\mathbf{2}}{Ph_2C{=}C{=}O} + Ph_2PBr_2$$

The acetyl bromide **1** was first prepared by Staudinger[5] from the addition of bromine to diphenylketene. A subsequent preparation of the dibromide from benzylic acid by the action of phosphorus pentabromide was reported.[6] Its preparation from diphenylacetic acid does not appear to have been reported. This source of the acyl bromide proved to furnish easily purified product. The usual bromination procedure was modified to use phosphorus pentabromide prepared *in situ*, followed by additional bromine to complete the reaction. In contrast the dihalide obtained from the benzylic acid bromination, in our hands, was difficult to purify, resulting in a considerable loss of product.

To obtain diphenylketene from the dibromide **1**, the solutions of acyl halide and triphenylphosphine were mixed. A mildly exothermic reaction occurred which was accompanied by the formation of a precipitate and an intense yellow color. The precipitate when removed under nitrogen was found to fume in moist air. Complete hydrolysis of the solids produced triphenylphosphine oxide.

The reaction of triethylphosphite with chloroacetyl chloride is presumed to be initiated at the carbonyl carbon.[7] A similar reaction path for triphenylphosphine does not seem likely at first. The recent report of reaction between triphenylphosphine and chloroacetyl chloride indicates that at least some reaction is initiated at the α halogen.[8] When α-bromoisobutyryl bromide was added to a triphenylphosphine solution, the formation of a precipitate was very slow, and no evidence for dimethylketene was obtained. This suggests that stabilization of the displaced enolate anion is necessary. The fact that acyl halides do not appear to form phosphonium salts readily with triphenylphosphine might also be taken as evidence for a halogen displacement reaction. However, it is still possible that the type of reaction observed here occurs only when acyl phosphonium salts are formed first. While acetyl chloride or the bromide are unreactive, the presence of electron-withdrawing groups on the α carbon have been shown to enhance markedly the reactivity of acyl halides toward water and amines.[9] Trichloroacetyl chloride will react with 1 equiv of triphenylphosphine to give an ether insoluble solid. Methanolysis of this solid gave methyltrichloro acetate, thus indicating that an acyl phosphonium salt has been formed.

As would be expected for nucleophilic attack on the α halogen or the reaction of a less reactive acyl halide, α-chlorodiphenylacetyl chloride undergoes dehalogenation at a much slower rate than the dibromo compound.

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[2] (a) Taken from a dissertation submitted by R. L. Kidwell to the University of Southern California in partial fulfillment of the requirements for the Ph.D. degree. (b) Du Pont Teaching Fellow, 1963–1964; Stauffer Fellow, 1964–1965; National Science Foundation Summer Fellowship, 1965; Petroleum Research Fund Fellow, 1965–1966.

[3] For recent reviews, see (a) H. Hoffman and H. S. Diehr, *Angew. Chem. Intern. Ed. Engl.*, **3**, 737 (1964); (b) B. Miller in "Topics in Phosporus Chemistry," Vol. 2, M. Grayson and E. J. Griffith, Ed., John Wiley & Sons, Inc., New York, N. Y., 1965, pp 133–195.

[4] W. E. Hanford and John C. Sauer, *Org. Reactions*, **3**, 120 (1946).

[5] H. Staudinger, *Ann.*, **356**, 121 (1907).

[6] H. K. Kinger and G. Nickell, *ibid.*, **390**, 365, 371 (1912).

[7] Reference 3b, p 179.

[8] P. A. Chapared, *J. Org. Chem.*, **31**, 107 (1916).

[9] J. Ugi and F. Beck, *Ber.*, **94**, 1839 (1961).

Diphenylketene 2 has been prepared from the dibromide 1 through zinc dehalogenation[4] as well as from various other precursors.[10]

The advantages of this procedure over all others to date are many. Some of these are the elimination of unstable intermediates such as phenylbenzoyldiazomethane, the use of mild reaction conditions, the formation of salts which do not appear to catalyze readily polymerization of the ketene, and an economy of materials. In addition, the dibromophosphorane can be recovered for use in the conversion of alcohols and phenols into bromides[11] or the cleavage of ethers.[12]

The reactions of unsubstituted and monosubstituted α-haloacetyl halides is also being studied. These systems give results different from those reported here. When they are fully characterized, the data will be reported.

Experimental Section[13]

2-Bromo-2,2-diphenylacetyl Bromide.—Phosphorus pentabromide was prepared from 17.1 g (0.55 mol) of red phosphorus in a 1-l. one-neck flask fitted with a Claisen adaptor holding an efficient coil condenser and a 100-ml Hirschberg-type dropping funnel. A 200-ml portion of dry carbon tetrachloride was added to cover the phosphorus. The addition of 220 g (75.2 ml, 1.4 mol) of reagent bromine as rapidly as possible (10 min) produced considerable heat which maintained the dark solution in a state of reflux. When the reaction had subsided, 106 g (0.5 mol) of diphenylacetic acid (Matheson) was stuffed into the flask. The flask was heated on a steam bath to reflux. After a short period copious hydrogen bromide fumes were evolved. When the gas evolution had diminished and the bromine color dissipated, an additional 28 ml (88 g, 0.55 mol) of bromine was added rapidly from the dropping funnel. Heating at reflux was maintained until hydrogen bromide evolution ceased (5 hr). The carbon tetrachloride and excess bromine were removed under vacuum, and the mobile liquid product was poured onto a mixture of 500 g of ice and 200 ml of water with rapid stirring. The mass solidified but soon melted from the heat of the hydrolysis reaction. Stirring was continued until the mass again solidified. Trituration of the solids with water completed the hydrolysis of the phosphorus halides. The solids were taken up in 1.2 l. of benzene, and the organic layer was washed twice with water. After drying the benzene solution over magnesium sulfate, the solvent was removed under vacuum. To the liquid residue was added approximately 200 ml of dry *n*-pentane. Upon scratching, crystals were deposited and continued to grow while the mixture was stirred and cooled.

The product was separated by filtration on a sintered glass funnel and washed twice with cold pentane. The yield of white crystals was 152 g, mp 65–66.5° (lit.[5] mp 65–66°). From the mother liquors an additional 7 g of similar crystals was obtained. Its melting point was 63.5–65° thus bringing the total yield to 89%.

Diphenylketene. Procedure A.—A 500-ml three-neck flask containing a stopcock at the bottom was fitted with a mechanical stirrer, Hirschberg dropping funnel, and large Büchner-type sintered glass funnel with a receiver. The entire system was flame dried under vacuum and placed under a nitrogen atmosphere. A coil of copper tubing was placed around the outside of the flask, and salt brine was circulated through it for cooling. The flask was charged with a solution of 20.8 g (0.079 mol) of triphenylphosphine dissolved in 270 ml of sodium dried *n*-heptane.

A solution of 25.7 g (0.073 mol) of the dibromide in 180 ml of dry *n*-heptane was placed in the dropping funnel. When the temperature of the phosphine solution reached 20° the compound began to crystallize out. Addition of the dibromide solution was carried out rapidly (10 min) keeping the temperature of the reaction between 20.5 and 22.5°. An immediate precipitation occurred with the formation of a yellow solution. After 15 min a sample was withdrawn for spectral analysis. Whereas the original halide solution in heptane showed absorption at 1770 cm^{-1}, nothing was now observed in this region. Only a new sharp peak at 2060 cm^{-1} was evident.

The mixture was drawn out of the flask into the funnel, and the orange-yellow filtrate was collected in a Dry Ice cooled receiver. The solids were washed with three 50-ml portions of dry *n*-heptane. Some precipitate formed in the filtrate on standing. Hydroquinone was added and the filtrate was evaporated under high vacuum (less than 0.5 mm) in a short-path distillation apparatus with a Dry Ice cooled receiver. The distillation pot was not heated during this period. When the heptane had been removed, the residue was transferred under nitrogen to a 50-ml distillation flask, connected to a short-path distillation setup, and a fraction collector. After the addition of more hydroquinone, the liquid was distilled, bp 96–99° at 0.02 mm (lit.[7] bp 119–121° at 3.5 mm), yielding 7.2 g (51%) of the product. The orange-yellow product readily solidified, mp 8–9°. A sample was dissolved in carbon tetrachloride, and the following infrared absorptions were recorded: 3020 (w), 2090 (s), 2050 (w), 1600 (m), 1490 (s), 1460 (w), 1290 (w), 1120 (w), 1080 (w), 1040 (w) cm^{-1}.

Procedure B.—In a 1-l. three-neck flask fitted with a mechanical paddle stirrer, thermometer, and Hirschberg dropping funnel was placed 137 g (0.55 mol) of triphenylphosphine, a few crystals of hydroquinone, and 300 ml of C_6H_6. The benzene solution was distilled to remove 50 ml, thereby drying the solution. After the system was placed under nitrogen, the dropping funnel was charged with a solution of 177 g (0.5 mol) of α-bromo-α,α-diphenylacetyl bromide in 250 ml of dry benzene, the system was evacuated to degas the liquids, and dry nitrogen was readmitted. When the contents of the flask had been cooled to 0°, the halide solution was added rapidly over 25 min keeping the temperature between 5 and 10°. A thick sludge formed which made mixing less efficient. After all of the solution had been added, an additional 300 ml of dry benzene was added. The mixture was allowed to stir after the addition for 45 min while being cooled in an ice bath. A connection was made from the flask to a closed 80 mm coarse sintered glass Büchner funnel, and the sludge was transferred under nitrogen. Filtration under nitrogen was slow requiring about 2 hr. The filtrates were cooled in an ice bath. After the initial filtration, the solids were washed with two 150-ml portions of dry benzene. The benzene was removed at room temperature on a rotary evaporator and nitrogen was readmitted into the system before disconnecting the flask. The contents were poured into a 250-ml round-bottom flask; a small amount of hydroquinone was added; and the residual benzene was removed under high vacuum into a Dry Ice cooled receiver. Nitrogen was readmitted into the system, and a short-path distillation head was attached to the flask. The system was again placed under vacuum, and the pot was heated with an oil bath and stirred with a magnetic stirrer. No forerun was obtained as the light orange liquid distilled. The product was collected in the boiling range of 95–96° at 0.5 mm with a bath temperature of 130–140°. The yield of product was 79 g (81.5%).

The spectral properties of this oil were exactly as before. A melting point determination gave 9.4–10.4°. The purity of the product was ascertained through an anilide derivative. When 1 g of diphenylketene was added to 2 ml of aniline dissolved in 25 ml of benzene an immediate reaction took place. The solution was warmed on a steam bath for a short period, and then an equal volume of petroleum ether, bp 30–60, was added. Crystallization took place immediately and was completed with cooling. The crystals were removed and washed with petroleum ether, bp 30–60°. The yield was 1.41 g (95.3%) of pure white solid, mp 181–182° (lit.[14] mp 180°).

Registry No.—Diphenylketene, 525-06-4; triphenylphosphine, 603-35-0; α-bromodiphenylacetyl bromide, 17397-37-4.

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[10] L. I. Smith and H. H. Hoelm, "Organic Syntheses," Coll. Vol. III, John Wiley & Sons, Inc., New York, N. Y., 1955, p 356, and references therein.

[11] G. A. Wiley, R. L. Hershkowitz, B. M. Rein, and B. C. Chung, *J. Amer. Chem. Soc.*, **86**, 964 (1964).

[12] A. G. Anderson, Jr., and F. S. Freenor, *ibid.*, **86**, 5037 (1964).

[13] All melting points and boiling points are corrected.

[14] F. Klingemann, *Ann.*, **275**, 84 (1893).