

THE REACTION OF α -BROMOKETONES WITH TRIPHENYLPHOSPHINE - I

A NOVEL DEBROMINATION REACTION

I.J. Borowitz*¹ and L.I. Grossman²

Department of Chemistry, The City College, New York

(Received 11 April 1962)

THE reaction of phenacyl halides with triphenylphosphine is known to give the corresponding phenacyltriphenylphosphonium halides via nucleophilic displacement of halogen.³ We have found that secondary and tertiary α -bromoketones, in contrast, react with triphenylphosphine in refluxing benzene-methanol to give the debrominated ketone, triphenylphosphine oxide and methyl bromide.⁴ The results are summarized in Table 1.

TABLE 1
Debromination of α -Bromoketones

α -Bromoketone ^a	Product	Yield (%)
2-Bromocyclohexanone	Cyclohexanone	62 ^b
2-Methyl-2-bromocyclohexanone	2-Methylcyclohexanone	60 ^b
2- α -Bromocholestan-3-one	Cholestan-3-one	60 ^c
2-Bromodimedone	Dimedone	68 ^d
2-Bromobenzylphenylketone	Benzylphenylketone	70

^a All starting compounds and products gave satisfactory infrared or nuclear magnetic resonance spectra or correct m.p. and m.m.p. with genuine samples.

^b Further identified by comparison of the 2,4-DNP derivative with a genuine sample.

^c This experiment was performed by Mr. E. Axelrod, Columbia University.

^d Identified by comparison with the formaldehyde derivative with a genuine sample: m.p. and m.m.p. 188-189.5° (corr.).

* Present address: Department of Chemistry, Lehigh University, Bethlehem, Pa., U.S.A.

¹ Work done at the Department of Chemistry in Columbia University.

² N.S.F. Undergraduate Research Participant, City College, 1960-1961.

³ F. Ramirez and S. Dershowitz, *J. Org. Chem.* 22, 41 (1957).

⁴ Identified by the isolation of triphenylmethylphosphonium bromide resulting from reaction with excess triphenylphosphine.

No quarternary phosphonium bromides resulting from nucleophilic displacement of bromide were observed. Phenacyltriphenylphosphonium bromide was found to be stable to refluxing methanol, being recovered in 90 per cent yield.⁵ The use of moist benzene as a solvent led to the formation of triphenylphosphine oxide hydrobromide hydrate.⁶

In view of these facts we propose that secondary and tertiary α -bromoketones react with triphenylphosphine to give enol phosphonium salts⁷ as illustrated.

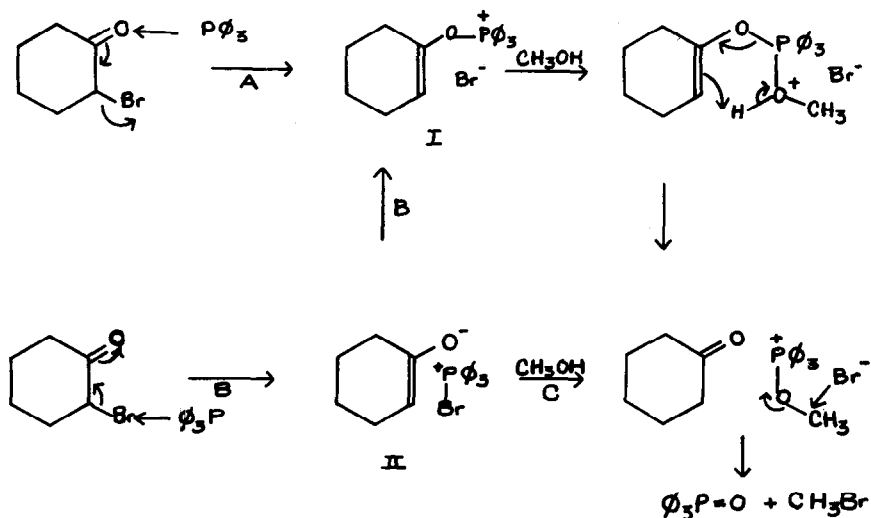


FIG. 1

Paths A and B represent alternate possibilities of initial attack of triphenylphosphine on the bromoketone leading to the enol phosphonium salt

⁵ L.I. Grossman, unpublished result.

⁶ Identified by elemental analysis, I.R. and NMR spectra and conversion to triphenylphosphine oxide.

^{7a} Similar conclusions involving path A have been reached by S. Trippett, *Proc. Chem. Soc.* 106 (1962); and A.J. Speziale, L.R. Smith and R.C. Freeman, Abstracts of Papers presented at the Meeting of the American Chemical Society, Chicago, p. 54Q (1961), propose enol phosphonium salt intermediates in the reactions of haloacetamides with phosphines.

^g The possibility of initial attack by triphenylphosphine on the carbonyl carbon with subsequent rearrangement to I must also be considered.

(I). The reaction of I with methanol or with water leads to the observed products. Path C, a formal possibility, involves the protonation of cyclohexanone enolate to give cyclohexanone directly without the intermediate formation of I.

The reaction of 2-bromodimedone (III) with triphenylphosphine in refluxing benzene led to triphenylphosphine oxide and a 29 per cent yield of 5,5-dimethyl-3-bromocyclohexenone (V). The structure of V follows from its analysis (Found: C, 47.41; H, 5.28%); its infrared spectrum (CCl_4): 5.97 and 6.24 μ (corr.); its ultraviolet spectrum which exhibited $\lambda_{\text{max}}^{\text{EtOH}}$: 245 $m\mu$ (13,400); its NMR spectrum (CCl_4) which had signals at integrated τ -values of: 3.72 (1), 7.38 (2), 7.85 (2) and 8.93 (6) and conversion to the formaldehyde derivative of dimedone (m.p. and m.m.p. 186-189°).

The formation of V provides evidence for the intermediacy of the enol phosphonium salt (IV). Michael addition of bromide ion to IV and subsequent elimination of triphenylphosphine oxide leads to V.

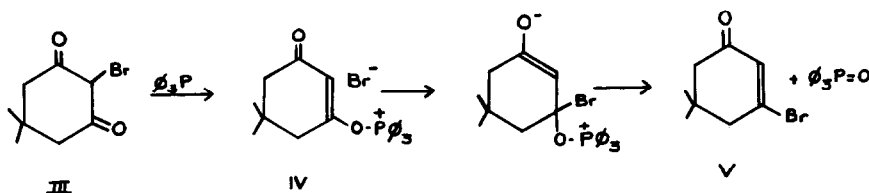


FIG. 2

Under conditions similar to those employed for bromoketones, 2-chlorocyclohexanone was dechlorinated to only a slight extent and direct quaternization was not detected.⁸

The reactions of *o*- and *p*-bromophenols with triphenylphosphine leading to debromination in the presence of water and aryl bromide formation under

⁸ I.J. Borowitz and Rhoda S. Weinberg, unpublished results.

anhydrous conditions⁹ can be rationalized by analogous mechanisms involving keto forms of the phenols. Hoffman and Michael¹⁰ have proposed positive bromine removal similar to path B for the debromination of *o*- and *p*-bromoamines with triphenylphosphine.

It has been reported¹¹ that α -chlorobenzylphenylketone reacts with triphenylphosphine in refluxing benzene to yield diphenylacetylene (VIII) and triphenylphosphine oxide. We propose that acetylene formation occurs via the initially obtained enol phosphonium salt (VII).

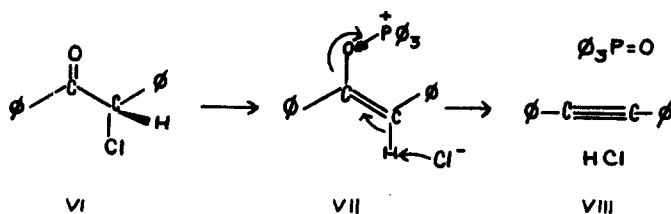


FIG. 3

Thus under appropriate conditions enol phosphonium salts may lead to debrominated ketones, β -bromoenones and possibly to acetylenes.

Further work on extending these observations is in progress.

Acknowledgements - We wish to express our gratitude to Professor Gilbert Stork of Columbia University for stimulating discussions and research facilities and to thank the City College Fund for a Research Grant.

⁹ H. Hoffman, L. Horner, H.G. Wippel and D. Michael, *Chem. Ber.* 95, 523 (1962).

¹⁰ H. Hoffman and D. Michael, *Chem. Ber.* 95, 528 (1962).

¹¹ S. Trippett and D.M. Walker, *J. Chem. Soc.* 2976 (1960).