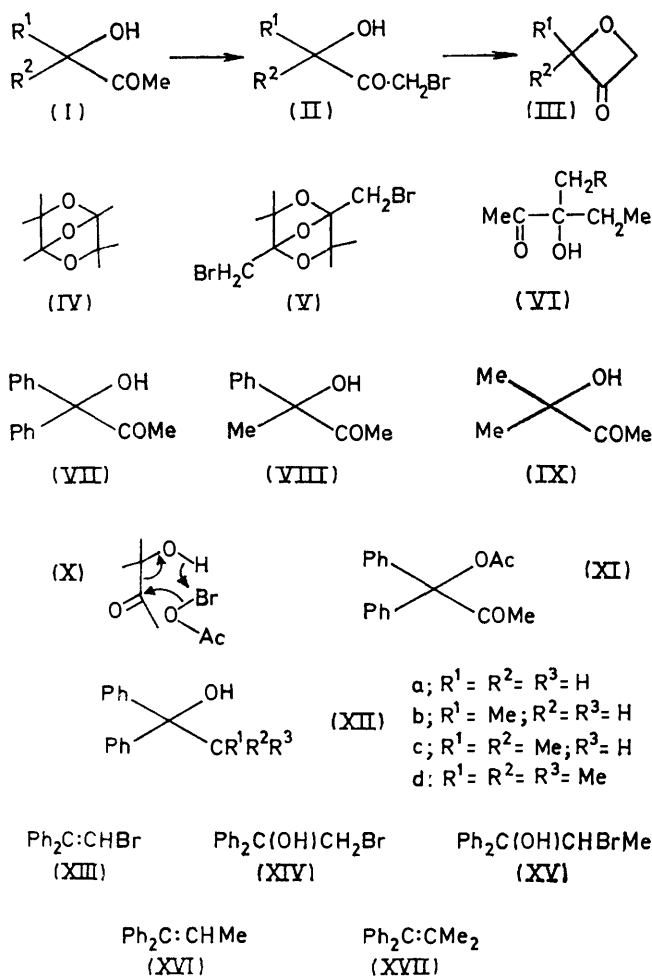


Brominative Cleavage of α -Ketols

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Bromination of some α -ketols resulted in cleavage of the carbonyl-carbinol bond; 1-hydroxy-1,1-diphenylacetone, for example, gave benzophenone. Bromination of diphenyl-substituted tertiary alcohols does not cause degradation and the products are bromohydrins and/or substituted alkenes.

As yet, there is no convenient general synthesis¹ of oxetan-3-ones. A possible route to 2,2-disubstituted oxetanones (III) lies in the halogenation of α -ketols (I) followed by the cyclisation of the resulting acyl halides (II). Hoey *et al.*² have successfully synthesised



2,2,4,4-tetraphenylloxetanone by this method and, as we required 2,2-disubstituted oxetanones for a study

¹ For a review on oxetan chemistry see S. Searles in 'Heterocyclic Compounds with Three- and Four-membered Rings,' ed. A. Weissberger, Interscience, New York, 1964, vol. 2, 983.

² G. B. Hoey, D. O. Dean, and C. T. Lester, *J. Amer. Chem. Soc.*, 1955, **77**, 391; see also A. T. Rowland, P. J. Bennett, and T. S. Shoupe, *J. Org. Chem.*, 1968, **33**, 2426.

³ J. A. Donnelly, J. G. Hoey, and R. O'Donnell, unpublished work.

⁴ G. F. Hennion and E. J. Watson, *J. Org. Chem.*, 1958, **23**, 658.

of the rearrangement they undergo³ with Grignard reagents, we attempted to extend this synthesis.

Hennion and Watson⁴ have observed that α -ketols have a marked tendency to form dimers (IV) during bromination and that the products usually are the dibrominated dimers (V). Nevertheless, they successfully formed the bromo-ketols of 3-hydroxy-3-methylpentan-2-one (VI; $R = H$) and 3-hydroxy-3-ethylpentan-2-one (VI; $R = Me$). The α -ketols that we examined, however, were usually difficult to brominate even with a variety of brominating agents and the reaction observed was cleavage of the ketol; an effect reminiscent of several other brominative cleavages.⁵

Bromination of 1-hydroxy-1,1-diphenylpropanone (VII) in carbon tetrachloride gave, as the only product, benzophenone. Irradiation with u.v. light during the bromination had little effect on the result but the use of the more powerful brominating agent, acetyl hypobromite,⁶ resulted in an almost quantitative yield of benzophenone. Treatment of 3-hydroxy-3-phenylbutan-2-one (VIII) with acetyl hypobromite gave a 52% yield of acetophenone, while 3-hydroxy-3-methylbutan-2-one (IX) gave acetone in small (17%) yield.

It is suggested that cleavage of these α -ketols by acetyl hypobromite may involve a six-membered cyclic transition state such as (X). This is in accord with the fact that protection of the hydroxy-group by acetylation completely suppressed the cleavage reaction; 2-oxo-1,1-diphenylpropyl acetate (XI) was unreactive towards acetyl hypobromite. It was also unaffected by bromine in carbon tetrachloride and by cupric bromide.⁷

The presence of the carbonyl group is essential for cleavage. Bromination of a series of diphenyl-substituted tertiary alcohols occurred^{8,9} without degradation; no trace of benzophenone was detected. 1,1-Diphenylethanol (XIIa), on reaction with acetyl hypobromite or with bromine in carbon tetrachloride, gave a mixture of 2-bromo-1,1-diphenylethylene (XIII) and 2-bromo-1,1-diphenylethanol (XIV). Bromination of 1,1-diphenylpropan-1-ol (XIIb) in carbon tetrachloride

⁵ For examples see E. M. Arnett and G. B. Klingensmith, *J. Amer. Chem. Soc.*, 1965, **87**, 1023; J. J. Beirne, A. M. Coyle, and J. A. Donnelly, *Tetrahedron*, 1970, **26**, 3809.

⁶ Y. Hatanaka, R. M. Keefer, and L. J. Andrews, *J. Amer. Chem. Soc.*, 1965, **87**, 4280.

⁷ K. B. Doifode and M. G. Marathe, *J. Org. Chem.*, 1964, **29**, 2025; L. C. King and G. K. Ostrum, *ibid.*, p. 3459.

⁸ V. I. Pansevich-Kolyada and N. A. Prilezhaev, *J. Gen. Chem. (U.S.S.R.)*, 1951, **21**, 571.

⁹ L. J. Andrews and R. M. Keefer, *J. Amer. Chem. Soc.*, 1953, **75**, 3557.

Substrate ^a	Amount (g)	Reagent ^b	Amount (g)	t/h	Product(s) ^c	Amount (g)	M.p. (°C)	Lit. m.p. (°C)	N.m.r. spectrum ^d (τ values)
(VII) ¹⁰	0.85	Bromine	0.61	18	Benzophenone	0.02	47	49	
	4.9	Bromine and u.v. light ^e	3.9	3	Substrate	0.6	63—65	63—65 ¹⁰	OH 5.17; COMe 7.70
	0.1	Bromine and silver acetate ^f	0.07	0.2	Benzophenone	0.13	47	49	
			0.08		Substrate	2.13	63	63—65 ¹⁰	
(XI)	0.52	Bromine	0.3	24	Benzophenone	0.08	48	49	
	0.3	Cupric bromide ^g	0.45	5	Substrate	0.35			COMe 7.91; Ac 7.95
	0.2	Bromine and silver acetate ^f	0.13	4.5	Substrate	0.24			
			0.14		Substrate	0.15			
(VIII) ¹¹	0.1	Bromine and silver acetate ^f	0.11	0.2	Acetophenone	0.38			COMe 7.42
			0.11		Substrate	0.15			OH 5.81; COMe 7.95; Me 8.29
(IX) ¹²	2.0	Bromine and silver acetate ^f	3.2	0.5	Acetone ^h	0.8 ^h	125—126	125—126 ¹⁷	
			3.3						
(XIIa) ¹³	0.1	Bromine	0.08	3	(XIII)	0.06	48	49—50 ¹⁸	CHBr 3.32
					(XIV)	0.03	68	73 ¹⁹	CH ₂ Br 5.88; OH 7.10
	0.5	Bromine and silver acetate ^f	0.45	18	(XIII)	0.28	48	49—50 ¹⁸	
			0.5		(XIV)	0.14	68	73 ¹⁹	
(XIIb) ¹⁴	0.23	Bromine ⁱ	0.17	3	(XV)	0.16	56	57 ⁸	CHBr 4.77; OH, 7.15; Me 8.45
					(XVI)	0.03	50	49 ²⁰	CHMe 3.79; Me 8.23
(XIIc) ¹⁵	0.36	Bromine	0.28	0.5	(XVII) ¹⁵	0.2			Pr ¹ 8.17
(XIId) ¹⁶	0.69	Bromine	0.50	18	Substrate	0.50			OH 7.79; Bu ^t 8.82

^a Unless otherwise stated, a carbon tetrachloride solution (ca. 10%) of the substrate was used. ^b Bromine was added as a solution (ca. 25%) in the solvent. ^c T.l.c. of the crude reaction products showed no other products than those mentioned. ^d All products were examined. Only non-aromatic signals are given. ^e From a 125 W medium pressure lamp, with or without a Pyrex glass filter. ^f Silver acetate was suspended in the substrate solution prior to bromine addition. ^g Solvent system for this reaction was refluxing chloroform-ethyl acetate (1:1). ^h As its 2,4-dinitrophenylhydrazone. ⁱ Compound (XV) has been obtained ⁸ from this reaction in warm 80% acetic acid.

gave 2-bromo-1,1-diphenylpropan-1-ol (XV) and 1,1-diphenylpropene (XVI). Similarly, 2-methyl-1,1-diphenylpropan-1-ol (XIIc) gave 2-methyl-1,1-diphenylpropene (XVII), while the highly substituted alcohol, 2,2-dimethyl-1,1-diphenylpropan-1-ol (XIId), was unreactive.

EXPERIMENTAL

N.m.r. spectra were obtained at 60 MHz with a Perkin-Elmer R12 or a Varian HR 60A spectrometer in deuteriochloroform with tetramethylsilane as internal reference. M.p.s were taken with a Kofler hot stage apparatus.

¹⁰ C. L. Stevens and C. T. Lenk, *J. Org. Chem.*, 1954, **19**, 538.
¹¹ I. I. Lapkin and A. I. Golovkova, *J. Gen. Chem. (U.S.S.R.)*, 1949, **19**, 669.

¹² J. G. Aston and R. B. Greenburg, *J. Amer. Chem. Soc.*, 1940, **62**, 2590.

¹³ C. F. H. Allen and S. Converse, *Org. Synth., Coll. Vol. I*, 1946, 226.

¹⁴ C. Hell and H. Bauer, *Ber.*, 1904, **37**, 230.

¹⁵ J. Levy, *Bull. Soc. chim. France*, 1921, **29**, 878.

Silica gel (Merck HF₂₅₄₊₃₆₆ and PF₂₅₄₊₃₆₆) was used for t.l.c. The products of all brominations were purified by p.l.c.

The details of the bromination reactions are given in the Table.

2-Oxo-1,1-diphenylpropyl Acetate (XI).—A solution of 1-bromo-1,1-diphenylpropanone ¹⁰ (14.2 g) and potassium acetate (8.7 g) in acetic acid (215 ml) was refluxed for 1 h and diluted with water. Extraction with ether gave the ester (11 g), b.p. 164° at 1.5 mmHg (lit.,²¹ b.p. 125° at 0.03 mmHg).

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¹⁷ J. D. Roberts and C. Green, *J. Amer. Chem. Soc.*, 1946, **68**, 214.

¹⁸ G. Wittig and R. Kethur, *Ber.*, 1936, **69**, 2078.

¹⁹ S. J. Cristol, J. R. Douglas, and J. S. Meek, *J. Amer. Chem. Soc.*, 1951, **73**, 816.

²⁰ R. Greenwald, M. Chaykovsky, and E. J. Corey, *J. Org. Chem.*, 1963, **28**, 1128.

²¹ V. Rosnati, D. Misiti, and F. de Marchi, *Gazzetta*, 1966, **96**, 497.