Favorsky Rearrangement under Reformatsky Conditions. The Zinc-induced Debromination of 1,3-Dibromo-1,1-diphenylpropan-2-one in Methanol as Solvent

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Summary Zinc-promoted debromination of 1,3-dibromo-1,1-diphenylpropan-2-one (**1**) in methanol affords methyl 3,3-diphenylpropionate (**8**) as the major product.

The Favorsky rearrangement of α-halogeno-ketones into carboxylic acids is generally induced by bases which either abstract a proton to produce an enolate ion and thence an intermediate cyclopropanone or, alternatively, add to the carbonyl group to trigger a benzylic acid-like shift.[1] We here report an unusual example in which a cyclopropanone intermediate arises from an αα′-dibromo-ketone in a protic solvent under Reformatsky conditions.

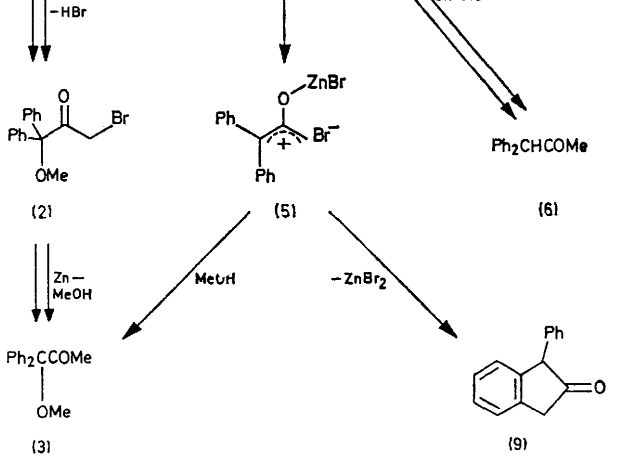
Previous work on a variety of acyclic αα′-dihalogeno-ketones has shown that dehalogenation with Zn–Cu in MeOH affords the α-methoxy-ketone (*via* an allyl cation) and parent ketone (by reductive removal of both halogens) in a clean reaction.[2] In contrast the dibromopropanone (**1**) has now been found to give the propionic ester (**8**) under similar conditions (Table). The same ester (**8**) is already known from the work of Bordwell to arise from both isomeric monohalogeno-ketones $Ph_2CXCOMe$ (**10a**) and $Ph_2CHCOCH_2X$ (**10b**) by conventional Favorsky rearrangement, *i.e.* on treatment with alkali.[3a]

Table Products from the Zn–Cu-promoted debromination of (**1**)[a] in MeOH.

Entry	T/°C	Period of addition of (**1**) min	(**2**)	(**3**)	(**6**)	(**8**)
1	25	210	25%	30	—	45
2	0	210	—	35	—	65
3		20	5	3	12	80
4		5	—	7	16	77
5	−35 to −40	210	42	16	—	42
6		5	16	26	11	47
7	−85	210	48[b]	—	—	—

[a] Prepared from 1,1-diphenylpropan-2-one (*Org. Synth. Coll. Vol.* 3, 1955, p. 343) and Br_2 in CCl_4; colourless crystals, m.p. 75°; $\delta(Me_4Si)$ 4·32 (2H, s) and 7·29 (10H, s). [b] 52% starting material (**1**) remaining.

Of the other products the α-methoxy-ketone (**3**) is formed in minor amount when methanolysis of the rather labile starting material (**1**) is minimised by fast addition (Table, entry 3). For this reason the α-methoxy-ketone (**3**) arises by conventional reduction of the bromoketone (**2**), which can also be detected by n.m.r. spectroscopy as an



Scheme. Simplified diagram for the formation of products from the αα′-dibromo-ketone (**1**).

intermediate (*cf.* Scheme). Furthermore, an allyl cation such as (**5**) or the equivalent 2-hydroxyallyl cation is likely to cyclize to 1-phenylindan-2-one (**9**)[3] which was absent under our conditions.†

The parent ketone (**6**) which emerges as a minor product on fast addition of (**1**) can be visualized to arise *via* ketonization of (**4**) with acid, followed by further reduction. Since acid is generated more quickly on fast addition, formation of (**6**) is facilitated and also reduction of the bromo-ketone (**2**) into the α-methoxy-ketone (**3**) (entries 3 and 4, 5 and 6, respectively).

That the Favorsky ester (**8**) is formed at all suggests that the enolate carbon in (**4**) is fairly nucleophilic. Presumably, the phenyl groups in (**4**) are twisted out of plane, nonbonding repulsion being relieved on rotation and conversion into (**7**). Quite generally, the formation of Favorsky ester, rare as it may be under Reformatsky conditions in methanol, might serve as a useful pointer towards an enhanced driving force for cyclopropanone[4] formation.

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† The absence of the indanone (**9**) in weakly acidic medium seems to argue against a rapid cyclopropanone ⇌ oxyallyl equilibrium, which has been discussed to account for the formation of (**9**) on Favorsky rearrangement of (**10a**) and (**10b**) with dilute base;[3a,b] see also D. B. Sclove, J. F. Pazos, R. L. Camp, and F. D. Greene, *J. Amer. Chem. Soc.*, 1970, **92**, 7488 and ref. 1a, p. 1096.

[1] (a) C. Rappe in 'The Chemistry of the Carbon-Halogen Bond,' ed., S. Patai, Wiley, London, 1973, Ch. 17; (b) A. A. Akhrem, T. K. Ustynyuk, and Y. A. Titov, *Russ. Chem. Rev. Engl. Transl.*, 1970, **39**, 732; (c) A. S. Kende, *Org. Reactions*, 1960, **11**, 261.

[2] H. M. R. Hoffmann, T. A. Nour, and R. H. Smithers, *J.C.S. Chem. Comm.*, 1972, 963. For further mechanistic and synthetic background see H. M. R. Hoffmann, *Angew. Chem. Internat. Edn.*, 1973, **12**, 819.

[3] (a) F. G. Bordwell and R. G. Scamehorn, *J. Amer. Chem. Soc.*, 1971, **93**, 3410; (b) F. G. Bordwell and J. G. Strong, *J. Org. Chem.*, 1973, **38**, 579; (c) P. Beltrame, V. Rosnati, and F. Sannicolo, *Tetrahedron Letters*, 1970, 4219.

[4] Reviews: H. H. Wasserman, G. M. Clark, and P. C. Turley, *Fortschr. Chem. Forsch.*, 1974, **47**, 73; N. J. Turro, *Accounts Chem. Res.*, 1969, **2**, 25.