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NOVEL REACTIONS PRODUCING 1,2-DIBENZOYLETHANES

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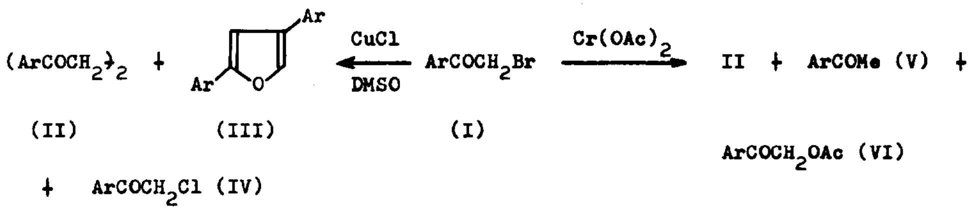
Few examples have been recorded with respect to the formation of 1,2-dibenzoylethanes II which involves dehalogenation condensation of phenacyl bromides I or recombination of phenacyl radicals. Interestingly, treatment of Ia with $Ni(CO)_4$ gives IIa in THF, whereas the same components afford 2,4-diphenylfuran (IIIa) in DMF solvent (1). Photolysis of dimethylphenacylsulphonium bromide in aqueous solution produces IIa along with acetophenone and phenacyl bromide (2). We report two related approaches: (a) treatment of I with lower valent metal salts of Cu(I) and Cr(II) both complexed with DMSO solvent and (b) photolysis of methyl phenacyl sulphoxide.

Table 1 summarizes the product distribution of the first method. Wurtz-type dehalogenation of benzylic and allylic halides was previously recorded to occur by means of CuCl in DMSO (3). Extention of this reaction to I has been shown to produce II, byproducts being III and phenacyl chlorides (IV). Reactions of organic halides with Cr(II) sulphate in aqueous DMF were extensively studied by Kochi, Castro and coworkers (4,5). A novel modification using anhydrous Cr(II) acetate in DMSO has been found to transform I into a mixture of II, acetophenones V and α-acetoxyacetophenones VI.

The DMSO-solvated Cu(I) and Cr(II) salts give II and S_N products IV and VI in common. Furan formation in dehalogenation of α-haloketones was previously recorded in the reaction with zero-valent metals such as $Ni(CO)_4$/DMF (1), Mg/THF (6) and Zn/PhH-DMSO (7). These reactions would involve the respective metal enolates, which are transformed into III either by (A) aldol addition and the subsequent cyclization under HBr elimination or,



Ia-VIa: Ar = Ph, Ib-VIb: Ar = p-BrC_6H_4-

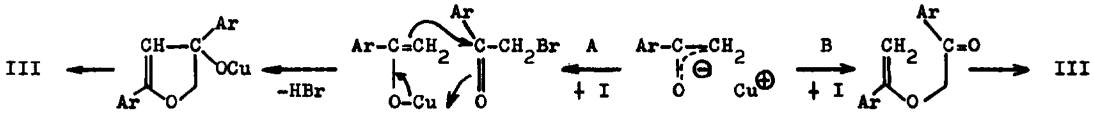


Table 1. Reaction of I with metal salts in DMSO [a]

Ar	CuCl Reaction				$Cr(OAc)_2$ Reaction			
	Reaction time (hr)	Yield in %, m.p. °C II	III	IV	Reaction time (hr)	Yield in % II	V	VI
a	18.5	13, 148-50[b]	14, 111[c]	39	12.5	28	--	43
b	38.5	11, 180[c]	13, 160[c]	43	23	16	32	18

[a] Carried out in N_2 atm. with 1 M salt solution (I/metal = 1:2.5). [b] Prepared by reduction of 1,2-dibenzoylethylene. See ref. (9). [c] Synthesized by means of $Ni(CO)_4$. See ref. (1).

alternatively, by (B) S_N attack on I at the enolate oxygen followed by ring-closure (8). The phenacyl Cr(II) compound is far less prone to this kind of condensation possibly due to the more covalent metal-carbon bonding and its protonolysis gives the reduction products V. The reaction under Castro's condition (5) in aqueous solvent gives almost quantitative yield of V along with II in trace amount at most.

In contrast to the sulphonium salt photolysis (2), irradiation of phenacyl sulphones (10) or sulphides (11) has been reported to give acetophenones V exclusively. Methyl phenacyl sulphoxides ($ArCOCH_2SOMe$) were subjected to photolysis in 0.1 M solutions with Pyrex-filtered high press Hg arc to afford a mixture of II, V, ArCOOH (VII) and $MeSO_2SMe$ (VIII). Yields (%) of isolated products are given together with Ar specification, solvent, time of irradiation: Ph, EtOH, 8 hr, IIa 32, Va 19; Ph, Me_2CHOH, 8 hr, IIa 24, Va 20, VIII 8; Ph, PhH, 8 hr, IIa 62, Va tr, VIII 61; p-$MeOC_6H_4$, EtOH, 2 hr, Vc 88; p-MeC_6H_4, EtOH, 6 hr, IId (m.p. 158-59°) 25, Vd 30; p-ClC_6H_4, EtOH, 5 hr, IIe (m.p. 161°) 78, Ve 9, VIIe 13; α-naphthyl, EtOH, 70 hr, Vf 63. The remarkable substituent effect has been observed and the possible account for this would be given in the full paper.

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