Reduction of α,α′-Dibromoketones by Ultrasonically Dispersed Mercury in Some Aliphatic Ketone Solvents. A Convenient Synthesis of 4-Isopropylidene-1,3-dioxolans

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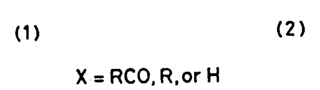
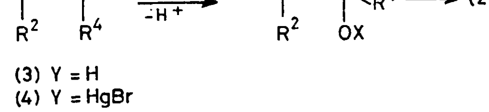
Summary Reduction of 2,4-dibromo-2-4-dimethylpentan-3-one by finely dispersed mercury in ketonic solvents provides a simple synthesis of the 4-isopropylidene-5,5-dimethyl-1,3-dioxolan ring system.

We have previously described the conversion of α,α′-dibromoketones (**1**) into α-substituted ketones (**2**) under reducing conditions, either electrochemically[1–3] or by ultrasonically dispersed mercury,[4] and have pointed out[1,4] the relative merits of this 'reductive substitution' process compared to conventional procedures for introducing nucleophilic substituents, such as acetoxy, alkoxy, or hydroxy groups α to a ketonic carbonyl. The key intermediate in the conversion of (**1**) into (**2**) is a 2-oxyallyl cation [(**3**) in the electrochemical reaction; (**4**) in the mercury reduction], which suffers nucleophilic attack by the hydroxylic solvent to afford the observed product.[1–4]



(1) (2)

X = RCO, R, or H

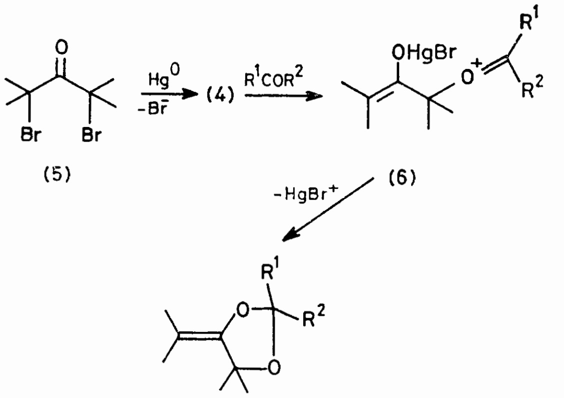


(3) Y = H
(4) Y = HgBr

It is apparent that nucleophiles not bearing a proton directly bound to the nucleophilic atom cannot readily form α-substituted ketones by reaction with (**3**) or (**4**), and they would be expected to show more complex behaviour. We now report that reduction of 2,4-dibromo-2,4-dimethylpentan-3-one (**5**) by ultrasonically dispersed mercury in ketonic solvents affords the 4-isopropylidene-1,3-dioxolans (**7**)—(**10**). The reaction presumably proceeds by nucleophilic attack by the ketone oxygen atom upon (**4**), followed by collapse of the initial adduct (**6**).

Although the yields are modest, the reaction is experimentally very simple and permits construction of the uncommon 4-methylene-1,3-dioxolan ring system[5] in one step from readily available starting materials. Material losses arise primarily by attack of adventitious water on (**4**) to afford the α-hydroxyketone (**11**) and proton loss from (**4**) to afford the methylene ketone (**12**). Attempted reaction between (**4**) and acetaldehyde resulted in conversion of the aldehyde into the corresponding trimer, possibly under electrophilic catalysis by $\mathrm{Hg^{II}}$ species.

Hoffmann and his co-workers[6,7] have reported formation of 2-dimethylamino-4-methylene-1,3-dioxolans through reduction of dibromoketones by zinc in dimethylformamide

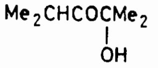


(7) $R^1 = R^2 = Me$, 49 %

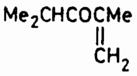
(8) $R^1 = Me, R^2 = Et$, 59 %

(9) $R^1 = R^2 = Et$, 25 %

(10) $R^1 = Me, R^2 = Pr^i$, 47 %


$\mathrm{Me_2CHCO}\underset{\mathrm{OH}}{\underset{|}{\mathrm{C}}}\mathrm{Me_2}$

(11)


$\mathrm{Me_2CHCO}\underset{\mathrm{CH_2}}{\underset{\|}{\mathrm{C}}}\mathrm{Me}$

(12)

and dimethylacetamide. A mechanism similar to that invoked in the present work was advanced, involving a zinc oxallyl cation intermediate analogous to (**3**) and (**4**). Introduction of oxygen at the more highly substituted α-position of the dibromoketone was observed, and this regioselectivity was used to support the hypothesis of an allylic cationic intermediate.[7]

In a typical procedure a solution of (**5**) (10 mmol) in 15 ml of ketone was placed in a 25 ml Erlenmeyer flask together with 5 ml of mercury. The stoppered flask was then placed in a 150 W laboratory ultrasonic cleaner thermostatted at 25 °C until t.l.c. demonstrated the disappearance of (**5**) (1—2 days). Mercury and mercuric salts were removed by centrifugation and excess of ketone was removed by rotary evaporation to afford the crude heterocycle, which could be purified by v.p.c. N.m.r., i.r., and mass spectral properties were consistent with the assigned structures.†

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† Typical spectroscopic data for (**7**) were: δ 1·67 (s, 3H), 1·62 (s, 3H), 1·47 (s, 6H), and 1·40 (s, 6H); ν 1710 cm^{-1} (C=C) (*cf.* ref. 5 and R. A. Johnson, F. H. Lincoln, J. L. Thompson, E. G. Nidy, S. A. Mizsak, and U. Axen, *J. Amer. Chem. Soc.*, 1977, **99**, 4182); *m/e* 43 (86%), 69 (100), 84 (73), 97 (42), 112 (98), and 170 (63). Data for (**8**)—(**10**) were analogous.

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