BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 2917—2918 (1973)

The Oxidation of Alkylbenzenes and Acylcarbinols by Means of Benzopinacol Diesters

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(Received March 30, 1973)

The thermal decomposition of benzopinacol diesters (I) in benzene at 150—160 °C results in the (a) cleavage of the central carbon-carbon bond of I, followed by the acyl radical-release or hydrogen-abstraction of the resulting acyloxydiphenylmethyl radical, thus affording benzophenone (II) and benzhydryl esters (III). The trace amount of tetraphenylethylene (IV) ($<5\%$) thus obtained was ascribed to the (b) cleavage.[1,2]

I (a: R=Et)

We have found that benzopinacol dipropionate (Ia) serves as a catalyst in the autoxidation of ethylbenzene, cumene, and tetralin. Table 1 summarizes the yields of the resulting ketones, acetophenone and α-tetralone, and of the products (II and IV) arising from Ia. No trace of III has been observed. Each mol of Ia accounted for *ca.* 20 mol of acetophenone or α-tetralone.

We found also that benzoin and an acyloin were oxidized to the corresponding α-diketones by Ia. The heating of a 0.1 M anisole solution of benzoin and Ia in a mol ratio of 2: 1 at 130 °C under a nitrogen atmosphere gave a quantitative yield of benzil, the Ia being converted to II (43) and IV (26%). The reaction of 2-hydroxycyclododecanone with Ia under the same conditions gave cyclododecane-1,2-dione in a 50% yield, besides II (34) and IV (31%). The yields are based on the amount of each component consumed, either the substrate or Ia. In order to examine the possible autoxidation, a mixture of benzoin and Ia in a mol ratio of 4: 1 was heated under an oxygen atmosphere. About 50% of benzoin was oxidized to afford the corresponding yield of benzil. 2-Hydroxycyclododecanone also behaved similarly, or it was not autoxidized at all under such conditions.

TABLE 1. AUTOXIDATION OF ALKYLBENZENES IN THE PRESENCE OF BENZOPINACOL DIPROPIONATE

Substrate	Reaction[a)] temp °C	hr	Product (%)[b)]	Ph_2CO[c)]	$Ph_2C=CPh_2$[c)]
Ethylbenzene	150	48	Acetophenone 47 (30)	67	33
Cumene	150	48	Acetophenone 36 (84)	60	12
Tetralin	120	17	α-Tetralone 45 (50)	32	25

a) A mixture of Ia and the alkylbenzene in a mol ratio of *ca.* 1: 200 was heated in oxygen atmosphere.
b) The yields of products are based on the consumed amount of the hydrocarbon. Data in the parentheses show the conversion (%) of hydrocarbons.
c) The yields are based on the added amount of Ia.

The exact nature of this stoichiometric oxidation is still not known, but the oxidation of benzylic methylene is apparently catalyzed by radicals generated from Ia. It should be added that the reaction of *N*,*N*-dimethylaniline as a solvent with Ia and Cu(II)Cl_2 (in a mol ratio of 1: 2) afforded an acylated product, *N*-methyl-

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[1] T. Shirafuji, Y. Yamamoto, and H. Nozaki, This Bulletin, **45**, 2574 (1972).

[2] Copper (II) carboxylates in aqueous DMF catalyze the decomposition of diphenyldiazomethane to afford benzopinacol diesters. This reaction constitutes the only available approach to the novel class of I esters. See T. Shirafuji, Y. Yamamoto, and H. Nozaki, *Tetrahedron*, **27**, 5353 (1971).

propionanilide (V), in a 44% yield (based on both propionyl groups of Ia). In the absence of Cu(II), the formation of V was not detected. This can be explained by assuming that the intermediary propionyl radical, after having been generated *via* the cleavage (a), is oxidized by Cu(II) to the acyl cation.³⁾ The ion is trapped by *N*,*N*-dimethylaniline to afford the intermediate, $(Me_2N(Ph)\text{-}COEt)^+$, which loses its methyl cation to provide V.

The acyloxy and alkyl radicals assumed to be generated *via* the (b) cleavage have not yet been characterized, but we cannot exclude the possibility of their being due, partly at least, to the oxidations mentioned above. The reasons are that consistently higher yields of IV have been obtained in these cases and IV can not be ascribed to diphenylcarbene,⁴⁾ but instead possibly results from the acyloxydiphenylmethyl radical in the (a) cleavage.

Experimental

All the melting and boiling points are uncorrected. The glc analyses and separations were performed with columns (1 m) packed with HVSG (30%) on Celite 545 or SE 30 (5%) on Chromosorb. Unless otherwise stated, the yields were estimated by glc analyses.

The Oxidation of Ethylbenzene by Means of the Oxygen-Benzopinacol Dipropionate (Ia) System. A mixture of ethylbenzene (0.95 g, 9.0 mmol) and Ia (25 mg, 0.050 mmol) was heated under stirring and refluxing (140—150 °C) in an oxygen atmosphere for 48 hr. The reaction mixture was first heated at 60 °C for 30 min with 2 N aqueous NaOH (1 ml), neutralized with aqueous sulfuric acid, and then extracted with ether. The extract was washed with an aqueous solution (1%) of $FeSO_4$, dried (Na_2SO_4), and concentrated *in vacuo*. Glc separation (HVSG 30%, 1 m; 150 °C) gave acetophenone (0.15 g, 47%), benzophenone (15 mg, 67%), tetraphenylethylene (6.0 mg, 33%), and the recovered ethylbenzene (0.66 g, 70%).

The Oxidation of Benzoin by Ia. An anisole solution (5 ml) of a mixture of benzoin (0.21 g, 1.0 mmol) and Ia (0.24 g, 0.50 mmol) was heated at 130 °C for 24 hr under a nitrogen atmosphere. The concentration of the reaction mixture *in vacuo*, followed by glc separation (SE 30 30%, 1 m; 180 °C), gave benzil (0.20 g, 95%), benzophenone (80 mg, 43%), and tetraphenylethylene (40 mg, 26%).

The Reaction of N,N-*Dimethylaniline with Ia in the Presence of Cupric Chloride.* A mixture of *N*,*N*-dimethylaniline (1 ml), Ia (0.10 g, 0.20 mmol), and $CuCl_2 \cdot 2H_2O$ (70 mg, 0.40 mmol) was heated at 150—160 °C for 17 hr under stirring in a nitrogen atmosphere. Heating was continued until the solution turned blue. The reaction mixture was then washed with aqueous $NaHCO_3$ and extracted with benzene. The extract was concentrated and subjected to glc (SE 30 30%, 1 m; 150 °C) to afford *N*-methylpropionanilide (30 mg, 44%), benzophenone (40 mg, 60%), and tetraphenylethylene (15 mg, 22%). The *N*-methylpropionanilide (mp 56 °C (lit,⁵⁾ 56—58 °C)) was identical with an authentic sample⁵⁾ (IR, NMR, MS, and glc retention time).

Financial support from the Ministry of Education, Japanese Government, is acknowledged with pleasure.

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3) C. L. Jenkins and J. K. Kochi, *J. Amer. Chem. Soc.*, **94**, 843, 856 (1972).

4) H. Nozaki, H. Takaya, S. Moriuti, and R. Noyori, *Tetrahedron*, **24**, 3655 (1968).

5) L. M. Norton and A. W. Allen, *Ber.*, **18**, 1998 (1885).