

his associates at the Chester Beatty Research Institute. Several of them exhibited antitumor activity. The effects of the different locations of the alkyl groups are to be discussed in a later paper.

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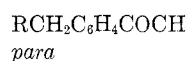
(7) C. T. Bahner, C. Cook, J. Dale, J. Fain, P. Smith, and J. Wilson, *J. Org. Chem.*, **23**, 1060 (1958).

Sodium Hypochlorite Oxidation of *p*-Methylacetophenone

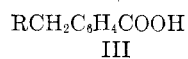
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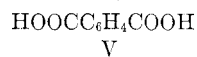
The recently proposed mechanism for sodium hypochlorite oxidations of *para*-methylene groups in acetophenone systems¹ (I), expressed in terms of the *a priori*-unlikely² enolization through the *para*-methylene group (e.g. II) and imputing a vital role to the acetyl group¹, is not supported by experimental evidence.



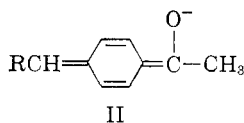
I



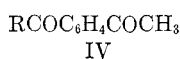
III



V



II



IV

e.g., R = a, H; b, CH₃

The experiment described below, under identical conditions, in which *p*-toluic acid (IIIa) was isolated in 77% yield after seven minutes, and was oxidized further to terephthalic acid (V) upon continuation of this treatment, demonstrates that in fact the vulnerable² acetyl group does not survive to give IV, and thus cannot participate in the oxidation of the aryl methyl or methylene group. The steps involved therefore are I → III → V, and the oxidation of the aryl methyl or methylene must be explained in terms of the effects of the first-formed carboxyl or carboxylate group.

EXPERIMENTAL

Oxidation of p-methylacetophenone (Ia). (A) A mixture of 5.0 g. of Ia and 800 ml. of commercial 5% sodium hypochlorite solution was refluxed gently under vigorous stirring

(1) D. D. Neiswender, Jr., W. B. Moniz, and J. A. Dixon, *J. Am. Chem. Soc.*, **82**, 2876 (1960).

(2) Cf. The first point of attack of hypochlorite on *p*-alkylated acetophenones is the acetyl group. [A. M. Van Arendonk and M. E. Cupery, *J. Am. Chem. Soc.*, **53**, 3184 (1931); R. C. Fuson, *J. Am. Chem. Soc.*, **56**, 1417 (1934)].

and a nitrogen atmosphere.¹ After 7 min., a 100-ml. aliquot upon cooling and treatment with sodium bisulfite and acidification, precipitated 0.48 g. (77%) of pure *p*-toluic acid (m.p. 176–178°, identified as its amide and anilide). From the remainder of the reaction mixture after 28 hr., 2.9 g. of solid (m.p. >250°) was similarly obtained which upon washing with ether to remove *p*-toluic acid yielded 1.6 g. (30%) of pure terephthalic acid (V, subl. >300°, identified as its dimethyl and diethyl esters). Evaporation of the ether washings produced 1.3 g. (26%) of *p*-toluic acid containing chlorinated impurities (identified by infrared spectrum) which on oxidation under the above conditions gave only pure V (65% by weight).

(B) In a similar oxidation with added base (4.1 g. of sodium hydroxide), after 10 min., a 100-ml. aliquot yielded 0.62 g. (98%) of pure *p*-toluic acid, and the remainder of the reaction mixture after 44 hr. gave 1.26 g. (23%) of pure terephthalic acid and 2.34 g. (53%) of pure *p*-toluic acid.

Oxidation of p-toluic acid (IIIa, 4.3 g.) under the above conditions without adjusting for reagent changes entailed in the primary and rapid destruction of the acetyl group starting from Ia (24 hr.), gave 2.95 g. of solid (m.p. >240°) which was purified by washing with ether [1.65 g. (32%)] and identified as V by infrared spectrum. Evaporation of the ether washings produced 1.3 g. of impure IIIa.

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Reactions of *N,N*-Dichloroamines

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N-Chlorinated derivatives of amines can be prepared by a number of methods involving hypochlorous acid or its derivatives.^{1,2,3} *N*-Chloro-*prim*-alkylidenimines have been prepared by the reaction of aldehydes with chloramine⁴ and *N*-chloro-*sec*-alkylidenimines have been postulated as intermediates in the preparation of α -amino-ketones from *N,N*-dichloro-*sec*-alkylamines.³ The preparation of *N*-chlorocyclohexanimine has been claimed by the reaction of cyclohexanone with chloramine.⁵

We have found that *N*-chloro-*sec*-alkylidenimines can be prepared from *N,N*-dichloro-*sec*-alkylamines by the action of bases. For example, *N,N*-dichloro-cyclohexylamine yields *N*-chlorocyclohexanimine.⁶ Such widely different bases as tertiary amines and

(1) A. Berg, *Ann. chim. et phys.*, **3**, 289 (1894).

(2) G. F. Wright, L. K. Jackson, and G. N. R. Smart, *J. Am. Chem. Soc.*, **69**, 1539 (1947).

(3) (a) H. E. Baumgarten and F. A. Bower, *J. Am. Chem. Soc.*, **76**, 4561 (1954); (b) H. E. Baumgarten and J. M. Petersen, *J. Am. Chem. Soc.*, **82**, 459 (1960).

(4) C. R. Hauser, *J. Am. Chem. Soc.*, **52**, 1108 (1930).

(5) B. Rudner (to W. R. Grace & Co.), U. S. 2,894,028 (1959), "Cyclohexylideneimino Compounds."