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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Sodium Hypochlorite Oxidation of *p*-Methylacetophenone

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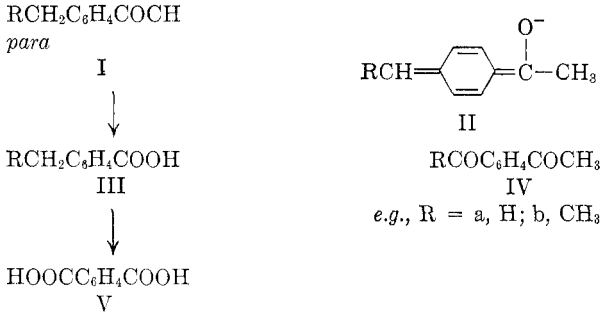
The recently proposed mechanism for sodium hypochlorite oxidations of *para*-methylene groups in acetophenone systems[1] (I), expressed in terms of the *a priori*-unlikely[2] enolization through the *para*-methylene group (e.g. II) and imputing a vital role to the acetyl group[1], is not supported by experimental evidence.



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 vulnerable[2] 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 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 chloroamine[4] and *N*-chloro-*sec*-alkylidenimines have been postulated as intermediates in the preparation of α-aminoketones 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*-dichlorocyclohexylamine yields *N*-chlorocyclohexanimine.[6] Such widely different bases as tertiary amines and

(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 hypohalite 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)].

(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."

potassium hydroxide in aqueous dioxane can be used successfully.

Certain aromatic *N*-chloroimines yield amides by a Beckmann rearrangement.[7] We were unsuccessful in attempts to obtain ε-caprolactam by treatment of *N*-chlorocyclohexanimine with such reagents as sulfuric acid, boron trifluoride, stannic chloride, and antimony pentachloride. Only cyclohexanone was isolated from the complexes after hydrolysis.

We have found that 2-aminocyclohexanone hydrochloride[3a] can be readily converted to 2-aminocyclohexanone oxime hydrochloride. A Beckmann rearrangement of this oxime should give either 2-oxo-7-aminohexamethylenimine or 2-oxo-3-aminohexamethylenimine. The latter could presumably be hydrolyzed to lysine. Paper chromatographic analysis of the products of an attempted Beckmann rearrangement of the oxime showed no ninhydrin-positive compounds, indicating that 2-oxo-7-aminohexamethylenimine was probably formed and was hydrolyzed to the *gem*-diamino derivative which would be expected to lose ammonia and be hydrolyzed to adipaldehydic acid. The presence of ammonia was noted during addition of base to the acid treated oxime. This direction of ring opening parallels the results of McLaren and Ungnade with 2-alkylcyclohexanone oximes.[8]

EXPERIMENTAL

Preparation of N-chloroimines. (a) *Triethylamine method.* To a solution of triethylamine in a solvent such as dry hexane or benzene was added an equimolar amount of the *N,N*-dichloroamine. The solution was stirred at room temperature for a short time and then at reflux temperature for 1–3 hr. The amine salt was filtered off and the filtrate was distilled at reduced pressure.

(b) *Potassium hydroxide method.* To a solution of potassium hydroxide in aqueous dioxane (0.1 mole per 120 cc. of water and 200 cc. of dioxane) was added an equimolar amount of the *N,N*-dichloroamine with vigorous stirring, maintaining the temperature below 35° during the addition and during a subsequent 15–30 min. reaction period. The solution was saturated with ammonium chloride and extracted thoroughly with ether. The combined extracts were dried and distilled from a water bath at reduced pressure.

N-Chlorocyclohexanimine. This compound was prepared in 52% yields by method (a) and 30% yields by method (b). It had b.p. 33–35°/1 mm., n_D^{25} 1.5053.

Anal. Calcd. for $C_6H_{10}ClN$: C, 54.76; H, 7.66; Cl, 26.95. Found: C, 54.09; H, 7.45; Cl, 26.42.

Its infrared absorption spectrum was consistent with an *N*-chloroimine structure and it could be hydrolyzed to cyclohexanone, identified as its 2,4-dinitrophenylhydrazone.

N-Chloroisopropylidenimine. This compound was prepared in 40% yields by method (a). It had b.p. 54–55°/100 mm.

Anal. Calcd. for C_3H_6ClN: C, 39.46; H, 6.61; Cl, 38.74; N, 15.31. Found: C, 39.59; H, 6.82; Cl, 38.41; N, 15.41.

Hydrolysis with dilute acid gave acetone, identified as its 2,4-dinitrophenylhydrazone.

2-Aminocyclohexanone oxime hydrochloride. 2-Aminocyclohexanone hydrochloride[3a] (9 g., 0.06 mole) in 15 cc. of water was added to 4.9 g. (0.07 mole) of hydroxylamine hydrochloride and 3.2 g. (0.03 mole) of sodium carbonate in 10 cc. of water. The solution was warmed on the steam bath 1.5 hr., cooled in ice, and filtered. The filtrate was concentrated and filtered again. The total solids were dissolved in methanol, treated with activated charcoal and filtered. Ether was added to the filtrate to precipitate the 2-aminocyclohexanone oxime hydrochloride, 7.1 g. A second crop of crystals was obtained by concentrating the mother liquor and adding ether. Total yield 7.9 g., 80%. An analytical sample was obtained by recrystallization from methanol-ether mixtures. It melted at 225° dec. Its infrared spectrum was consistent with an oxime structure.

Anal. Calcd. for $C_6H_{13}ClN_2O$: C, 43.75; H, 7.95; N, 17.01. Found: C, 43.94; H, 7.96; N, 17.16.

Beckmann rearrangement of 2-aminocyclohexanone oxime hydrochloride. One gram of the oxime was dissolved in 1 cc. of sulfuric acid containing one drop of water. After hydrogen chloride evolution ceased, the solution was heated to 120° for 2 min., cooled, diluted with 9 cc. of water, let stand several hours. Lysine hydrochloride (0.1 g.) was treated in the same way, as a control. The solutions were treated with saturated barium hydroxide solution at 80° to *p*H 10 ("pHydrion" test paper) and centrifuged. The *p*H was adjusted to 5 with dilute sulfuric acid and the solutions were chromatographed on Whatman No. 1 filter paper with a phenol solvent.[9] The chromatograms were dried, sprayed with ninhydrin solution, and developed in an oven at 35° for 1 hr. A well defined spot appeared for the lysine control but no spot appeared for the oxime rearrangement product.

In another experiment after the oxime had been heated with acid and diluted with water, cold potassium hydroxide solution was added until the solution was strongly basic. Ammonia was evolved as evidenced by its odor and reaction with moist indicator paper held above the solution.

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(6) *N*-Chlorocyclohexanimine was subsequently prepared independently by W. S. Knowles and G. Alt, *J. Org. Chem.*, **25**, 2047 (1960), and shown to be an intermediate in the transformation of *N,N*-dichlorocyclohexylamine to 2-aminocyclohexanone.

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The Identity of Nottbohm's "C_6H_6O" with Sorbanilide

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In 1916 Nottbohm[1] reported a synthesis of dienoic acids by the sequence illustrated. The intermediate anilide dianilium sulfonates (II. a,b,c) were obtained in good yield as crystalline solids. Refluxing these with hydrochloric acid followed by refluxing with concentrated sodium hydroxide solution and acidification afforded the dienoic acids in good yield. However, if IIa or IIb were refluxed with concentrated sodium hydroxide

(1) O. Nottbohm, *Ann.*, **412**, 49 (1916).