Degradation of Acids to Alcohols by the Carboxy-Inversion Reaction

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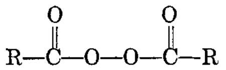
Received May 26, 1965

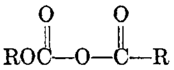
The rearrangements of acyl aroyl peroxides RCOOOCOAr, Ar = m-ClC_6H_5 and p-$NO_2C_6H_5$, R = primary, secondary, or tertiary alkyl, to mixed carbonates, ROCOOCOAr, have been studied. It has been found that mixed peroxides derived from m-chloroperbenzoic acid rearrange smoothly to the mixed carbonates which decompose to some extent under the conditions of the reaction to give alkyl m-chlorobenzoates. Saponification of these reaction mixtures yields alcohols, ROH. The yields of alcohol are greater than 50%. The rates of the rearrangements depend on the nature of R with tertiary > secondary > primary.

The carboxy-inversion reaction of diacyl peroxides (I) has been studied in great detail from the theoretical point of view.[2] The results of these studies clearly demonstrate that the reaction is strongly affected by polar factors including those of substituents and the medium. The initial product of the reaction is mixed carbonate, II. Subsequent decomposition of II often occurs under the conditions of the reaction to give an ester, carbonate, carbon dioxide, and an anhydride.



I

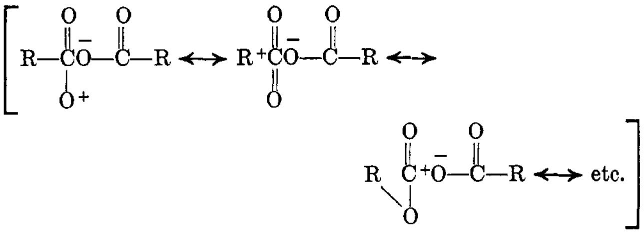
$$R-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-R$$



II

$$RO\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R$$

The mechanistic studies have indicated that the transition state for the conversion of I to II is polarized in such a way that a potential carboxylate ion is developed and a partial positive charge is distributed over the triad of atoms involved in the 1,2 shift from carbon to oxygen.[3] This concept can be summarized, in part at least, by the resonance structures illustrated. Consideration of these structures and available experimental data indicates that the group, R, which migrates to oxygen in an unsymmetrical diacyl peroxide will be that one which can support a positive charge most effectively. Similarly, the potential carboxylate ion will be derived from the most stable carboxylate ion. It seemed reasonable to suggest that unsymmetrical diacyl peroxides could be prepared which would undergo the carboxy-inversion reaction in an entirely predictable manner. If this goal could be achieved, then the carboxy-inversion reaction could be used as a means of converting an acid into an alcohol with the loss of one carbon atom.

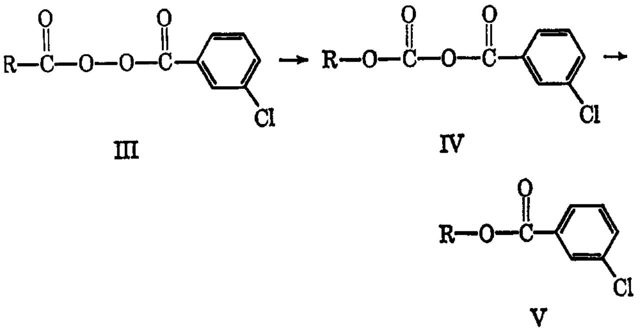


Results and Discussion

It has been found that mixed peroxides can be prepared readily by reaction of acid chlorides with either m-chloroperobenzoic acid[4] or p-nitroperbenzoic acid.[5] The acylation reaction is modeled after the procedure of Silbert and Swern.[6] The yields of mixed peroxides are usually greater than 80%.[7]

Studies of the carboxy-inversion reactions of these peroxides were conducted on purified peroxides, solutions in which the peroxides were prepared but from which acids, bases, and salts had been removed, and finally the peroxides were allowed to rearrange in the solutions in which they were prepared without any treatment. The effect of antimony pentachloride on the rearrangements of several representative peroxides was also studied.

The results of these experiments showed that carboxy-inversion was the predominant mode of decomposition of mixed peroxides, III, derived from m-chloroperbenzoic acid. It was also found that the rates of rearrangement depend on the nature of the R group in III. The rates varied as expected with R tertiary > secondary > primary. Convenient rates were found at *ca.* −30° for R tertiary, 25° for secondary, and 60–100° for primary. Under these conditions the rearrangements are completed in 8–12 hr. Some typical alcohol yields based on the conversion of acid chlorides to alcohols, *i.e.*, RCOCl → ROH, are for primary groups: tridecyl, 58%; octyl, 58%; and hexyl, 66%. For secondary R groups, yields are 2-ethylpentyl, 73%; cyclohexyl, 69%; and 3-pentyl, 70%. Two tertiary



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[1] Trubek Fellow in Chemistry, 1962–1964.

[2] (a) J. E. Leffler, *J. Am. Chem. Soc.*, **72**, 67 (1950); (b) D. B. Denney, *ibid.*, **78**, 590 (1956); (c) D. B. Denney and D. Z. Denney, *ibid.*, **79**, 4806 (1957); (d) D. Z. Denney, T. M. Valega, and D. B. Denney, *ibid.*, **86**, 46 (1964); (e) R. Huisgen and W. Edl, *Angew. Chem.*, **74**, 588 (1962); (f) J. T. Edward, H. S. Chang, and S. A. Samad, *Can. J. Chem.*, **40**, 804 (1962); (g) F. D. Greene, H. P. Stein, C. Chu, and F. M. Vane, *J. Am. Chem. Soc.*, **86**, 2080 (1964); (h) C. Walling, H. N. Moulden, J. H. Waters, and R. C. Neuman, *ibid.*, **87**, 518 (1965).

[3] This transition state may lead to an ion pair(s) before collapse to II.

[4] m-Chloroperbenzoic acid is commercially available from FMC Corp.

[5] M. Vilkas and R. W. Cummins, *Bull. soc. chim. France*, 1401 (1959).

[6] L. S. Silbert and D. Swern, *J. Am. Chem. Soc.*, **81**, 2364 (1959).

[7] In early experiments the mixed peroxides from both m-chloroperbenzoic acid and p-nitroperbenzoic acid were isolated and their arrangements were then studied under a variety of conditions. No difficulty was experienced with those peroxides derived from m-chloroperbenzoic acid; however, several incidents occurred with those derived from p-nitroperbenzoic acid. For example, cyclohexanoyl p-nitrobenzoyl peroxide, 6.0 g., decomposed at room temperature without explosion but with the evolution of oxides of nitrogen.

examples are *t*-butyl, 40% yield, and 2,4,4-trimethylpentyl, 50% yield. These results were obtained without the use of catalysts and in most cases without processing the solutions in which the peroxides were prepared. The reaction mixtures were extracted to remove acids. The solvent was removed and replaced by methanolic potassium hydroxide. After saponification the alcohols were isolated by conventional means.

The results of these experiments indicate that thermal, uncatalyzed rearrangements of mixed peroxides from *m*-chloroperbenzoic acid and the types of acids described provides a good route for the degradation of these acids to alcohols with the loss of the carboxyl carbon atom. The best results were obtained under these conditions and attempts to use various Lewis acids as catalysts led to lower yields of the desired products. Indeed, when antimony pentachloride was used, a considerable amount of ester, RCO_2R, was always formed. This may have been due to disproportionation of the mixed peroxide to the symmetrical peroxide, $(RCO_2)_2$, which then rearranged.

Experimental Section

Reagents.—The acid chlorides were prepared by heating with excess pure thionyl chloride. The acid chlorides were distilled. Their boiling points and infrared spectra agreed with reported values. Pyridine was stored over potassium hydroxide. *m*-Chloroperbenzoic acid (85%) was obtained from FMC Corp.; allowance was made for the 15% contamination by *m*-chlorobenzoic acid when the peroxides were prepared. All solvents were distilled and dried.

General Procedure.—A solution of the acid chloride and *m*-chloroperbenzoic acid, either in solution or as a suspension, was treated dropwise with pyridine at the appropriate temperature with cooling and stirring. After the addition of the pyridine the mixture was stirred at the desired temperature until the infrared spectrum indicated that the peroxide had decomposed and a test for peroxide was negative. The solvent was decanted from the gummy precipitate of pyridine hydrochloride, which was washed with solvent. Evaporation of the solvent and replacement with methanolic potassium hydroxide followed by saponification gave the desired alcohols. The alcohols were isolated by concentration of the methanolic solution followed by extraction with diethyl ether. The alcohols were identified by boiling point, infrared and n.m.r. spectra, and conversion in some cases to solid derivatives. Several specific examples of these procedures are outlined below.

Conversion of 2-Ethylhexanoyl Chloride to 3-Heptanol.—A stirred mixture of 6.60 g. (0.0324 mole) of 85% *m*-chloroperbenzoic acid and 5.30 g. (0.0324 mole) of 2-ethylhexanoyl chloride in 70 ml. of hexane at 0° was treated dropwise with 2.72 g. (0.034 mole) of pyridine in 10 ml. of cyclohexane. The mixture was allowed to warm to room temperature with stirring. After 18 hr. the infrared spectrum and a peroxide test indicated no peroxide remained. The solution was decanted from the pyridine hydrochloride and the hexane was evaporated and replaced with 175 ml. of 1 *N* methanolic potassium hydroxide. The solution was heated under reflux for 18 hr. and then most of the methanol was distilled. The residue was treated with 50 ml. of ether and 50 ml. of water. The ether was separated, dried, and distilled to give 2.68 g. (73%) of 3-heptanol, b.p. 156–157° (lit.[8] b.p. 156°). The n.m.r. and infrared spectra were in complete agreement with the structural assignment. The 3,5-dinitrobenzoate was prepared, m.p. 62–64° (lit.[8] m.p. 64°).

Acidification of the aqueous solution yielded *m*-chlorobenzoic acid, m.p. 156–157° (lit.[9] m.p. 158°). The yield was quantitative.

2,2,4-Trimethyl-2-pentanol from 2,2,4,4-Tetramethylpentanoic Acid.—2,2,4,4-Tetramethylpentanoic acid was prepared by the method of Koch and Haaf.[10] The acid chloride, 8.16 g. (0.050 mole), and 10.05 g. (0.050 mole) of *m*-chloroperbenzoic acid in 125 ml. of pentane at −45° were treated with 4.00 g. (0.050 mole) of pyridine. The stirred mixture was allowed to warm to room temperature over a 40-hr. period. Isolation as before gave 3.26 g. (50%) of 2,4,4-trimethyl-2-pentanol, b.p. 147–149° (lit.[11] b.p. 146.5–147.5°). The infrared and n.m.r. spectra were identical with those of a sample prepared by another method.[11] The 3,5-dinitrobenzoate was prepared, m.p. 87–90° (lit.[12] m.p. 89.5–90.5°).

Preparation of *n*-Heptanoyl *m*-Chlorobenzoyl Peroxide.—A stirred mixture of 8.12 g. (0.040 mole) of 85% *m*-chloroperbenzoic acid and 6.00 g. (0.040 mole) of *n*-heptanoyl chloride in 150 ml. of hexane was treated dropwise with 3.20 g. (0.040 mole) of pyridine in 15 ml. of hexane. The temperature was maintained at −20° during the addition and for 5 hr. thereafter. The hexane solution was filtered to separate it from pyridine hydrochloride. It was then extracted with 50 ml. of 10% hydrochloric acid, 50 ml. of water, 50 ml. of 10% sodium bicarbonate solution, and 50 ml. of water. The hexane solution was dried and evaporated to give 11.28 g. (95%) of a liquid. Active oxygen analysis[13] showed 96% of that expected for *n*-heptanoyl *m*-chlorobenzoyl peroxide. The infrared spectrum was in agreement with that expected.

Rearrangement of *n*-Heptanoyl *m*-Chlorobenzoyl Peroxide.—The peroxide, 5.20 g. (0.0182 mole), was heated under reflux in a solution of 30 ml. of hexane and 20 ml. of cyclohexane for 10 hr. At this time the infrared spectrum and a qualitative peroxide test indicated the peroxide had decomposed. Isolation, as before, provided 1.26 g. (69%) of 1-hexanol whose infrared and n.m.r. spectra were identical with those of a known sample.

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(8) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 280.

(9) Reference 8, p. 278.

(10) H. Koch and H. Haaf, *Ann.*, **618**, 251 (1958).

(11) J. J. Ritter, *J. Am. Chem. Soc.*, **70**, 4253 (1948).

(12) R. C. Hutson and R. B. Smith, *J. Org. Chem.*, **15**, 1074 (1950).

(13) L. S. Silbert and D. Swern, *Anal. Chem.*, **30**, 385 (1958).