The Reaction of Olefins with Carboxylic Acid Anhydrides

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The acylation of olefins with monocarboxylic acid anhydrides to form unsaturated ketones was first reported by Kondakov (10), who found acetic anhydride and zinc chloride to convert trimethylethylene to 3,4-dimethyl-3-penten-2-one (as well as to the adduct, 2,3-dimethyl-4-oxo-2-pentyl acetate, and *tert*-pentyl acetate) and isobutylene to mesityl oxide and *tert*-butyl acetate.

$$2(CH_3)_2C{=}CH_2 + (CH_3CO)_2O \xrightarrow{ZnCl_2} (CH_3)_2C{=}CHCOCH_3 + CH_3COOC(CH_3)_3$$

The reaction has occasionally been restudied, chiefly with a view toward converting diisobutylene into a marketable ketonic solvent by acetylation (2,3,6,11). A systematic investigation (15) of the cyclohexene-acetic anhydride reaction achieved a maximum yield of 54 per cent of cyclohexenyl methyl ketone; a reasonable, typical Friedel-Crafts carbonium-ion mechanism was proposed. Such acetylation of still other olefins has received some attention (5,7,8,9,12,14).

The present study was designed to extend this reaction to olefins and anhydrides not previously tried, particularly cyclic dicarboxylic anhydrides.

EXPERIMENTAL

To gain experience, several known reactions were effected first. The zinc chloride-catalyzed reaction of diisobutylene (112 g., one mole) and acetic anhydride (102 g., one mole) at 20-30° gave 59 g. (36.7%) of isomeric methyl octenyl ketones, b.p. 186-196°, and 24 g. of recovered olefin. A similar run with one-half mole of cyclohexene produced only 6.6 g. (11%) of cyclohexenyl methyl ketone, b.p. 203-6°. Isobutylene gave only insignificant yields of mesityl oxide, whether it was used at one atmosphere or two, and whether the catalyst was zinc chloride or acetylsulfoacetic acid.

2-METHYL-2-HEXEN-4-ONE. Propionic anhydride (130 g., one mole) and anhydrous zinc chloride (68 g., one-half mole) were stirred and treated with a stream of isobutylene by way of a gas-dispersing tube for one hour at about 18°. The dark brown liquid was decanted, kept overnight in the refrigerator, diluted with ether, washed with dilute alkali and water, dried over calcium chloride, and distilled in a Todd column to yield 16 g. (14%) of crude 2-methyl-2-hexen-4-one, b.p. 148-157°. This gave a semicarbazone melting at 162°, the same as the literature value (1) for this derivative.

CYCLOHEXENYL ETHYL KETONE. In essentially the same way, cyclohexene (82 g., 1 mole), one mole of propionic anhydride, and 0.5 mole of zinc chloride gave 23 g. (17%) of cyclohexenyl ethyl ketone, b.p. 217-220°. Although the literature value (16) for this boiling point is "about 218°", the compound has never been definitely characterized. It was therefore further studied.

Analytical data: Calculated for $C_9H_{14}O$; C, 78.21; H, 10.21; molecular weight, 138. Found: C, 78.18, 78.44; H, 10.12, 10.28; molecular weight (cryoscopically, in benzene), 132.

The semicarbazone was found to melt at 186-189°.

CYCLOHEXENYL PHENYL KETONE. The reaction of benzoic anhydride with excess cyclohexene gave no ketone when boron trifluoride or zinc chloride was used as catalyst, but aluminum chloride or concentrated sulfuric acid so used produced a small amount of a steam-volatile ketonic oil. This material boiled at 130-135° at 8 mm .upon repeated fractional distillation and could not be made to give the recorded boiling point (147° at 8 mm. (4)) nor other expected values for pure cyclohexenyl phenyl ketone. Calculated for $C_{13}H_{14}O$: molecular weight, 186; molecular refraction, 50.8. Found: molecular weight, 207; molecular refraction, 53.9.

UNSUCCESSFUL TRIALS. Saturated ketones result from the reaction of acid chlorides with olefins if aluminum chloride is used as catalyst, and cyclohexane as the solvent and source of hydrogen (13). However, cyclohexene and acetic anhydride thus treated gave no significant amount of material boiling at 179-80°, the boiling point of cyclohexyl methyl ketone, and the tiny fraction obtained gave positive tests for unsaturation.

No ketone could be isolated from reaction mixtures of acetic anhydride with the olefins in Table I.

TABLE I

Trials of Various Olefins with Acetic Anhydride.

OLEFIN	CATALYST	RESULTS
Propylene	Acetylsulfoacetic acid	Polymerization
Styrene	Sulfuric acid	Exothermic polymerization
α-Pinene	Zinc chloride	Exothermic polymerization
Vinyl bromide	Sulfuric acid	No reaction
Vinyl acetate	Sulfuric acid	No reaction
Trichloroethylene	Aluminum chloride	No reaction
Allyl chloride	Aluminum chloride	Polymerization
Allyl chloride	Zinc chloride	Polymerization

Chloracetic anhydride similarly gave no ketone with cyclohexene and either sulfuric acid or acetylsulfoacetic acid as catalyst.

Reactions between the olefins and cyclic anhydrides in Table II were followed, except as noted, by extraction with aqueous alkali to remove the expected keto-acid. In no case was any found.

TABLE II

Trials of Olefins with Cyclic Anhydrides.

ANHYDRIDE	OLEFIN	SOLVENT	CATALYST
Maleic	Propylene	Ethyl ether	Boron trifluoride
Maleic	Isobutylene	Ethyl ether	Boron trifluoride
Maleic	Cyclohexene	Ethyl ether	Boron trifluoride
Maleic (molten)	Cyclohexene	None	Zinc chloride
Maleic*	Diisobutylene	Isopropyl ether	Zinc chloride
Maleic*	Diisobutylene	None	Zinc chloride
Maleic*	Styrene	None	Zinc chloride
Succinic	Cyclohexene	Dioxane	Boron trifluoride
Succinic	Cyclohexene	None	Zinc chloride
Phthalic (molten)	Isobutylene	None	Zinc chloride
Phthalic	Cyclohexene	None	Boron trifluoride

* Product tested directly for ketones without extraction.

Finally, the passage of vaporized acetic anhydride and isobutylene over activated alumina at 250-340° gave no ketone except acetone, derived from pyrolysis of the anhydride.

DISCUSSION

A predominance of poor yields and failures in this work indicates that acid anhydrides are generally inferior to acid chlorides as reagents for acylating olefins, in spite of the contrary observation of Royals and Hendry (15) for the one acylation they studied intensively, and of the presumable success of Cook, Krimmel, and Whitmore (5). It may be presumed that carbonium ion formation is less easy from the anhydrides, especially the cyclic ones, and that the competing polymerization of the olefin via the derived alkylcarbonium ion almost or entirely dominates the process. Polymerization of the olefins was worse when no solvent other than excess olefin was used, but it was never thoroughly repressed by any change of solvent, catalyst, or temperature. Indeed, more severe conditions appeared only to increase the amount of polymer without improving the yield of ketone. It is of course possible that part of the observed polymerization was that of the unsaturated ketone, as suggested by Royals and Hendry (15).

LITERATURE CITED

1. BLAISE, E. E. AND M. MAIRE. 1908. Syntheses with mixed organometallic derivatives of zinc. β-ketonic alcohols and α, β-unsaturated acyclic ketones. Ann. chim. phys. 15:556 (in French).

2a. BYRNS, A. C. 1944. Ketones. U. S. Patent 2,355,703, as cited by Chem. Abstracts 39:87 (1945).

2b. ————. 1949. Ketones. U. S. Patent 2,463,742, as cited by Chem. Abstracts 43:4685 (1949).

3. BYRNS, A. C. AND T. F. DOUMANI. 1943. Ketone synthesis—condensation of acid anhydrides with olefins. Ind. Eng. Chem. 35:349.

4. CHRIST, R. E. AND R. C. FUSON. 1937. Application of the principle of vinylogy to unsaturated ketones. J. Am. Chem. Soc. 59:895.

5. COOK, N. C., J. A. KRIMMEL, AND F. C. WHITMORE. Unpublished work cited by Brooks, The chemistry of the nonbenzenoid hydrocarbons, 2d ed.: New York: Reinhold Publishing Co., 1950, p. 398.

6a. DOUMANI, T. F. AND J. F. CUNEO. 1946. Unsaturated ketones. U. S. Patent ,2411,823, as cited by Chem. Abstracts 41:1234 (1947).

6b. ————. 1948. Unsaturated ketones. U. S. Patent 2,438,334, as cited by Chem. Abstracts 42:4602 (1948).

7. EBEL, F. AND M. W. GOLDBERG. 1927. Action of acetic anhydride containing sulfoacetic acid on aliphatic double bonds. Helv. Chim. Acta 10:677 (in German).

8. GUTSCHE, C. D. AND W. S. JOHNSON. 1946. Some observations on Friedel-Crafts reactions involving unsaturated ketones. 9-Keto-4b, 5, 6, 7, 8, 8a, 9, 10-octahydrophenanthrene. J. Am. Chem. Soc. 68:2239.

9. JOHNSON, C. E. 1949. Ketones. U. S. Patent 2,458,603, as cited by Chem. Abstracts 43:3441 (1949).

10. KONDAKOV, J. 1894. On the compounds formed from olefins and acid anhydrides under the influence of zinc chloride. J. Russ. Phys.-Chem. Soc. 26:232, as cited by Ber. 27:R941 (1894) (in German).

11. LUKES, G. E. AND R. C. SWANN. 1948. Unsaturated ketones. U. S. Patent 2,457,696, as cited by Chem. Abstracts 43:3442 (1949).

12. MESCHERYAKOV, A. P. AND L. V. PETROVA. 1951. Synthesis of unsaturated ketones from di- and triisobutylenes by the Kondakov reaction. Izvest. Akad. Nauk S. S. S. R., Otdel Khim. Nauk, 576, as cited by Chem. Abstracts 46:7043 (1952).

13. NENITZESCU, C. D. AND E. CIORANESCU. 1936. Reactions catalyzed by aluminum chloride. XV. Preparation of saturated ketones by addition of acid chlorides to olefins and hydrogenation by means of aluminum chloride. Ber. 69B:1820 (in German).

14. PETROV, A. D. AND E. P. KAPLAN. 1947. Chemistry of the Grignard reaction. I. Reaction of Grignard reagents with carbonyl compounds. Izvest. Akad. Nauk. S. S. S. R., Otdel Khim. Nauk, 295, as cited by Chem. Abstracts 43:1718 (1949).

15. ROYALS, E. E. AND C. M. HENDRY. 1950. Acylation of olefins. I. Acetylation of cyclohexene. J. Org. Chem. 15:1147.

16. WALLACH, O. 1908. Contribution to our knowledge of the terpenes and the ethereal oils. XCII. The preparation of ring hydrocarbons with semicyclic linking and their application to new synthesis. Ann. 360:26 (in German).