m. p. 58–60°. After two recrystallizations from ethanol it melted at 63–64°.

*Anal.* Calcd. for $C_{21}H_{26}O_2$: C, 81.3; H, 8.4. Found: C, 81.4; H, 8.6.

**6-(1-Hydroxyheptyl)-1,2,3,4-tetrahydroanthracene** (NIH 2192).—Seven grams of 6-heptanoyltetrahydroanthracene was reduced with 40 cc. of 1 *M* aluminum isopropoxide (one hour). Solvent was evaporated *in vacuo*, and the residue was partitioned between dilute hydrochloric acid and ether. Drying and evaporation of the ether gave an oil which crystallized from aqueous methanol in a yield of 6 g. (86%). After two recrystallizations from methanol it melted at 75.5–77°.

*Anal.* Calcd. for $C_{21}H_{28}O$: C, 85.1; H, 9.5. Found: C, 85.0; H, 9.6.

## Summary

6-Butyryl- and 6-heptanoyl-1,2,3,4-tetrahydroanthracenes have been synthesized and their structures proved by oxidation to the corresponding carboxylic acid.

6-Butyryl- and 6-heptanoyl-1,2,3,4-tetrahydro-9,10-anthraquinones are without value in *gallinaceum* malaria.

BETHESDA 14, MARYLAND RECEIVED JULY 7, 1947

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[CONTRIBUTION NO. 627 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

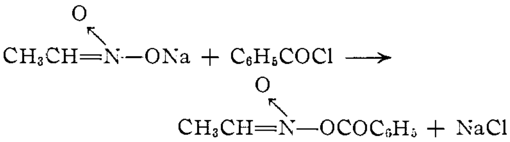
# The Reaction of 2-Nitropropane with Acid Anhydrides[1,2]

BY EUGENE P. STEFL[3] AND MALCOLM F. DULL

With the exception of a few which contain aromatic groups, no stable acyl derivative of the aci-nitroparaffins has been described. Thus, Nenitzescu and Isacescu[4] obtained acetyl aci-phenylnitromethane by the action of ketene with the aci-form of phenylnitromethane. These same investigators prepared acetyl and benzoyl aci-9-nitrofluorene by treatment of the potassium salt with the corresponding acid chlorides. Thurston and Shriner[5] obtained benzoyl aci-phenyl nitroacetonitrile by reaction of benzoyl chloride with both the sodium and silver salts of the nitro-compound.

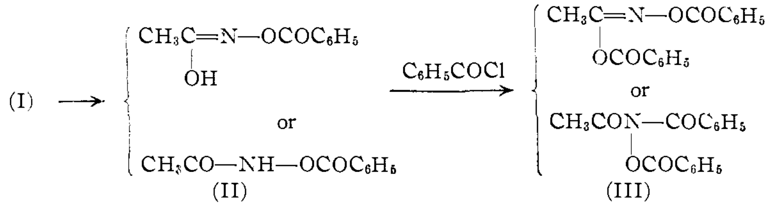
The action of acetyl and benzoyl chlorides on simple primary nitroparaffins or their salts causes molecular rearrangements.[6] Jones,[7] for example, found the product of the action of benzoyl chloride on sodium aci-nitroethane to be dibenzoylacethydroxamic acid (III), probably by the following reactions.

(1)



$$CH_3CH{=}\overset{O\nwarrow}{N}{-}ONa + C_6H_5COCl \longrightarrow CH_3CH{=}\overset{O\nwarrow}{N}{-}OCOC_6H_5 + NaCl$$

(I)



$$(I) \longrightarrow \left\{\begin{matrix} CH_3\underset{OH}{\underset{|}{C}}{=}N{-}OCOC_6H_5 \\ \text{or} \\ CH_3CO{-}NH{-}OCOC_6H_5 \end{matrix}\right. \xrightarrow{C_6H_5COCl} \left\{\begin{matrix} CH_3\underset{OCOC_6H_5}{\underset{|}{C}}{=}N{-}OCOC_6H_5 \\ \text{or} \\ CH_3CO\underset{OCOC_6H_5}{\underset{|}{N}}{-}COC_6H_5 \end{matrix}\right.$$

(II) (III)

The aci-benzoate (I) was not isolated, but was assumed to rearrange to (II), which on further reaction gave (III). That acylation may in certain instances occur on the carbon atom adjacent to the nitro group is evident from experiments by Gabriel,[8] who treated phthalic anhydride with sodium nitromethane and obtained, after acidification, small amounts of 2-nitroacetylbenzoic acid.

The present investigation reveals that a secondary nitroparaffin or its salt may give rise to a relatively stable aci-ester or mixed anhydride, $(CH_3)_2C{=}\overset{O\nearrow}{N}{-}OCOR$ (IV), by reaction with aliphatic acid anhydrides. Acetyl and propionyl 2-aci-nitropropane were prepared by reaction of the acid anhydrides directly with 2-nitropropane in anhydrous toluene solution in the presence of potassium acetate, or with an ether suspension of sodium 2-nitropropane, both reactions being highly exothermic. In reactions with sodium 2-nitropropane cooling in an ice-bath was required. Yields were low, acetyl 2-aci-nitropropane being obtained in yields averaging 7.5% directly from the nitroparaffin and 17.3% from the sodium salt. Propionyl 2-aci-nitropropane was isolated in 9.5% yields from the nitroparaffin and 5.6% from its salt.

In every instance the reaction was accompanied by a slow and unexplained evolution of carbon dioxide and the development of a bright blue color, the latter possibly attributable to the monomolecular form of isopropyl pseudonitrole.[9,10] It distilled with the solvent and excess of reactants at the conclusion of the reaction, and could not be separated from them by distillation through a 38-cm. packed column. On prolonged standing the blue color disappeared, and after the ether or toluene solution had stood for a considerable time in contact with water a positive brown ring test

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[1] Abstracted from a thesis submitted by Eugene P. Stefl in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Presented before the Organic Division of the American Chemical Society at the Atlantic City Meeting, April 17, 1947.

[3] Present address: Firestone Tire and Rubber Company, Akron, Ohio.

[4] Nenitzescu and Isacescu, *Bull. soc. chim. Romania*, **14**, 53 (1932) (*C. A.*, **27**, 964 (1933)).

[5] Thurston and Shriner, *J. Org. Chem.*, **2**, 183 (1937).

[6] Gilman, "Organic Chemistry, an Advanced Treatise," Vol. 1, John Wiley and Sons, Inc., New York, N. Y., 1938, p. 626.

[7] Jones, *Am. Chem. J.*, **20**, 1 (1898).

[8] Gabriel, *Ber.*, **36**, 570 (1903).

[9] Scholl, *ibid.*, **21**, 508 (1888).

[10] Piloty and Stock, *ibid.*, **35**, 3093 (1902).

was obtained. When some of the excess anhydride separated from the reaction mixture was refluxed the blue color soon vanished, the brown fumes of nitrogen dioxide were observed, and acetone was subsequently detected.

The evolution of carbon dioxide was measured in reactions involving the sodium 2-nitropropane, and was liberated in quantities of approximately 0.2 mole per mole of salt reacting. It is apparent that at least one and possibly several other reactions occur in addition to simple acylation. The nature of these other reactions has not yet been established but is being studied.

Both acetyl and propionyl 2-aci-nitropropane are colorless liquids which distil with some decomposition even at 1 mm. pressure. The acyl derivatives were characterized by the reactions

$$\text{IV} + H_2O \longrightarrow (CH_3)_2CO + RCOOH + {}^1/_2H_2N_2O_2 \quad (2)$$

$$\text{IV} + C_2H_5OH \longrightarrow (CH_3)_2CO + RCOOC_2H_5 + {}^1/_2H_2N_2O_2 \quad (3)$$

$$\text{IV} + C_6H_5NH_2 \longrightarrow (CH_3)_2CO + RCONHC_6H_5 + {}^1/_2H_2N_2O_2 \quad (4)$$

$$\text{IV} + 2H_2 \longrightarrow (CH_3)_2CO + RCOONH_4 \quad (5)$$

The reactions with water and aniline occurred slowly at room temperature, while that with ethanol required refluxing in the presence of a drop of sulfuric acid. The expected decomposition products of hyponitrous acid were identified. Mellor[11] states that the decomposition of hyponitrous acid may occur in three ways

$$H_2N_2O_2 \longrightarrow N_2O + H_2O \quad (6)$$

$$3H_2N_2O_2 \longrightarrow 2NH_2OH + 2N_2O \quad (7a)$$

$$\searrow 2NH_3 + 2N_2O_3 \quad (7b)$$

while hydroxylamine in turn decomposes in alkaline solution to ammonia, nitrous oxide, and nitrogen.[12] It will be noted that equation (7a) does not balance. In the reaction of the aci-acetate and propionate with water (equation 2) nitrous oxide and hydroxylamine or its salt were identified when water alone or dilute hydrochloric acid were employed, while ammonia, nitrous oxide, and nitrogen were produced when 10% sodium hydroxide was used. The latter were also formed in the reaction with aniline, probably because of the basic character of the reagent. In the reactions with ethanol (equation 3) and aniline (equation 4) no free hydroxylamine, and only a little acetone, was found. Acetoxime was isolated instead.

Several attempts to prepare benzoyl 2-aci-nitropropane by reaction of the sodium salt, first with benzoic anhydride, and then with benzoyl chloride, were unsuccessful. The anhydride failed to react on prolonged refluxing in ether or toluene solution. The acid chloride readily reacted, but although anhydrous conditions were employed only benzoic acid, formed in considerable quantity, was identified. This reaction will be investigated further.

## Experimental[13]

**Acetyl 2-Aci-nitropropane from 2-Nitropropane.**—To a mixture of 45 g. (0.51 mole) of 2-nitropropane and 60 g. (0.59 mole) of acetic anhydride in 100 g. of dry toluene contained in a flask attached to a reflux condenser was added 5 g. of anhydrous potassium acetate. The mixture was warmed gently to initiate the reaction, after which it was maintained at reflux temperature by frequent addition of small portions of potassium acetate. After a total of 30 g. had been added, no further reaction was evident. Additional refluxing of the mixture had no noticeable effect upon the yield. During the reaction the mixture rapidly acquired a bright blue color, and slowly evolved carbon dioxide.

The cooled reaction mixture was filtered from the precipitated molecular compound of potassium acetate and acetic acid, $CH_3COOK{\cdot}CH_3COOH$ (m. p. 148°), and the toluene and excess anhydride were removed by distillation *in vacuo*. The blue color distilled and recondensed with the distillate, leaving a residue possessing a brown color due to some charring which occurred during the reaction. This residue was distilled through a 38-cm. fractionating column packed with 3-mm. glass helices. The portion distilling at 47° at 1 mm.[14] was collected, giving 6.0 g. (8.9%) of colorless product. In other runs the yield varied from 7.2 to 9.1%, the average being 7.5%.

**From Sodium 2-Nitropropane.**—In 200 g. of anhydrous ether in a three-necked flask, fitted with a dropping funnel, thermometer and mechanical stirrer, was suspended 20 g. (0.18 mole) of sodium 2-nitropropane. The mixture was cooled to 5° in an ice-bath and 25 g. (0.24 mole) of acetic anhydride added slowly and with stirring over a period of one hour. A bright blue color was developed in the mixture during the reaction. When the addition was complete the mixture was allowed to return to room temperature. After standing thus for about thirty minutes an evolution of carbon dioxide, extending over a period of about eighteen hours, was noted. In duplicate determinations by absorption with ascarite it was found that 0.2 mole of carbon dioxide was evolved per mole of sodium 2-nitropropane used. The precipitated sodium acetate was filtered off and the ether removed on a steam-bath. The blue color distilled and condensed with the ether. Excess anhydride was removed by distillation *in vacuo*, carrying with it the remainder of the blue color. The residue was distilled through the packed column at 1 mm., and gave 4.5 g. (19.0%) of pale yellow product boiling at 47°.

In other experiments the yield varied from 16.7 to 19.1%, and averaged 17.3%.

Samples of the acetyl compound obtained by both methods, recrystallized from anhydrous ether by immersing in an ethanol–solid carbon dioxide-bath, exhibited the following characteristics: b. p. 50° (1 mm.); $n^{25}_D$ 1.4308; $d_{25}$ 1.017.

*Anal.* Calcd. for $C_5H_9O_3N$: N, 10.69; mol. wt. 131. Found: N, 10.52, 10.66; mol. wt. (f. p. depression of benzene) 120.

**Reactions of Acetyl 2-Aci-nitropropane with Water.**—A mixture of 5 g. of acetyl 2-aci-nitropropane with an equal amount of water was refluxed for fifteen minutes. The evolved gas was identified as nitrous oxide by means of a glowing splint after it had been absorbed in ethanol and expelled through a drying train into a nitrometer.

Fractionation of the liquid mixture through the packed column gave approximately quantitative amounts of acetone and acetic acid, identified by conversion to the 2,4-dinitrophenylhydrazone, and by boiling point and density, respectively. Vacuum distillation of the residue from a

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(11) Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. 8, Longmans, Green and Co., New York, 1928, p. 407.

(12) Mellor, *ibid.*, p. 287.

(13) All boiling points are corrected.

(14) Distillation of the acyl 2-aci-nitropropane was carried out many times without difficulty. On one occasion, however, a violent explosion occurred, the cause of which has not been ascertained.

small flask gave hydroxylamine, converted to acethydroxamic acid (m. p. 87°) by addition of acetyl chloride.

**With Dilute Hydrochloric Acid** (2:1).—A mixture of 2 g. of acetyl 2-aci-nitropropane with 6 ml. of dilute hydrochloric acid was refluxed for ten minutes. Fractionation gave acetone and acetic acid, while a residue of 250 mg. of hydroxylamine hydrochloride remained.

**With 10% Sodium Hydroxide.**—Reaction of 2 g. of the acetyl compound with 6 ml. of 10% sodium hydroxide occurred rapidly at room temperature. Acetone and sodium acetate were formed, and a mixture of ammonia, nitrous oxide and nitrogen, all separately identified, was evolved. No hydroxylamine was noted.

**With Ethanol.**—No reaction occurred on refluxing acetyl 2-aci-nitropropane with either ethanol or 1-butanol alone.

A mixture of 2 g. of the acetyl compound with 4 g. of ethanol and one drop of 100% sulfuric acid was refluxed for one hour and fractionated. A trace of acetone was identified by conversion to the 2,4-dinitrophenylhydrazone, and an almost quantitative amount of ethyl acetate was separated and identified by odor, boiling point, and density. From the residue was obtained 300 mg. of acetoxime.

**With Aniline.**—A mixture of 4 g. of acetyl 2-aci-nitropropane and 8 g. of aniline was gently warmed on the water-bath for about ten minutes, during which ammonia was evolved. The resulting white crystalline product, representing quantitative formation of acetanilide, was identified as such after recrystallization from carbon tetrachloride. Distillation of the unreacted aniline gave a small amount of acetone, and a residue of 400 mg. of acetoxime. No free hydroxylamine was detected.

**Propionyl 2-Aci-nitropropane** (from 2-Nitropropane).—The procedure employed in preparing the acetyl derivative was used here. A mixture of 89 g. (1 mole) of 2-nitropropane, 130 g. (1 mole) of propionic anhydride and 10 g. of anhydrous potassium acetate in 200 g. of toluene was warmed to refluxing temperature. With the heat removed the reaction was continued by frequent additions of potassium acetate until no further reaction was noted. This required a total of 70 g. Removal of the insoluble salt, solvent and unreacted anhydride as before gave a pale yellow product. This was distilled through the packed column, giving 15.0 g. (10.3%) of substance boiling at 69° at 1 mm. In several runs an average yield of 9.5% was obtained.

**From Sodium 2-Nitropropane.**—To a mixture of 100 g. (0.90 mole) of sodium 2-nitropropane in 1000 g. of anhydrous ether, 140 g. (1.08 mole) of propionic anhydride was added over a period of one hour, the temperature being maintained at 5° for three hours after the addition was complete. On warming to room temperature the usual evolution of carbon dioxide occurred. The precipitated salt, the ether and unreacted anhydride were removed as before, and the crude yellow product distilled through the packed column, giving 8.0 g. (6.1%) of propionyl 2-aci-nitropropane, boiling at 68° at one mm. In a series of experiments an average yield of 5.6% was obtained.

Samples for analysis were further purified by recrystallization from anhydrous ether in an ether–solid carbon dioxide-bath. The following characteristics were observed: b. p. 70° (1 mm.); $n^{25}_{D}$ 1.4340; $d_{25}$, 0.9850.

*Anal.* Calcd. for $C_6H_{11}O_3N$: N, 9.70; mol. wt., 141. Found: N, 10.03, 10.05; mol. wt., 140.

The reactions of propionyl 2-aci-nitropropane with water, ethanol and aniline were similar to those observed for the acetyl compound.

**Reaction of Sodium 2-Aci-nitropropane with Benzoyl Chloride.**—In several experiments benzoyl chloride was found to react slowly with an anhydrous ether suspension of sodium 2-aci-nitropropane at reflux temperature. Removal of the precipitated sodium chloride and distillation of the solvent left a residue of benzoic acid, although anhydrous conditions were maintained throughout. The reaction will be investigated further.

**Acknowledgments.**—We are indebted to the Commercial Solvents Corporation for supplying the 2-nitropropane employed in this investigation, and to the Buhl Foundation for its support during the final stages of the work. The microanalyses were performed by Mr. George Stragand.

## Summary

The preparation of acetyl and propionyl 2-aci-nitropropane has been accomplished. They are reactive substances, being converted by action of water, alcohols, amines and hydrogen (catalytically) to acetone or acetoxime, the carboxylic acids, their esters and N-substituted amides, and nitrogeneous compounds whose formation can be traced to the decomposition of initially formed hyponitrous acid.

PITTSBURGH, PA. RECEIVED MAY 3, 1947

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[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

# Hydrogenation of Esters to Alcohols over Raney Nickel. I

BY HOMER ADKINS AND A. A. PAVLIC[1]

Ovakimian, Kuna and Levene[2] reported the hydrogenation of the esters of certain amino acids to amino alcohols over Raney nickel in the temperature range of 35 to 100°. The conversion of a carbalkoxy to a carbinol group, under such mild conditions, was apparently due to the use of a high ratio of nickel to ester. Early attempts in this Laboratory to reproduce the results and develop a procedure of preparative value, gave rather erratic results. These successes and failures led to a modification of the procedure for the preparation of Raney nickel from the nickel aluminum alloy. The original process recommended by Raney,[3] as developed by Covert,[4] involved a prolonged digestion of the alloy at 115° or higher for about ten hours. According to a later and better process described by Mozingo[5] the digestion was for eight hours at 80°.

In attempting to obtain a very active catalyst, uniformly effective for the hydrogenation of α-amino esters, a process for preparing the catalyst was developed,[6] in which the digestion was at 50°

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[1] Du Pont Fellow at the University of Wisconsin 1941–1942.

[2] Ovakimian, Kuna and Levene, *J. Biol. Chem.*, **135**, 91 (1940).

[3] Murray Raney, U. S. Patent 1,628,190 (1927).

[4] Covert and Adkins, THIS JOURNAL, **54**, 416 (1932).

[5] Mozingo, "Organic Syntheses," **21**, 15 (1941).

[6] Pavlic and Adkins, THIS JOURNAL, **68**, 1471 (1946).