[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF THE JOHNS HOPKINS UNIVERSITY AND YALE UNIVERSITY]

The Acylation of Salts of Secondary Nitroparaffins[1]

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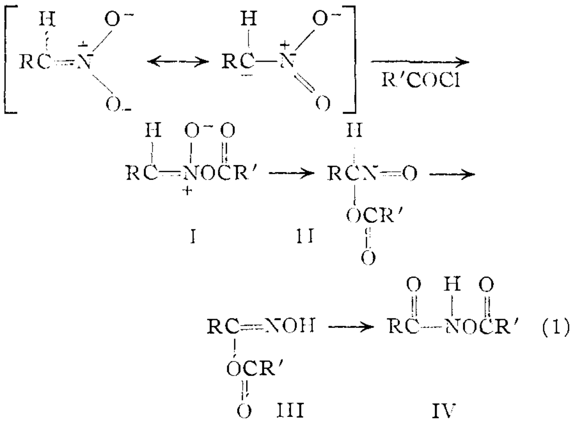
RECEIVED JULY 1, 1957

The reaction of benzoyl chloride with a salt of a secondary nitroparaffin yields the O-acylated derivative (a nitronic anhydride VII) as the initial product. The nitronic anhydride can be cleaved by ammonia to benzamide and the ammonium salt of the nitroparaffin. In general, the nitronic anhydrides are quite unstable and at temperatures well below 0° they rearrange to the corresponding nitrosoacyloxy compounds VIII. The latter compounds were synthesized independently in the present study by the reaction of lead tetrabenzoate with the corresponding oximes. Pertinent infrared absorption data are presented and the reactions are discussed.

The reaction of acid chlorides with salts of primary nitroparaffins has been reported by a number of investigators to yield various acylated hydroxamic acids (IV and related derivatives).[3] The following rational sequence accounts for the products of the reaction.



$$\left[\overset{\text{H}}{\text{RC}}{=}\overset{+}{\text{N}}\begin{smallmatrix}\text{O}^-\\ \text{O}^-\end{smallmatrix} \longleftrightarrow \overset{\text{H}}{\underset{-}{\text{RC}}}{-}\overset{+}{\text{N}}\begin{smallmatrix}\text{O}^-\\ \text{O}\end{smallmatrix}\right] \xrightarrow[\text{R'COCl}]{} \overset{\text{H}}{\text{RC}}{=}\underset{+}{\overset{\text{O}^-}{\text{N}}}\text{O}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{R'} \longrightarrow \text{R}\overset{\text{H}}{\underset{\text{OCOR'}}{\text{C}}}\text{N}{=}\text{O} \longrightarrow \underset{\text{OCOR'}}{\text{RC}}{=}\text{NOH} \longrightarrow \text{R}\overset{\text{O}}{\overset{\|}{\text{C}}}{-}\overset{\text{H}}{\text{N}}\text{O}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{R'} \quad (1)$$

I II III IV

Although the initial formation of the nitronic anhydride I was proposed as early as 1896,[3b] no direct evidence has been presented for the intermediacy of I or II.[4]

Even less has been published about the acylation of secondary nitroparaffins. The nitroso compounds VIII had not been identified as reaction products prior to our work, although several investigators[5] reported "transient blue colors" characteristic of nitroso compounds. In all but one[6] of the acylation reactions which have been reported, the authors claim to have isolated the nitronic anhydride VII as the principal reaction product. Forster[7] reported the anhydride of benzoic acid and *aci*-nitrocamphor as a dark green viscous oil. It was not characterized and the color indicates at least the presence of nitroso compounds in the oil. Stefl and Dull and later Urbanski reported a low yield of a high boiling oil from the reaction of acetic anhydride with salts of 2-nitropropane.[5] In view of the extreme instability that we have found to be a general property of the unconjugated nitronic anhydrides, these investigators could not have isolated VIIe. The remaining two reports concerning the synthesis of nitronic anhydrides are correct. Thurston and Shriner[8] synthesized and proved the structure of O-benzoyl-*aci*-nitrophenylacetonitrile (VI) and Nenitzescu[3f] has reported the synthesis of O-benzoyl-9-*aci*-nitrofluorene (V). We have repeated the latter synthesis and have confirmed the structure assigned. Both of these compounds are highly conjugated nitronic anhydrides; they are relatively stable and the reactions which they undergo are different from those of the alkyl nitronic anhydrides. These reactions will be covered elsewhere.[9] In this paper we show that the salts of nitroparaffins do yield nitronic anhydrides as initial products of the acylation reaction and that the latter compounds are quite unstable; at relatively low temperatures, they rearrange to the corresponding nitroso acyloxy compounds (equation 2).[10]

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[1] Taken in part from a thesis submitted by William J. Considine to the faculty of the Graduate School of Yale University in partial fulfillment of the requirements for the Ph.D. degree. Presented before the Division of Organic Chemistry at the 130th Meeting of The American Chemical Society, Atlantic City, N. J., September 21, 1956.

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[3] (a) J. Kissel, *Ber.*, **15**, 727 (1882); (b) J. U. Nef, *ibid.*, **29**, 1221 (1896); see also L. W. Jones, *Am. Chem. J.*, **20**, 1 (1898); (c) M. A. F. Holleman, *Rec. trav. chim.*, **15**, 359 (1896); (d) M. A. Van Raalte, *ibid.*, **18**, 392 (1899); (e) Wieland, *Ber.*, **62**, 1252 (1929); (f) C. D. Nenitzescu and D. A. Isacescu, *Bull. soc. chim. Romania*, **14**, 53 (1932); (g) T. Urbanski, *J. Chem. Soc.*, 3374 (1949); (h) R. H. Terss and W. E. McEwen, THIS JOURNAL, **76**, 580 (1954).

[4] Nenitzescu (footnote 3f) has reported that ketene and *aci*-nitrophenylmethane yield the corresponding nitronic anhydride. The compound was not characterized and in view of the properties reported it is, in all probability, compound III, R = C_6H_5, R' = CH_3.

[5] E. Stefl and M. Dull, THIS JOURNAL, **69**, 3037 (1947); T. Urbanski and W. Gurzynska, *Roczniki Chem.*, **25**, 183 (1951).

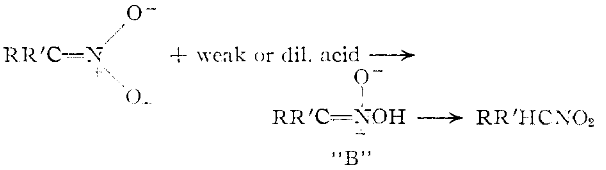
[6] In this case (W. Wislicenus and K. Pfeilsticker, *Ann.*, **436**, 40 (1924)), the authors claim to have isolated 1-benzoyl-3-nitroindene from the reaction of benzoyl chloride with the potassium salt of 3-nitroindene. The compound was not characterized and since the related nitrofluorene under similar conditions yielded the stable nitronic anhydride[9] V, the compound in question is probably O-benzoyl-3-*aci*-nitroindene.

[7] M. O. Forster, *J. Chem. Soc.*, **77**, 251 (1900).

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

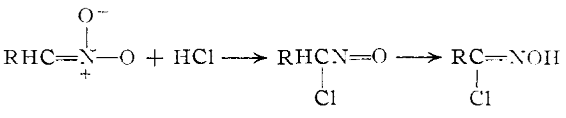
[9] E. H. White and W. J. Considine, *ibid.*, **22**, 1745 (1957).

[10] The reactions of nitronate ions with acids are formally analogous to those of equations 1 and 2.



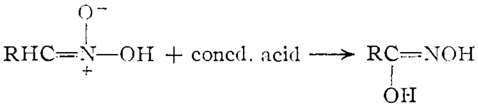
$$\text{RR'C}{=}\overset{+}{\text{N}}\begin{smallmatrix}\text{O}^-\\ \text{O}^-\end{smallmatrix} + \text{weak or dil. acid} \longrightarrow \underset{\text{"B"}}{\text{RR'C}{=}\underset{-}{\overset{\text{O}^-}{\text{N}}}\text{OH}} \longrightarrow \text{RR'HCNO}_2$$

N. Kornblum and G. E. Graham, THIS JOURNAL, **73**, 4041 (1951).



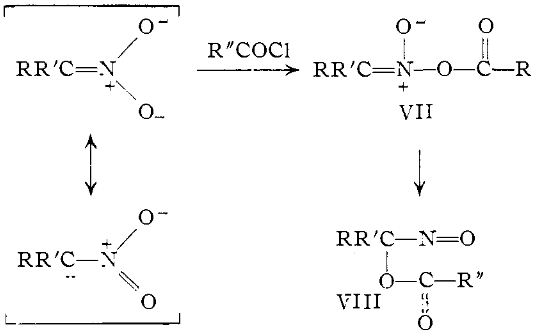
$$\text{RHC}{=}\underset{+}{\overset{\text{O}^-}{\text{N}}}{-}\text{O} + \text{HCl} \longrightarrow \text{RH}\underset{\text{Cl}}{\text{C}}\text{N}{=}\text{O} \longrightarrow \underset{\text{Cl}}{\text{RC}}{=}\text{NOH}$$

W. Steinkopf and B. Jürgens, *J. prakt. Chem.*, [2] **84**, 711 (1911).



$$\text{RHC}{=}\underset{+}{\overset{\text{O}^-}{\text{N}}}{-}\text{OH} + \text{concd. acid} \longrightarrow \underset{\text{OH}}{\text{RC}}{=}\text{NOH}$$

S. B. Lippincott and H. B. Hass, *Ind. Eng. Chem.*, **31**, 119 (1939).



(2)

VIIa, R = R′ = CH_3, R″ = C_6H_5
VIIb, R = CH_3, R′ = R″ = C_6H_5
VIIe, R = R′ = R″ = CH_3
VIIIa, R = R′ = CH_3, R″ = C_6H_5
VIIIb, R = CH_3, R′ = R″ = C_6H_5
VIIIc, R = R′ = CH_3, R″ = p-$NO_2C_6H_4$
VIIId, R + R′ = C_5H_{10}, R″ = C_6H_5

A mixture of benzoyl chloride and sodium 2-propanenitronate was allowed to react for 24 hours at −80° in methylene chloride and infrared spectra were taken of the colorless liquid phase at −80°. The absorption bands of benzoyl chloride gradually disappeared and the bands attributed to O-benzoyl-2-*aci*-nitropropane (VIIa) gradually appeared (Table I). The absorption bands in the double bond stretching region of the spectrum were similar to those of the stable nitronic anhydrides V and VI (Table I). The structure of the product was confirmed by ammonolysis at −80° to benzamide and ammonium 2-propanenitronate. O-Benzoyl-2-*aci*-nitropropane was isolated as a faintly colored solid at −80°; upon being warmed, the solid became noticeably blue at −60° and a deep blue melt was formed at *ca.* −30°.

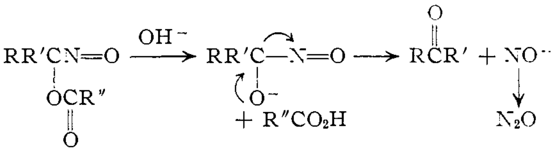
TABLE I

SPECTROSCOPIC ABSORPTION BANDS[a]

Compound		Solvent	Absorption C=O, μ	Absorption C=N, μ	Absorption N=O, μ	Absorption N=O, mμ
A. Nitronic anhydrides	V	$CHCl_3$	5.67[b]	6.16[c]		
	VI	$CHCl_3$	5.67[b]	6.18[c]		
	VIIa	CH_2Cl_2	5.71[b]	6.09[c]		
	VIIb	CH_2Cl_2	5.68[b]	6.21[c]		
B. Nitroso compounds	VIIIa	$CHCl_3$	5.78[e]		6.34[d]	663[d,f]
	VIIIb	CH_2Cl_2	5.77[e]		6.36[d]	
	VIIIc	$CHCl_3$	5.78[e]		6.35[d]	
	VIIId	CH_2Cl_2	5.80[e]		6.39[d]	667[d]
C. Nitro ketone[g]	IXa	$CHCl_3$	5.92[e]			

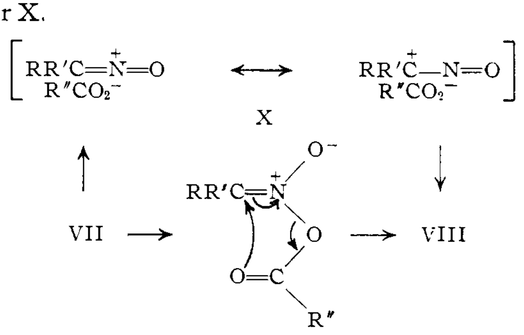
[a] Determined with recording spectrophotometers, a Perkin-Elmer I.R. (model 21) and a Cary U.V. (model 11S). The spectra of VIIa and VIIb were measured at −80°; all the others were measured at room temperature. [b] Substituted vinyl esters have been reported to absorb at 5.70 μ (R. N. Jones and F. Herling, *J. Org. Chem.*, **19**, 1252 (1954)). [c] Oximes have C=N absorption bands at 6.10 μ (A. Palm and H. Werbin, *Can. J. Chem.*, **32**, 858 (1954)). [d] For 1-chloro-1-nitrosocyclohexane, Müller (*Ber.*, **87**, 1449 (1954)) lists $\lambda_{\max}$ 6.37–6.40 μ, $\lambda_{\max}^{C_6H_{12}}$ 655 mμ (ε 22). [e] R. N. Jones ("Chemical Applications of Spectroscopy," Vol. IX, Technique of Organic Chemistry, Interscience Publishers, Inc., New York, N. Y., 1956) lists 5.80 μ for esters of aromatic acids (p. 454) and 5.92 μ for aryl ketones (p. 448). [f] Measured in CH_2Cl_2. [g] Also had a prominent band at 6.47 μ (NO_2).

A solution of VIIa in methylene chloride was allowed to warm to room temperature. The solution became deep blue and the infrared spectrum gradually developed into that of pure 2-nitroso-2-benzoyloxypropane (VIIIa). The nitroso compound was isolated as a rather unstable blue oil which was decomposed rapidly by acids and by visible light. After storage at −45° for several days, it crystallized as the colorless dimer. The structure of VIIIa was confirmed by an independent synthesis (*vide infra*) and by hydrolysis to benzoic acid, acetone and nitrous oxide.[11]



$$\underset{\substack{|\\ OCR''\\ \|\\ O}}{RR'CN{=}O} \xrightarrow{OH^-} \underset{\substack{|\\ O^-\\ +\ R''CO_2H}}{RR'C{-}N{=}O} \longrightarrow \overset{\substack{O\\ \|}}{RCR'} + \underset{\substack{\downarrow\\ N_2O}}{NO^-} \quad (3)$$

The rearrangement of VIIa in the presence of *p*-nitrobenzoic acid yielded both VIIIa and the product of exchange, 2-nitroso-2-(*p*-nitrobenzoyloxy)-propane (VIIIb). Although the benzoyl derivative VIIIa was shown to be stable to *p*-nitrobenzoic acid, the information on hand is insufficient to decide whether the exchange occurred with VII or through a reaction intermediate such as the ion-pair X.



For identification purposes, the nitroso compounds VIII were prepared by an independent method. Iffland[12] recently showed that lead tetraacetate reacts with ketoximes to form the corresponding acetoxy nitroso compounds (VIII, R″ = CH_3). We have found that lead tetrabenzoate can also be used in the synthesis. The reaction of

$$RR'C{=}NOH + Pb(O_2CC_6H_5)_4 \longrightarrow \text{VIII } (R'' = C_6H_5)$$

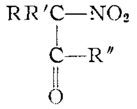
acetoxime with lead tetrabenzoate yielded 2-nitroso-2-benzoyloxypropane (VIIIa) identical in all respects with the compound obtained from the rearrangement of VIIa. 1-Nitroso-1-benzoyloxycyclohexane (VIIId) also was prepared from the corresponding oxime by this method.

Nitronate ions are "ambident"[13] ions and bond formation could occur, *a priori*, either with oxygen or with carbon. In the acylation just discussed, only the O-acylated product was obtained. The C-acylated analog 2-benzoyl-2-nitropropane (IXa) was prepared by the chromic acid oxidation of 1-phenyl-2-nitro-2-methylpropanol. Compared with VIIa and VIIIa, it is a relatively stable compound.

(11) The nitroxylate ion (eq. 3) was identified by the method of Nast (*Z. anorg. u. allgem. Chem.*, **267**, 304 (1952)). Zintle has shown that water reacts rapidly with the nitroxylate ion to form nitrous oxide (*Ber.*, **66**, 760 (1933)). The hydrolysis reaction (eq. 3) is closely related to the Nef reaction (M. F. Hawthorne, THIS JOURNAL, **79**, 2510 (1957)); in effect, the sequence of reactions in eq. 2 and 3 represents an alternate method for carrying out the Nef reaction.

(12) D. Iffland and G. Criner, *Chemistry & Industry*, 176 (1946).

(13) N. Kornblum, R. A. Smiley, R. K. Blackwood and D. C. Iffland, THIS JOURNAL, **77**, 6269 (1955).


$RR'C(NO_2)-C(=O)-R''$

IX

IXa, $R = R' = CH_3$, $R'' = C_6H_5$

Examination of the infrared spectrum of the reaction mixture from benzoyl chloride and sodium 2-propanenitronate (heterogeneous system) indicated that less than 1% of the C-acylated product could have been formed. The reaction of benzoyl chloride with ammonium 2-propanenitronate (homogeneous system) also yielded only the O-acyl derivative.

Experimental[14]

Infrared Cell.—The following assembly was used for the low temperature runs. A 0.1-mm. liquid-type Perkin-Elmer cell was positioned in a brass box fitted with NaCl windows. The cell was clasped by hollow tubes which could be filled with the coolant material from the outside of the box. Usually the cell was cooled with a Dry Ice-ether mixture; about 30 minutes was required for the cell to reach the lowest temperature. The cell was filled by a hypodermic syringe through a rubber disk on the outer box. Although the outer box could be evacuated, we found that operation with a dry atmosphere was satisfactory. A small heater was usually placed under the outer box to keep it and the NaCl windows near room temperature.

Reagents.—The commercially available nitroparaffins, 2-nitropropane and nitrocyclohexane, were purified before use.[15] The sodium nitronates were prepared by the method of Seigle and Hass[16] and the ammonium salt by the method of Watt and Knowles.[17] The benzoyl chloride was distilled at 1 mm. before use. The methylene chloride was refluxed with and distilled from phosphorus pentoxide.

O-Benzoyl-2-*aci*-nitropropane (VIIa).—Sodium propane-2-nitronate (1.11 g., 0.01 mole) was suspended in 15 ml. of dry methylene chloride in a three-neck flask provided with a syringe cap, a mercury-seal stirrer and a dropping funnel protected from the atmosphere by a drying tube. The flask was immersed in a cooling bath and it was held at Dry Ice-acetone temperatures throughout the experiment. A solution of benzoyl chloride (0.70 g., 0.005 mole) in 10 ml. of dry methylene chloride was added dropwise to the stirred mixture. After 24 hours of stirring, a sample was removed through the syringe cap with a pre-cooled hypodermic syringe. The needle was replaced with one bearing a plug of cotton which served to filter the solution. The cold, clear solution (colorless in this case) containing VIIa was then introduced into a low temperature infrared cell. The infrared spectrum at −80° showed prominent bands at 5.71 and 6.09 μ. (Benzoyl chloride under the same conditions has bands at 5.62 and at 5.77 μ.) When this sample was allowed to warm to room temperature, the spectrum gradually changed, becoming identical with that of 2-nitroso-2-benzoyloxypropane (5.75 and 6.37 μ in CH_2Cl_2).

The experiment was repeated except that the reaction flask was provided with a sintered glass filter stick connected by a Tygon tube to another flask which was protected from the atmosphere by a drying tube. After the reaction was complete, the filter stick was lowered into the reaction mixture and its extruding part, the Tygon tube, and the receiving flask were covered with Dry Ice. The reaction mixture was filtered by forcing it through the filter stick under a pressure of dry nitrogen gas. The flask containing the filtrate (very light green in color) was connected through a liquid nitrogen trap to a vacuum pump. The solvent was removed at a vacuum of 1 mm. and a pot temperature of −80° to yield a faintly blue-green solid. Upon warming the product, a deepening of the blue color was observed at −60°. At 35°, the solid softened somewhat, melting to a mobile blue liquid at −30 to −15°.

2-Nitroso-2-benzoyloxypropane (VIIIa). (A).—Sodium propane-2-nitronate (1.0 g., 9.0 mmoles) was suspended in 35 ml. of alcohol-free chloroform (methylene chloride was used in later runs) and the mixture was cooled in an ice-salt-bath. Benzoyl chloride (1.14 g., 8.1 mmoles) dissolved in 15 ml. of alcohol-free chloroform was added with stirring over 0.5 hour. Stirring was continued for an additional three hours at −10°. At this point, an infrared spectrum of the filtered blue solution showed that no benzoyl chloride remained and that the product consisted of a mixture of the nitroso derivative VIIIa (90–95%) and 2-nitropropane (5–10%). No 2-nitro-2-benzoylpropane (IXa) was detected. Since IXa has intense absorption bands at 10.25, 11.25 and 11.85 μ and since VIIIa is transparent at these wave lengths, we estimate that less than 1% of IXa could have been present.

The blue reaction mixture was then washed with 25 ml. of a 2.5 *N* sodium hydroxide solution and with 25 ml. of water; it was dried over anhydrous potassium carbonate. The solvent was removed at the water-pump without heating and the resulting bright blue oil was dried for three hours at 1 mm.; yield 0.96 g. (4.9 mmoles, 61% based on benzoyl chloride), λ_{max} 663 mμ (ϵ 23.7) in CH_2Cl_2 (see Table I). The compound is rather unstable; however, it can be distilled in a molecular still at room temperature. It is decomposed quite rapidly by visible light.

When kept at −45° for several days, the blue oil changed to a crystalline powder which was obtained nearly white by washing with cold pentane. The dimer melted at 61–62.5° when the bath was heated at 2°/min. The m.p. is sensitive to the rate of heating, since monomer is formed at temperatures below the m.p.

Anal. Calcd. for $C_{10}H_{11}O_3N$: C, 62.16; H, 5.74; N, 7.25. Found: C, 62.18; H, 5.81; N, 7.26.

Solutions of the solid in methylene chloride are deep blue in color; the infrared spectrum in this solvent (Table I) does not change when the sample is cooled to −80°.

Similar results were obtained from the benzoylation of the ammonium salt. Ammonium 2-propanenitronate was prepared by the method of Watt and Knowles.[17] A freshly made solution of the salt (3.14 g., 29.6 mmoles) in dry methanol (25 ml.) was diluted with 50 ml. of methylene chloride and the solution was cooled to −50°. A solution of benzoyl chloride (2.81 g., 20 mmoles) in methylene chloride (30 ml.) was added slowly and the solution was allowed to warm to 10°. Ammonium chloride gradually separated and the solution became deep blue in color. After two hours, the solvents were removed at 1 mm. and the remaining solid was extracted with pentane. The solution was washed with a dilute solution of sodium carbonate, then dried; the pentane was removed *in vacuo* leaving a blue oil, the infrared spectrum of which was identical to that of authentic VIIIa.

(B) Method of Iffland and Criner.[12]—Acetoxime (2.7 g., 0.037 mole) was added in small portions over a period of 45 minutes to a stirred suspension of lead tetrabenzoate[18] (28 g., 0.041 mole) in 50 ml. of methylene chloride at 0°. Stirring was continued for 15 minutes and then 10 ml. of water was added. Stirring was continued for an additional 10 minutes, after which the bright blue reaction mixture was filtered. The voluminous white precipitate was washed with 25 ml. of methylene chloride. The filtrate and washes were combined and washed with 25-ml. portions of a 5% sodium bicarbonate solution (until the aqueous layer remained basic to litmus) and with 25 ml. of water. The blue solution was dried over anhydrous potassium carbonate. The solvent was removed at the water-pump without heating and the resulting bright blue oil was dried for 3 hours at 1 mm.; yield 4.91 g. (0.027 mole, 69% based on acetoxime). When stored in the deep-freeze for several days, the blue oil changed to a crystalline powder which could be obtained nearly white by washing with cold pentane; m.p. 61–62.5° (heated at 2°/min.). The infrared spectrum was identical in every respect with that of material obtained by method A.

2-Nitro-2-benzoylpropane (IXa).—A sample of 1-phenyl-2-nitro-methylpropanol[19] was recrystallized from hexane; m.p. 65–67°. A solution of chromic anhydride (3.42 g., 0.034 mole) in a mixture of 10 ml. of water and 20 ml. of acetic acid was added over the course of 0.5 hour to a stirred solution of the purified 1-phenyl-2-nitro-2-methylpropanol (5.0 g., 0.025 mole) in acetic acid. The mixture was cooled

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(14) All m.p.'s are corrected.

(15) The chemical treatments described by C. J. Thompson, H. J. Coleman and R. V. Helm (THIS JOURNAL, **76**, 3445 (1954)) were used. The compounds were then distilled through a small column.

(16) L. W. Seigle and H. B. Hass, *J. Org. Chem.*, **5**, 102 (1940).

(17) G. W. Watt and C. M. Knowles, *ibid.*, **8**, 540 (1943).

(18) C. Hurd and P. Austin, THIS JOURNAL, **53**, 1546 (1931).

(19) Kindly furnished by the Commercial Solvents Corp., Terre Haute, Ind.

in an ice-bath; after two hours the ice-bath was removed and the stirring was continued for an additional 48 hours. The reaction mixture was extracted with ether and the extract was washed with water (until the washes were colorless), with 5% sodium carbonate solution, and finally with water again. The ether solution was dried over anhydrous magnesium sulfate. The solvent was removed under vacuum to yield 4.48 g. of a yellow liquid, n^{25}D 1.5259. The liquid was chromatographed on silica gel. With 5% ether–hexane there was eluted 3.56 g. (0.018 mole, 72%) of a yellow liquid. The infrared spectrum showed strong carbonyl absorption (5.92 μ) and no trace of hydroxyl absorption.

Short path distillation of one of the chromatographic fractions (2.74 g.) gave these fractions:

No.	Wt., g.	n^{22}D
1	0.280	1.5279
2	1.148	1.5282
3	1.074	1.5282
	2.502	

Fraction 2 was analyzed. The infrared spectrum showed $\lambda_{max}^{CHCl_3}$ 5.92 μ (aromatic ketone), 6.47 μ (aliphatic nitro).

Anal. Calcd. for $C_{10}H_{11}O_3N$: C, 62.16; H, 5.74; N, 7.25. Found: C, 62.29; H, 5.75; N, 7.46.

Ammonolysis of O-Benzoyl-2-*aci*-nitropropane.—A solution of VIIa (6.25 mmoles) in 25 ml. of methylene chloride was prepared and filtered as described before. Liquid ammonia, 5 ml., was then condensed in the flask containing the solution and the reaction mixture was kept at −80° for one hour. The reaction mixture was then allowed to warm to room temperature. A white precipitate in a colorless mother liquor was obtained. The mixture was filtered and the precipitate was washed with two 25-ml. portions of dry methylene chloride. The white unstable powder obtained was dried in a vacuum desiccator; yield 0.279 g. (2.7 mmoles, 43%). The infrared spectrum had λ_{max}^{KBr} 3.68 μ (ammonium ion). This spectrum was identical with that of authentic ammonium propane-2-nitronate prepared by the method of Watt and Knowles.[17]

The filtrate and wash liquors were combined and evaporated to dryness. White plates, m.p. 128–130° (lit.[20] 128°) were obtained; yield, 0.556 g. (4.6 mmoles, 74%). The infrared spectrum of this material was identical with that of pure benzamide.

Attempted Ammonolysis of 2-Nitroso-2-benzoyloxypropane.—A deep-blue solution of 2-nitroso-2-benzoyloxypropane (0.48 g., 2.5 mmoles) in 12.5 ml. of dry methylene chloride was placed in a flask calibrated for a volume of 15 ml. The flask was provided with a gas-inlet tube and a drying tube filled with sodium hydroxide pellets. It was immersed in a Dry Ice–acetone-bath. Ammonia, 2.5 ml., was condensed in the flask and the reaction mixture was kept for one hour at −80° before it was allowed to warm to room temperature. The resulting deep-blue solution was washed with an equal volume of water and dried with anhydrous magnesium sulfate. The infrared spectrum of this solution was identical with that of authentic 2-nitroso-2-benzoyloxypropane.

Even when a solution, prepared as above, was saturated with ammonia at room temperature and stored for one hour at room temperature the infrared spectrum of the washed and dried final solution was that of 2-nitroso-2-benzoyloxypropane—no trace of benzamide could be detected.

Saponification of 2-Nitroso-2-benzoyloxypropane.—(A) A solution of 2-nitroso-2-benzoyloxypropane (1.0 g., 5.2 mmoles) in 4.5 ml. of methanol was placed in a flask connected with a gas buret filled with mercury, and 0.5 ml. of a 10 *M* aqueous potassium hydroxide solution was added to the flask. The solution became warm and evolution of a gas began. During 0.75 hour the color of the solution changed from deep-blue, through green, to yellow. At the end of this period the volume of evolved gas had reached a maximum value of 25 ml. at 24.0° and 768 mm. Correcting for the solubility of nitrous oxide in methanol (3.23 vol. N_2O/vol. CH_3OH at 24°[21]), the total volume becomes 41 ml., or 32 ml. at S.T.P. (1.4 moles, 27%). The infrared spectrum of the gas was identical with that of an authentic sample of nitrous oxide. The reaction mixture gave a negative test for the hyponitrite ion ($N_2O_2^{=}$).[22] When the saponification was repeated in an aqueous solution containing $K_2Ni(CN)_4$, a reddish-violet color appeared (a positive test for the nitroxylate ion, NO^-).[11]

(B) A saponification mixture, prepared as in part A, was cooled in an ice-bath and acidified with 10% sulfuric acid; a precipitate formed (benzoic acid). A solution of 2,4-dinitrophenylhydrazine (1.1 g., 5.6 mmoles) in 2.4 ml. of concentrated sulfuric acid and 16 ml. of methanol was added. A copious yellow precipitate formed; all of the material was then poured into a separatory funnel containing ether. The ether was washed with two portions of water, with a saturated sodium bicarbonate solution and finally with water. The ether solution was dried over anhydrous potassium carbonate and evaporated to give 1.19 g. (5 mmoles, 96%) of orange needles. One recrystallization from methanol gave long needles, m.p. 123–124°; the m.p. was undepressed when the sample was mixed with the authentic 2,4-dinitrophenylhydrazone of acetone (m.p. 123–124°).

(C) A saponification mixture, prepared as in part A, was poured into ether and the ether phase was washed with water. The ether was dried with anhydrous potassium carbonate and evaporated to give 0.14 g. (1.1 mmoles, 20%) of a yellow liquid, the infrared spectrum of which was identical with that of authentic methyl benzoate.

The combined alkaline layer and water washes from above were acidified with dilute hydrochloric acid and extracted with ether. The ether solution was dried over sodium sulfate and evaporated to give 0.36 g. (2.9 mmoles, 57%) of needle-like crystals, the infrared spectrum of which was identical with that of authentic benzoic acid.

Rearrangement of O-Benzoyl-2-*aci*-nitropropane in the Presence of *p*-Nitrobenzoic Acid.—A clear, colorless solution of O-benzoyl-2-*aci*-nitropropane (380 mg., 1.8 mmoles) in methylene chloride (9 ml.) at −80° was added to a stirred suspension of *p*-nitrobenzoic acid (637 mg., 1.8 mmoles) in methylene chloride at room temperature. When the reaction mixture was warmed to room temperature the now deep-blue solution was washed with 5 ml. of a 5% sodium hydroxide solution and dried over anhydrous magnesium sulfate. The infrared spectrum indicated a 1:1 ratio of VIIIa to VIIIc. Evaporation of the methylene chloride left a blue powder which, when crystallized from pentane, gave 26 mg. (0.11 mmole, 5.5%) of blue-green plates, m.p. 78.5–79.5° (heated at 2°/min.). The infrared spectrum was identical with that of an authentic sample of 2-(*p*-nitrobenzoyloxy)-2-nitrosopropane (VIIIc).

2-(*p*-Nitrobenzoyloxy)-2-nitrosopropane (VIIIc).—Sodium propane-2-nitronate (2.66 g., 0.022 mole) was suspended in 80 ml. of dry methylene chloride and the mixture was cooled in an ice-bath. Freshly prepared *p*-nitrobenzoyl chloride[23] (3.72 g., 0.020 mole) dissolved in 70 ml. of methylene chloride was added dropwise with stirring. Stirring was continued for an additional 3 hours at ice–salt temperatures. The blue reaction mixture was washed with 75 ml. of a 2.5% sodium hydroxide solution and with 75 ml. of water; it was then dried with anhydrous potassium carbonate. The solvent was removed at the water-pump without heating and the resulting light-blue powder, m.p. 62–68°, was dried for three hours at 1 mm. to yield 3.38 g. of VIIIc (0.014 mole, 71%). Sublimation at 0.1 mm. (bath temp. 70°) raised the melting point of the light-blue powder to 76–78° (heated at 2°/min.), unchanged by further sublimation. The infrared spectrum in $CHCl_3$ had bands at 5.78 (ester carbonyl), 6.35 (monomeric aliphatic nitroso) and 6.54 μ (aromatic nitro).

Anal. Calcd. for $C_{10}H_{10}N_2O_5$: C, 50.42; H, 4.23; N, 11.76. Found: C, 50.42; H, 4.43; N, 11.58.

Attempted Exchange of *p*-Nitrobenzoic Acid with 2-Nitroso-2-benzoyloxypropane.—A solution of 2-nitroso-2-benzoyloxypropane (0.309 g., 1.6 mmoles) in 50 ml. of methylene chloride was added to a suspension of *p*-nitrobenzoic acid (1.34 g., 8 mmoles) in 300 ml. of methylene chloride. The solution was stirred for one hour, then washed with 5% sodium hydroxide and dried over anhydrous mag-

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nesium sulfate. The methylene chloride was removed at the water-pump without heating. The infrared spectrum of the blue liquid obtained was that of 2-nitroso-2-benzoyloxypropane. No trace of the aromatic nitro absorption of VIIIc was evident.

1-Nitroso-1-benzoyloxycyclohexane (VIIId). (A).—Sodium cyclohexanenitronate (20 g., 0.132 mole) was suspended in 200 ml. of dry methylene chloride and the mixture was cooled in an ice-salt-bath. Benzoyl chloride (16 g., 0.111 mole) dissolved in 50 ml. of methylene chloride was added to the stirred suspension during 0.5 hour. Stirring was continued for an additional three hours at −10°. The green reaction mixture was washed with water, with 5% sodium hydroxide and with water again, and then dried over anhydrous potassium carbonate. The solvent was removed at the water pump without heating to yield 20.8 g. of a green oil (0.076 mole, 68% based on benzoyl chloride). No solid material was deposited when the green oil was stored in the deep freeze. The infrared spectrum in methylene chloride had bands at 5.80 (ester carbonyl) and 6.39 μ (aliphatic monomeric nitroso). During short path distillation (0.25 mm., bath temperature 70°) extensive decomposition occurred, but a small amount of a mobile bright blue oil was obtained, $n^{26}\text{D}$ 1.5250, λ_{max} 667 (ϵ 23.8) in CH_2Cl_2.

Anal. Calcd. for $C_{13}H_{15}O_3N$: C, 66.93; H, 6.48; N, 6.01. Found: C, 66.88; H, 6.64; N, 5.78.

(B) **Method of Iffland and Criner.**[12]—Lead tetrabenzoate[21] (25 g., 0.036 mole) was suspended in 100 ml. of methylene chloride and the mixture was cooled in an ice-bath. Cyclohexanone oxime (3.68 g., 0.033 mole) was added in small portions to the stirred suspension over a period of 45 minutes. Stirring was continued for 15 minutes and then 10 ml. of water was added to the green suspension. Stirring was continued for an additional ten minutes, during which time the green reaction mixture turned blue and a white precipitate was washed with 25 ml. of methylene chloride. The filtrate and washes were combined and washed with 25-ml. portions of a 5% sodium bicarbonate solution (until the aqueous phase remained basic to litmus) and then with 25 ml. of water. The bright blue solution was dried over anhydrous potassium carbonate. The solvent was removed at the water-pump without heating to give 6.6 g. (0.028 mole, 86% based on cyclohexanone oxime) of a bright blue liquid. Its infrared spectrum was identical in every respect with that obtained by method A.

α-Phenylnitroethane. Modification of the Method of Kornblum.[24]—α-Phenylethyl bromide (111 g., 0.595 mole) was added to a solution of urea (80 g., 1.33 moles), phloroglucinol (80 g., 0.64 moles) and sodium nitrite (72 g., 1.04 moles) in 1.2 l. of dimethylformamide. The reaction mixture was stirred at room temperature for 45 hours and then poured into 3 l. of ice-water. The water solution was extracted with five 200-ml. portions of pentane. The extracts were combined, washed with five 150-ml. portions of water and dried over anhydrous magnesium sulfate. Evaporation of the pentane gave 32 g. of a red liquid, the infrared spectrum of which showed the presence of a considerable amount of a carbonyl containing material (5.90 μ). To remove the carbonyl impurity, a Girard[25] separation was employed. The non-ketonic fraction from the Girard separation was distilled through a Vigreux column. The following fractions were obtained (colorless liquids):

Fraction	Wt., g.	B.p. °C.	Mm.	$n^{25}\text{D}$
1	4.95	68-78	0.65	1.5189
2	11.1	78-80	.65	1.5202
3	8.06	80	.65	1.5208

α-Phenylnitroethane has reported boiling points of 92° (2 mm.)[26] and 135° (25 mm.).[27] The literature values for the index of refraction are: $n^{20}\text{D}$ 1.5215[31] and $n^{25}\text{D}$ 1.5212.[27]

Fraction 1 was contaminated with carbonyl-containing substances as shown by the infrared spectrum (5.90 μ). Fraction 2 and 3 weighed 19.16 g. (0.127 mole, 21%). The infrared spectrum showed: $\lambda_{max}^{CHCl_3}$ 6.45 μ (aliphatic nitro), no peak was observed at 5.90 μ.

Benzoylation of Sodium α-Phenylethanenitronate.—Benzoyl chloride and sodium α-phenylethanenitronate were allowed to react at −80° as previously described for compound VIIa. The low temperature infrared spectrum of VIIb in methylene chloride had bands at 5.68 and 6.21 μ. Upon warming to room temperature, the spectrum changed to that of 1,1,1-benzoyloxynitrosophenylethane (VIIIb) with bands at 5.77 and 6.36 μ. In addition, a band appeared at 5.94 μ (probably acetophenone).

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Many-membered Carbon Rings. XVI. Acetolysis of 5,5-Dimethylcyclononanol Tosylate[1,2]

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RECEIVED SEPTEMBER 17, 1957

Acetolysis of 5,5-dimethylcyclononanol tosylate has been studied with the objective of ascertaining the role of annular methyl groups in medium size ring reactions. The rate of acetolysis at 35° was about half that observed for cyclononyl tosylate. Analysis of the acetolysis products indicated that transannular migration of methyl groups occurs to the extent of less than 5%, if at all.

Although a number of transannular hydride migrations have been observed in reactions of medium size rings,[3] there have been no reported instances of shifts of alkyl or aryl groups across such rings. It was of interest, therefore, to seek evidence for such phenomena. The first effort to discern the role of annular alkyl groups in medium size ring reactions has been a study of the acetolysis of 5,5-dimethylcyclononanol tosylate (I) under Winstein's "limiting conditions."[4] Some of the possible transformations that might be expected to occur in the acetolysis of I are indicated in the dia-

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[1] This study was supported by the National Science Foundation, Grant NSF-G2022.

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