[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Michael Type Additions with Secondary Nitro Olefins Prepared In Situ¹

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Michael type additions of primary or secondary nitro paraffins, gem-dinitro paraffins and nitramines are successfully carried out with secondary nitro olefins generated *in situ*. The nitro olefins form readily from the corresponding 2-nitroalkyl acetates, in the presence of sodium acetate or the salt of the nitro compound in hydroxylic and non-hydroxylic media.

Although Michael type additions of primary or secondary nitro paraffins to low molecular weight nitro olefins are well known,² the scope of the reaction has remained limited because of the difficulty involved in the preparation of the olefins. Sodium or potassium bicarbonate or carbonate, as well as sodium acetate has been widely used in the Schmidt and Rutz reaction for dehydroacetylating nitroalkyl acetates to nitro olefins.³ Gold⁴ converted nitroalkyl acetates and nitroalkyl chlorides to the corresponding nitro olefins by catalytic cleavage in the vapor phase and Buckley and Scaife⁵ decomposed β -nitroalcohols directly to nitro olefins in the presence of phthalic anhydride. In all these methods the olefin is removed from the reaction medium by distillation. The elevated temperatures are generally detrimental to the olefin, particularly in the case of long chain nitro olefins with high boiling points. A possible way of avoiding this difficulty is to produce the nitro olefin in situ at approximately room temperature while carrying out the Michael type addition. Thus, Fraser and Kon⁶ and Hass and Bourland⁷ prepared nitro olefins by the decomposition of the corresponding nitro alcohols in the presence of amines, while Snyder and Hamlin⁸ employed the degradation of the Mannich product derived from the reaction of primary nitro paraffins, formaldehyde and a secondary amine, to produce nitro olefins in situ for the preparation of polynitro paraffins. These methods though, were no real improvement over preparing the nitro olefins separately, since high reaction temperatures were employed. Other methods described in the literature for the preparation of nitro olefins in situ in Michael type additions with anions other than nitronate ions, involved the decomposition of 2-nitroalkyl nitrates^{9a} and 2-nitroalkyl acetates.^{9b} The latter authors employed high temperatures to obtain the olefins. Recently, Gold et al.,¹⁰ established that 2-nitroalkyl acetates would react with alkaline sulfite solutions at room temperature in a double decomposition reaction to give the corresponding nitroalkyl sulfonates.

Because of the ease of their preparation from the corresponding nitro alcohols and their stability, 2-nitroalkyl acetates appeared to be the most promising precursor for the preparation of nitro olefins *in situ*, provided that the elimination of acetate ion would occur at mild temperatures. It has now been found that 2-nitroalkyl acetates react readily with sodium acetate or the sodium salt of the nitro paraffin at approximately room temperature or slightly higher temperatures in hydroxylic and nonhydroxylic solvents to afford the olefin *in situ*, which then undergoes the Michael addition.

In hydroxylic solvents, such as aqueous methanol or t-butyl alcohol, two methods were adapted for carrying out the reactions. The first involved the reaction of equivalent amounts of the salt of the nitro paraffin, 2-nitroalkyl acetate and sodium acetate. Under these conditions the pH of the reaction mixture began at nine and fell within fifteen minutes to approximately seven. The alternate method employed two equivalents of the

^{(1) (}a) From the Ph.D. thesis of Robert Miller, Purdue University, 1958; (b) presented before the Division of Organic Chemistry at the Symposium on Nitro Paraffins at the Atlantic City Meeting of the American Chemical Society, September 1959; (c) the application of our method to primary nitro olefins is currently under investigation and will be the subject of a forthcoming publication.

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⁽⁷⁾ H. B. Hass and J. F. Bourland (to Purdue Research Foundation), U. S. Patent 2,343,256 (March 7, 1944).

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Pseudo Acid	Product ^o	Yield, %	M.P.	B.P.	n ²⁰ _D	
2-Nitropropane	itropropane 2-Methyl-2,4-dinitrohexane ^{8,11}		<u> </u>	77 (0.75 mm.)	1.4530	
1-Nitropropane	3,5-Dinitroheptane ^{8,11}	15, ^a 13, ^b 19 ^{a,d}	33-34	82-86 (0.7 mm.)		
1.1-Dinitroethane	2.2.4-Trinitrohexane	65 ^a	29-29.5	90-92(0.2 mm.)	1.4667	
2-Nitro-1,3-propane- diol	2-Hydroxy-2,4-dinitro-1- hexanol	27 ^a	101-102	` `		
Ethylene dinitramine	5,8-Diaza-3,5,8,10-tetranitro- dodecane	81 ^a	131-132 100-101			
2-Hydro-6-hydroxy-3- pyridazinone	6-Hydroxy-(2H)2-(2-nitro- butyl)-3-pyridazinone	74 ^a	152-153	_		
Diethyl malonate	Ethyl 2-carbethoxy-4-nitro- hexanoate ¹²	52 ^{b,e}	—	101 (0.17 mm.)	1.4403	
Methanol	1-Methoxy-2-nitrobutane	34 ⁴		61 (4.6 mm.)	1.4203	
	Michael Additions wi	th 3-Nitro-2-buty	l Acetate			
2-Nitropropane	2,3-Dimethyl-2,4-dinitro- pentane ¹³	33, ^{b,d} 25, ^{a,f} 57, ^{b,f} 71, ^{c,f} 48 ^b		80 (0.5 mm.)	1.4650	
Ethylene dinitramine	4,7-Diaza-3,8-dimethyl-2,4,7,9- tetranitrodecane	21	124.5-125.5	-		

TABLE I MICHAEL ADDITIONS WITH 2-NITROBUTYL ACETATE

^a Equivalent amounts of reactants and sodium acetate. ^b 100% excess of the salt of the pseudo acid (no sodium acetate). ^c 200% excess of the salt of the pseudo acid (no sodium acetate). ^d The solvent was anhydrous tetrahydrofuran. ^e The solvent was absolute ethanol. ^f The solvent was aqueous *t*-butyl alcohol. ^e Reactions carried out in aqueous methanol unless otherwise specified. ^h The free pseudo acid and sodium acetate were employed. ^f Diastereoisomers.

TABLE II

MICHAEL ADDITIONS WITH 4-ACETOXY-2-BUTANONE

		Yield.			
Pseudo Acid	$Product^{b}$	%	M .P.	B.P.	n_{D}^{20}
2-Nitropropane	5-Methyl-5-nitro-2- hexanone ¹⁴	92 ^a		88-91 (2.0 mm.)	1.4450
1-Nitropropane	5-Nitro-2-heptanone	72^a		102 (4.8 mm.)	1.4410
	Michael Additions with	h 1,6-Diac	etoxy-2,5-dinitrohe	хале	
2-Nitropropane	2,9-Dimethyl-2,4,7,9- tetranitrodecane	98ª	193-194		
1,1-Dinitropropane	3,3,5,8,10,10-Hexanitro- dodecane	94ª	161–163° 158–159	_	—
1-Nitroamino- butane	5,12-Diaza-5,7,10,12- tetranitrohexadecane	88ª	139–140 dec.	—	

^a Equivalent amounts of reactants and sodium acetate. ^b Reactions carried out in aqueous methanol unless otherwise specified. ^c Diastereoisomers.

salt of the nitro paraffin to one of the 2-nitroalkyl acetate and no sodium acetate. The pH of this reaction started at approximately nine and only fell approximately one-half of a unit through the duration of the reaction. The first procedure afforded the product as the free nitro compound while the second gave the product in the form of its salt. The reactions were generally carried out in a temperature range of $30-40^\circ$ for fifteen to twenty hours. In nonhydroxylic solvents the reactions were performed analogously to the two methods employed in hydroxylic solvents. These reactions were carried out in anhydrous tetrahydrofuran, employing a temperature range of 35-45° for twentyfour to forty-eight hours. Generally, it was found that the reactions proceeded faster in hydroxylic than in nonhydroxylic solvents.

The utility of employing 2-nitroalkyl acetates directly in Michael type additions with pseudo acids was determined in a number of experiments. These results are compiled in Tables I and II.

Reactions of 2-nitrobutyl acetate. As is apparent from Table I, 2-nitrobutyl acetate gave high yields with such pseudo acids as secondary nitro paraffins, gem-dinitro paraffins and nitramines. In hydroxylic solvents, 1-nitropropane gave only a small amount of product. Distillation of the reaction

⁽¹¹⁾ C. T. Bahner and H. T. Kite, J. Am. Chem. Soc., 71, 3597 (1949).

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⁽¹³⁾ A. Lambert and H. A. Piggott, J. Chem. Soc., 1489 (1947).

⁽¹⁴⁾ H. Shechter, D. E. Ley, and L. Zeldin, J. Am. Chem. Soc., 74, 3664 (1952).

mixture afforded a large forerun as well as a sizable amount of undistillable higher molecular weight material. The infrared spectrum of the forerun indicated that it consisted of several compounds. Besides the expected absorption bands for the nitro group, maxima at 3.05μ (OH), 5.83μ (C = O) and 6.25μ (C = N) were present. These bands may be due to oxime and carbonyl containing materials. It should be noted that the assignment of the absorption band at 6.25μ to the C = N vibration of the oxime is questionable since Bellamy¹⁵ reports the absorption band for C = N in the range of $5.9-6.1\mu$, while Smith, *et. al.*¹⁶ have indicated a range of $6-6.3\mu$.

When sodium 1-propanenitronate, 2-nitrobutyl acetate and sodium acetate were allowed to react in anhydrous tetrahydrofuran, the expected product was obtained in somewhat higher yields, and the amount of forerun was reduced markedly.

The addition of a 2-nitroalkyl alcohol to a nitro olefin has never been reported in the literature. It is well established that nitro alcohols demethylolate readily in the presence of base, which is the catalyst in Michael additions. Since the pH of the acetate elimination reactions fell readily from nine to seven, it was believed that the reaction of a nitro alcohol with a nitro olefin would proceed with some success. When the sodium salt of 2nitro-1,3-propanediol (prepared by demethylolating trishydroxymethylnitromethane in a mixture of ether and methanol with sodium methoxide) was treated with equivalent amounts of 2-nitrobutyl acetate and sodium acetate in aqueous methanol, the expected product, 2-hydroxymethyl-2,4dinitro-1-hexanol, was isolated in a 27% yield.

$$\begin{bmatrix} HO-CH_2 \\ NO_2=C \\ HO-CH_2 \end{bmatrix}^{-} Na^{+} + CH_3-CH_2-C-CH_2-OAc \longrightarrow H \\ HO-CH_2 \end{bmatrix} \xrightarrow{-} Na^{+} + CH_3-CH_2-C-CH_2-CH_2-CH_2 \longrightarrow H \\ NO_2 \longrightarrow C-CH_2-C-CH_2-C-C_2H_5 \\ CH_2OH H \end{bmatrix}$$

The importance of the drop in pH is indicated by the fact that only an intractable oil was obtained when two equivalents of sodium 2-nitro-1,3propanediol and one equivalent of 2-nitrobutyl acetate were employed.

Reactions of 3-nitro-2-butyl acetate. The reactions of 3-nitro-2-butyl acetate with secondary nitro paraffins and nitramines were found to be much slower than with 2-nitrobutyl acetate, and the yields were usually lower.

The reaction of sodium 2-propanenitronate with 3-nitro-2-butyl acetate in methanol, afforded besides the expected product, a large amount of the methyl ether of 3-nitro-2-butanol. This compound resulted from the reaction of the solvent (methoxide ion) with the olefin, 2-nitro-2-butene. In an attempt to increase the yield of the desired Michael addition product, the reactions were carried out with tbutyl alcohol as the solvent, because it was believed that by increasing the steric requirements of the solvent, ether formation could be kept to a minimum. In this way the yield of product was increased by approximately 10% and practically no ether formation occurred. However, some unchanged 2-nitro-2-butene was obtained.

Reactions of 1,6-diacetoxy-2,5-dinitrohexane. 1,6-Diacetoxy-2,5-dinitrohexane reacted readily with secondary nitro paraffins, gem-dinitro paraffins and primary nitramines. Occasionally it was observed that the olefin produced in situ, 2,5dinitro-1,5-hexadiene, polymerized. This difficulty could be minimized by first carrying out the reaction at room temperature (25°) or lower for several hours and then increasing the temperature to 35-40° to bring the reaction to completion.

As in the case of 2-nitrobutyl acetate, 1-propanenitronate reacted with 1,6-diacetoxy-2,5dinitrohexane to afford a complex mixture, but in this instance, the expected product could not be separated from the byproducts.

Reactions of 4-acetoxy-2-butanone. 4-Acetoxy-2butanone reacted readily with pseudo acids to afford products derived from methyl vinyl ketone. This precursor of methyl vinyl ketone was found to be quite stable toward polymerization and could be stored readily at room temperature.

DISCUSSION

The observations and results of the reactions which were carried out in hydroxylic solvents, suggest the following reaction path:

$$[R'R-C=NO_{2}]^{-}Na^{+} + R''OH \underset{B}{\overset{A}{\underset{B}{\underset{B}{\xrightarrow{}}}}} R'R-CHNO_{2} + NaOR'' (1)$$

$$\begin{array}{c} \mathcal{C}-\mathcal{C}H_{2}OAc + NaOR'' \xrightarrow{F}_{B} \\ H \\ NO_{2} \\ R'''-\mathcal{C}=\mathcal{C}H_{2} + NaOAc + R''OH \quad (2) \\ NO_{2} \end{array}$$

$$\begin{bmatrix} \mathbf{R}'\mathbf{R} - \mathbf{C} = \mathbf{NO}_2 \end{bmatrix}^{-\mathbf{Na}^+} + \mathbf{R}''' - \mathbf{C} = \mathbf{CH}_2 \xrightarrow{\mathbf{A}}_{\mathbf{B}} \\ \begin{bmatrix} \mathbf{NO}_2 & \mathbf{NO}_2 \\ \mathbf{R}'\mathbf{R} - \mathbf{C} - \mathbf{CH}_2 - \mathbf{C} - \mathbf{R}''' \end{bmatrix}^{-1}_{\mathbf{Na}}$$
(3)

$$\begin{bmatrix} NO_2 & NO_2 \\ \vdots & \vdots \\ R'R-C-CH_2-C-R''' \end{bmatrix} \begin{bmatrix} Na^+ + R''OH \\ A \\ B \\ NO_2 \\ R'R-C-CH_2-C-R''' \\ H \\ H \\ \end{bmatrix} \begin{bmatrix} NO_2 \\ NO_2 \\ NO_2 \\ R''R-C-R''' \\ H \\ \end{bmatrix}$$
(4)

 ⁽¹⁵⁾ L. J. Bellamy, The Infrared Spectra of Complex Molecules, John Wiley and Sons, New York, 1954, p. 277.
 (16) D. C. Smith C. Y. Fan, and J. B. Nielsen, J. Chem.

⁽¹⁶⁾ D. C. Smith, C. Y. Fan, and J. R. Nielsen, J. Chem. Phys., 18, 707 (1950).

$$\begin{bmatrix} NO_2 & NO_2 \\ H & H & H \\ R'R-C-CH_2-C-R''' \end{bmatrix}^{-} \begin{array}{c} NO_2 \\ Na^+ + R'''-C=CH_2 \\ Higher mol. wt. products (5) \\ R, R' and R''' are H, alkyl or aryl \\ R' is alkyl \end{bmatrix}$$

...

In step (1), alkoxide ions form by the alcoholysis of the salt of the nitroparaffin. It should be noted that alkoxide ions could also form by alcoholysis of sodium acetate as evidenced by the fact that a 30-40% yield of 1-methoxy-2-nitrobutane was

$$\begin{array}{c} \operatorname{NO}_{2} \\ C_{2}H_{4} \longrightarrow C \longrightarrow CH_{2} \longrightarrow OAc + CH_{3}OH \xrightarrow{\operatorname{NaOAc}} \\ H \\ H \\ CH_{3} \longrightarrow O \longrightarrow CH_{2} \longrightarrow CH_{2}$$

obtained when 2-nitrobutyl acetate, sodium acetate and methanol were allowed to react at 40° . Although the equilibrium of step 1 of the proposed mechanism lies far to the left, the elimination of acetate ion from the 2-nitroalkyl acetate in the presence of alkoxide ion in step 2 shifts the equilibrium of step 1 to the right. Step 3 shows the addition of the anion to the olefin. The forward steps 1A and 4A explain the drop of the pH at the beginning of the reaction and the isolation of the Michael adduct as the free nitro compound. It is quite possible that the acidification of the salt of the product in step 4 is aided by the direct reaction with the free nitro paraffin produced in step 1A. However, this reaction would probably be comparatively unimportant because of the relatively large amount of solvent available for the protonation.

The marked drop in pH of the reaction mixture at the beginning of the reaction, indicates that the formation of the nitro olefin from the 2-nitroalkyl acetate is probably quite fast. This would indicate that some free nitro paraffin forms rapidly in step 1 while the alkoxide ion is utilized in step 2. Indeed the free nitro paraffin was isolated from those reactions in which step 3 was very slow as in the case of the 3-nitro-2-butyl acetate (vide supra). Step 5 offers a possible explanation for the fact that sometimes higher molecular weight compounds are obtained as undesirable byproducts. The free nitro paraffins which are produced in steps 1A and 4A compete for the available base. It is evident from the mechanism that if the starting nitro paraffin converts to the salt more readily than the expected Michael product (reaction 1B > 4B), the latter will form in high yields. However, if the desired Michael product forms the salt more readily (reaction 4B > 1B), it will react further with the nitro olefin forming high molecular weight materials which are difficult to isolate and to purify. In order to test whether there exists an

empirical correlation between the yields of product and the structural relationship of the starting nitro paraffin with that of the product, several reactions were carried out in aqueous methanol, employing equivalent amounts of the sodium salt of the nitro paraffin, 2-nitroalkyl acetate or 3acetoxy-2-butanone (precursor of methyl vinyl ketone) and sodium acetate. This correlation cannot be considered if the reaction is incomplete or if side reactions occur which are in competition with the Michael addition in steps 3 and 5 of the proposed mechanism. The results of these reactions are enumerated in Table III; they appear to indicate that several factors determine the yield of the desired Michael product.

(a) Number of reaction centers. The compound (i.e. the starting nitro paraffin or the expected Michael adduct) with the greater number of positions for salt formation will probably have the greater tendency to form the anion, provided of course that the other factors are approximately equal. Experiment 1 (Table III) demonstrates the yield when all the factors in both the starting nitro paraffin and product are approximately equal. In experiment 2 the number of reaction centers in the product is greater than in the starting nitro paraffin and as expected, the yield is lower than in experiment 1. It should be noted that experiment 2 gave besides higher molecular weight materials, a forerun (vide supra). Although it is difficult to evaluate experiment 2 in the light of the side reactions, the low yield obtained in nonhydroxylic solvents where very little forerun was obtained appears to justify factor (a).

(b) Number of active hydrogen atoms. The compound with the larger number of ionizable hydrogen atoms will form the salt faster. Maron and La Mer¹⁷ have reported that the rate of salt formation of the lower nitro paraffins decreases in the order of nitromethane>1-nitropropane>2-nitropropane. Experiment 3 in Table III demonstrates the approximate yield when the number of active hydrogens in the expected product and the starting nitro paraffin are different. The faster rate of salt formation in the primary nitro paraffin leads to high yields of the desired product. The yields in this case are notably higher than in experiment 1 where the factors are approximately equal.

In experiment 4 the yield is very high because there is no competition for the available base. The nitro group of the product is tertiary and the carbonyl group does not activate the α -hydrogens sufficiently to compete with the secondary nitro group of the starting pseudo acid.

(c) Importance of relative acidities. Although the pKa values listed in Table III are based on work carried out in aqueous systems, the trend will remain approximately the same in aqueous methanol.

⁽¹⁷⁾ S. H. Maron and V. K. La Mer, J. Am. Chem. Soc., 60, 2588 (1938).

	' pKa of	Prod- uct	œ	œ	80	١	%	×	ø	and on work
fins Prepared In Súu	Approximate	Pseudo Acid	8(7.8)	9 (8.9)	9(8.9)	8(7.8)	5.5	5.5(5.6)	œ	itro nereffine h
	Number of Active Hydrogens	Pseudo Prod- Acid uct	1 1	6	2	1 0	3	61	6	meavimete nKe of n
	Number of Re- action Centers	Pseudo Prod- Acid uct	1	1 2	1 1	1 0	5	5	5	linituchamona d Ar
I NITRO OLI		Yield, %	55	15	72-78	92	65	94	86	Antonia O E d
FACTORS INFLUENCING YIELD IN A MICHAEL ADDITION WI		Product	CH ₃ NO ₃ NO ₂ -C-CH ₂ -C-C ₃ H ₅	$\begin{array}{ccc} \mathrm{CH_3} & \mathrm{\dot{H}} \\ \mathrm{NO_2} & \mathrm{NO_2} \\ \mathrm{C_2H_3-C-CH_2-C-C_2H_3} \\ \mathrm{\dot{H}} & \mathrm{\dot{H}} \end{array}$	$\begin{array}{ccc} NO_2 & & O \\ C_2H_6 - CH_7 - CH_7 - CH_7 - CH_4 \\ H \end{array}$	CH, O NOI-C-CHI-CHI-CHI	$\begin{array}{cccc} NO_2 & NO_3 \\ H_3C-C-CH_2-C-R_2-C_3H_6 \\ H_3C-C-CH_2-C-R_3-R_6 \\ H_3C-R_3-R_6 \\ H_3C-R_6 \\ H$	$\begin{array}{cccccccc} \mathbf{n}0_{2} & \mathbf{n}0_{2} & \mathbf{N}0_{2} & \mathbf{N}0_{2} & \mathbf{N}0_{2} \\ \mathbf{n}0_{2} & \mathbf{H}_{1} - \mathbf{C} - \mathbf{C}\mathbf{H}_{1} - \mathbf{C} - \mathbf{C}\mathbf{H}_{2} \\ \mathbf{n}0_{2} & \mathbf{H} & \mathbf{H} & \mathbf{N}0_{1} \end{array}$	CH ₁ NO ₁ NO ₂ CH ₁ NO ₂ C-CH ₂ C-(CH ₁), CH ₂ CH ₂ CH ₁ CH ₁ H H CH ₂ CH ₄	
		Pseudo Acid	CH1 H-C-N0ga	CH₄ CH₂—CH₂—CH₂—NO₂ª	CH ₃ CH ₂ CH ₂ NO ₂ ^b	CH4 H-CN02 ^b CH4	NO ₂ H ₃ C-CH ²	NO2 NO2 CH2-CH2 NO2	CH ₄ H-C-NO ² CH ₄	
		Expt.	-	7	ę	4	сı	Q	4	

TABLE III

NITRO OLEFINS PREPARED In Silv. A no 2 N. 5 f

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d d c ^a Reacted with 2-nitrobutyl acetate. ^b Reacted with 4-acetoxy-2-butanone. ^c Reacted with 1,6-diacetoxy-2,5-by G. W. Wheland and J. Farr¹⁹ and H. Shechter, Ohio State University, Private Communication. gem-Dinitro paraffins¹⁸ have a much lower pKa than mononitro compounds¹⁹ and therefore undergo salt formation more readily. This is in agreement with the findings of Pearson and Dillon,²⁰ which indicate that gem-dinitro paraffins have a faster rate of ionization in water than mononitro paraffins. Relative acidities become important only when they exceed at least one pKa unit. This is demonstrated by the fact that, although 2-nitropropane is more acidic than 1-nitropropane, the rate of salt formation for the latter is faster by a factor of approximately fourteen.¹⁷

Experiment 5 then demonstrates the effect of relative acidities. As predicted, the yield of product was higher than in experiment 1, although on the basis of relative number of reaction centers and number of active hydrogens the yield should have been the same. It should be noted that the acidity of the product of experiment 5 would be slightly higher than that of a simple secondary nitro paraffin, because of the inductive effect of the gemdinitro group, which is located in the β -position.

(d) Solubility factor. If the product of the Michael addition is insoluble in the reaction solvent it will form in high yields because it will not compete with the starting pseudo acid for the available base. Experiments 6 and 7 demonstrate the high yields obtained due to the low solubility of the expected product, even though from consideration of the other factors, such as number of ionizable hydrogen atoms or number of reaction centers, lower yields would have been anticipated. That the low solubility of the Michael product might be responsible for a decrease of its reactivity was established in an experiment in which 3,3,5,8,10,10hexanitrododecane was heated to 35° in 50% aqueous methanol with excess sodium hydroxide for three days. Approximately 30% of the unreacted starting material was reclaimed. Thus even under these vigorous conditions only 70% of the material was converted to its salt.

The proposed mechanism further indicates that an excess of the salt of the pseudo acid in the reaction would favor step 3A over 5 in the mechanism, and the desired Michael product should form in higher yields. This generally has been found to be the case as illustrated in Table I. Only when two equivalents of sodium 1-propanenitronate and one equivalent of 2-nitrobutyl acetate were allowed to react was there no increase in the amount of expected product. Instead, as in the reaction of equimolar amounts of sodium 1-propanenitronate, 2-nitrobutyl acetate and sodium acetate, a large amount of by-product formation was observed (vide supra). The reaction path proposed for the reactions carried out in nonhydroxylic solvents is very similar to the one presented in hydroxylic solvents. The main difference lies in step 1 in which the salt of

$$R'R-CHNO_2 + NaOAc \stackrel{A}{\underset{B}{\longrightarrow}}$$

 $[R'R-C=NO_2]^-Na^+ + HOAc^-(2)$

$$\begin{bmatrix} \mathbf{R}'\mathbf{R} - \mathbf{C} = \mathbf{NO}_2 \end{bmatrix}^{-\mathbf{Na}^+} + \mathbf{R}'' - \mathbf{C} = \mathbf{CH}_2 \xrightarrow{\mathbf{A}}_{\mathbf{B}} \\ \begin{bmatrix} \mathbf{NO}_2 & \mathbf{NO}_2 \\ \vdots & \vdots \\ \mathbf{R}'\mathbf{R} - \mathbf{C} - \mathbf{CH}_2 - \mathbf{C} - \mathbf{R}'' \end{bmatrix}^{-1}_{\mathbf{Na}^+} (3)$$

$$\begin{bmatrix} NO_2 & NO_2 \\ R'R - C - CH_2 - C - R' \end{bmatrix}^{-1} Na^{+} + HOAc \xrightarrow{A}_{B}$$

$$NO_2 & NO_2$$

$$R'R - C - CH_2 - C - R' + NaOAc \quad (4)$$

$$H$$

$$\begin{bmatrix} NO_2 & NO_2 \\ I & I \\ R'R - C - CH_2 - C - R'' \end{bmatrix}^{-} Na^{+} + NO_2$$

$$R'' - C - CH_2 - H_2 - H_2 H_2 H_2 H_2 H_2 H_2 (5)$$

the nitro paraffin reacts directly with the 2nitroalkyl acetate (1A) to yield the nitro olefin. Furthermore the regeneration of the salt of the starting material (2A) and of the product (4B)occurs by the reaction with sodium acetate. As in hydroxylic solvents, step 5 accounts for the formation of higher molecular weight materials. In contrast to the reactions in hydroxylic solvents, the yield of product did not increase substantially when two equivalents of the nitronate salt to one of the 2-nitroalkyl acetate were employed. Presumably this was due to the insolubility of the extra equivalent of salt in the nonhydroxylic medium, thereby having very little effect on the reaction which occurred in solution.

Limitations of the reaction. The reaction of 2,4dinitrophenylnitramine with 2-nitrobutyl acetate in aqueous methanol in the presence of sodium acetate was unsuccessful. The 2,4-dinitrophenylnitramine was reclaimed quantitatively, while the nitro olefin produced *in situ* reacted with the solvent (*i.e.* methoxide ion) to afford the methyl ether of 2-nitro-1-butanol. It is thought that 2,4-dinitrophenylnitramine did not react because of the much greater stability of the anion of 2,4-dinitrophenylnitramine (I) over that of the expected product (II).

⁽¹⁸⁾ H. Shechter, Ohio State University, Private Communication.

⁽¹⁹⁾ G. W. Wheland and J. Farr, J. Am. Chem. Soc., 65, 1433 (1943).

⁽²⁰⁾ R. G. Pearson and R. L. Dillon, J. Am. Chem: Soc., 75, 2441 (1953).



Ingold²¹ has pointed out that the Michael addition will be reversed if the starting anion is much more stable than the anion of the product. Indeed, 3-(2,4-dinitrophenylnitramino)-2-propanone, which was obtained by treating 2,4-dinitrophenyl-nitramine with methyl vinyl ketone in the presence of a *catalytic* amount of base, was cleaved at room temperature to the starting materials upon the addition of aqueous sodium hydroxide.

A close analogy to these reverse Michael additions are the following acetate elimination reactions.

$$CH_{3}-CH_{2}-CH_{2}-CH_{2}-OAc \xrightarrow{RO^{-}}_{H}$$

$$H$$

$$NO_{2}$$

$$CH_{3}-CH_{2}-CH_{2}-CH_{2}+ -OAc + ROH$$

$$CH_{3} \xrightarrow{-C} -CH_{2} \xrightarrow{-CH_{2}} -OAc \xrightarrow{RO^{-}} O$$

$$CH_{3} \xrightarrow{-C} -CH \xrightarrow{-CH_{2}} + -OAc + ROH$$

In these examples, the anions of the ket ester and nitro ester are unstable with respect to the acetate ion, and they are converted to the corresponding olefins and sodium acetate, in the presence of alkoxide ions. The acidity of a compound is a measure of the stability of its corresponding anion. Since the acidity of 2,4-dinitrophenylnitramine (pKa 2.7) 's greater than acetic acid, it is probable that the product formed from 2,4-dinitrophenylnitramine under the conditions of the acetate elimination would be at least as unstable as the 2-nitroalkyl acetate and therefore could not be expected to form.

It may be stated then, that the acetate elimination reaction will not succeed to any great extent with any active hydrogen compound (pseudo acid), which is as acidic or more acidic than acetic acid. On the other hand, the reaction will proceed when the pseudo acid and the olefin are reacted in the presence of a catalytic amount of base.

EXPERIMENTAL

Reagents. 1-Nitropropane and 2-nitropropane (Commercial Solvents Corp.) were rectified prior to their use. The *gem*-dinitro paraffins were prepared by the ter Meer reaction²² of the corresponding chloronitroparaffins and anhydrous sodium acetate (Baker Chemical, Purified) was employed without further purification.

The 2-nitroalkyl alcohols²³ were prepared by an improved procedure, of which two examples are given below. These alcohols were converted to the corresponding acetates by treatment with acetic anhydride in the presence of a catalytic amount of sulfuric acid.

2,5-Dimme 2° inneatol. To a stirred solution of 40.5 g. (1.0 mole) of 98% assay sodium hydroxide in 250 ml. of water was added 74 g. (0.5 mole) of 1,4-dinitrobutane²⁴ at 0-5°. After salt formation was complete, 85 g. (1.05 mole) of 37% formalin solution was added dropwise over a 10-min. period, while the temperature was kept below 4°. After stirring the cold solution for 3 hr., 65 ml. of glacial acetic acid was added, keeping the temperature below 12°. The mixture was then stirred overnight at 25°, filtered and washed with water to yield 83.6 g. or an 80% yield of crude 2,5-dinitro-1,6-hexanediol, mp. 143-155°. The high melting diastereoisomer was isolated by recrystallizing the crude product from 95% ethanol (m.p. 163-165°). This isomer was previously isolated by Colwell.²⁵

Evaporation of the filtrates yielded the lower melting isomer $(95-105^{\circ})$. Recrystallization from aqueous ethanol raised its melting point to $112-113^{\circ}$.

Anal. Calcd. for $C_6H_{12}N_2O_6$: C, 34.62; H, 5.81; N, 13.46. Found: C, 34.80; H, 6.02; N, 13.44.

1,6-Diacetoxy-2,5-dinitrohexane from the high melting diol. A mixture of 6.24 g. (0.03 mole) of 2,5-dinitro-1,6-hexanediol (m.p. 163-165°), 36 ml. of acetic anhydride and 4 drops of concd. sulfuric acid was heated to 90-95° for 4 hr. with stirring. The reaction mixture was then poured onto cracked ice and the solid was filtered and washed with water to afford 8.15 g. (93% yield) of 1,6-diacetoxy-2,5-dinitrohexane, m.p. 105-107°. Two recrystallizations from ethanol raised the melting point to 111-112°.

Anal. Calcd. for $C_{10}H_{16}N_2O_6$: C, 41.10; H, 5.52; N, 9.59. Found: C, 41.25; H, 5.30; N, 9.73.

2-Nitrobutanol. To a stirred solution of 53.6 g. (1.3 mole) of 98% assay sodium hydroxide in 300 ml. of water was added 115.7 g. (1.3 mole) of 1-nitropropane all at once at 0-5°. After approximately 20 min. the reaction mixture was allowed to warm to room temperature to facilitate salt formation. After salt formation was complete, 105 g. (1.3 mole) of a 37% formalin solution was added dropwise over a 15-min. period at 0-5°. The reaction mixture was then allowed to come to room temperature and maintained there for 3 more hr. The temperature was again lowered to $0-5^{\circ}$ and 90 g. (1.5 mole) of glacial acetic acid was added dropwise. After approximately 2 hr. the aqueous solution was extracted with several portions of ether, the extracts were dried over magnesium sulfate, filtered, and the ether removed in vacuo. Distillation of the residual liquid afforded 132 g. (85% yield) of crude 2-nitro-1-butanol, b.p. 90–92° at 3 mm., $n_D^{20^{\circ}0}$ 1.4398; lit. value, $n_D^{20^{\circ}0}$ 1.4287.

The corresponding acetate was then prepared according to the procedure of Vanderbilt and Hass,²³ b.p. 70-72° at 2 mm., $n_2^{20.0}$ 1.4287.

2,2,4-Trinitrohexane. To a stirred solution of 2.40 g. (0.06 mole) of sodium hydroxide in 15 ml. of water at 0-5° were added 7.20 g. (0.06 mole) of 1,1-dinitroethane and 30 ml. of methanol. When salt formation was complete, 4.92 g. (0.06 mole) of sodium acetate, 9.66 g. (0.06 mole) of 2-nitrobutyl acetate, 5 ml. of water and 30 ml. of methanol were added. After 1 hr. at 0-5°, the reaction was run at room temperature for 19 hr. The solvents were removed

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in vacuo, the oily residue was taken up in water and ether, and the aqueous layer was extracted with ether. The combined extracts were dried over magnesium sulfate, leaving 11.64 g. of oil. Distillation of this oil yielded 8.56 g. (65%) yield) of liquid, b.p. 97° at 0.4 mm. to 91° at 0.2 mm., $n_D^{2°}$ 1.4651-1.4667. Redistillation gave material, b.p. 88-90° at 0.1 mm., $n_D^{2°}$ 1.4668, which solidified when cooled in Dry Ice to a yellow solid, m.p. 26-28°. Recrystallization from isopropyl ether raised the melting point to 29-29.5°.

Anal. Calcd. for $C_6H_{11}N_8O_6$: C, 32.58; H, 5.01; N, 19.00. Found: C, 32.70; H, 4.96; N, 18.93.

2-Methyl-2,4-dinitrohexane. (a) In the presence of sodium acetate in a hydroxylic solvent. A solution of 12.3 g. (0.3 mole) 98% assay sodium hydroxide in 40 ml. of water and 60 ml. of methanol was cooled to 0-5° and 26.7 g. (0.3 mole) of 2-nitropropane was added with stirring. The reaction was then allowed to come to room temperature and after salt formation was complete, 24.6 g. (0.3 mole) of anhydrous sodium acetate was added. Then 48.3 g. (0.3 mole) of 2nitrobutyl acetate dissolved in 100 ml. of methanol was added dropwise over a 60-min. period. The temperature was allowed to reach 28-29° and was maintained there for 45 hr. It was then raised to $37-39^{\circ}$ for 4 hr. more. At the end of this time, the solvent was removed in vacuo and the residual oily solid was taken up in water and extracted with small portions of ether. Evaporation of the solvent resulted in an oil. Vacuum distillation of this material yielded 31.4 g. (55% yield) of product (b.p. 77-83° at 1 mm.). Redistillation of this material yielded 2-methyl-2,4-dinitrohexane, b.p. 77° at 0.75 mm., $n_{D}^{20.5}$ 1.4530.

Anal. Calcd. for $C_7H_{14}N_2O_4$: C, 44.20; H, 7.42; N, 14.73. Found: C, 44.50; H, 7.39; N, 14.97.

(b) Using two equivalents of the nitronate salt in a hydroxylic solvent. In this procedure, 0.3 mole of sodium 2-propanenitronate, 0.15 mole of 2-nitrobutyl acetate and a solvent mixture consisting of 90 ml. of methanol and 25 ml. of water, were employed. The reaction mixture was heated for 13 hr. at $38-40^{\circ}$ and was then cooled to $0-5^{\circ}$ and 12 ml. of glacial acetic acid was added all at once. After the mixture was stirred for 1 more hr. and worked up as in procedure (a), an 87% yield of 2-methyl-2,4-dinitrohexane, $n_{\rm D}^{21.5}$ 1.4527, was obtained.

(c) Using two equivalents of the nitronate salt in a nonhydroxylic solvent. A mixture of 22.2 g. (0.2 mole) of anhydrous sodium 2-propanenitronate and 16.1 g. (0.1 mole) of 2-nitrobutyl acetate in 250 ml. of anhydrous tetrahydrofuran, was heated to 37-39° for 48 hr. The reaction mixture was then cooled to 0-5° and 8.5 ml. of glacial acetic acid was added all at once. After 15 min. the reaction mixture was filtered through a sintered glass funnel to remove the sodium acetate. The sodium acetate was dissolved in a minimum amount of water and extracted once with a small portion of ether. The ether extract was added to the previously obtained filtrate and the tetrahydrofuran and ether were removed in vacua leaving an oil. Vacuum distillation yielded 10.4 g. or 55% yield of crude 2-methyl-2,4-dinitrohexane, $n_D^{20.0}$ 1.4520.

(d) In the presence of sodium acetate in a nonhydroxylic solvent. In this experiment, 18.87 g. (0.17 mole) of anhydrous sodium 2-propanenitronate, 13.94 g. (0.17 mole) of anhydrous sodium acetate, and 27.37 g. (0.17 mole) of 2-nitrobutyl acetate in 350 ml. of anhydrous tetrahydrofuran were employed, otherwise procedure (c) was followed. The crude yield of 2-methyl-2,4-dinitrohexane, $n_{D}^{20.9}$ 1.4520, was 49%.

3,5-Dinitroheptane. Sodium acetate, 41.0 g. (0.5 mole)and 20.4 g. (0.5 mole) of 98% assay sodium hydroxide were dissolved in a mixture of 50 ml. of water and 170 ml. of methanol. The solution was cooled to 0-5° and 44.5 g. (0.5 mole) of 1-nitropropane was added with stirring. The reaction was then allowed to come to room temperature and after salt formation was complete, 80.5 g. (0.5 mole) of 2nitrobutyl acetate was added all at once. The temperature was maintained at 23-25° for 23 hr. and then raised to 34-35° for 19 hr. more. The solvent was then removed in vacuo, the residual oily solid taken up in water, extracted with small portions of ether and the solvent evaporated. The remaining oil was vacuum distilled with a large amount of decomposition. The product was collected at 76-84° and 0.6 mm. (13.8 g., 15% yield). Redistillation of this material yielded 3,5-dinitroheptane, b.p. 82-86° at 0.7 mm. Dissolving it in a small amount of 95% ethanol and cooling to -78° yielded oily white crystals which were filtered at ice bath temperature, m.p. 26-27°.

Anal. Calcd. for $C_7H_{14}N_2O_4$: C, 44.20; H, 7.42; N, 14.73. Found: C, 44.44; H, 7.33; N, 14.69.

Subsequent recrystallization of the analytical sample from 95% ethanol raised the melting point to $33-34^\circ$, indicating that the oily solid consisted of diastereoisomers.

6-Hydroxy-(2H)-2-(2-nitrobutyl)-3-pyridazinone. To a stirred solution of 2.04 g. (0.05 mole) of 98% assay sodium hydroxide and 5.60 g. (0.05 mole) of maleic hydrazide in 20 ml. of water and 50 ml. of methanol was added 4.1 g. (0.05 mole) of anhydrous sodium acetate. The reaction mixture was then heated to 35° and 8.05 g. (0.05 mole) of 2-nitrobutyl acetate dissolved in 25 ml. of methanol was added dropwise to the stirred solution over a 20-min. period. The reaction mixture was heated at 38-40° for 21 hr. and then filtered while hot. The methanol was removed from the filtrate *in vacuo*, and the solid precipitate was filtered. It was triturated twice with 25-30 ml. portions of cold water and then dried *in vacuo*, yielding 7.87 g. (74% yield) of product, m.p. 135-140°. Recrystallization twice from benzene gave 6-hydroxy-(2H)-2-(2-nitrobutyl)-3-pyridazinone, m.p. 152-153°.

Anal. Caled. for $C_8H_{11}N_3O_4$: C, 45.07; H, 5.16; N, 19.71. Found: C, 45.00; H, 5.35; N, 19.77.

2-Hydroxymethyl-2,4-dinitro-1-hexanol. A mixture of 14.3 g. (0.1 mole) of the sodium salt of 2-nitropropanediol, 8.2 g. (0.1 mole) of anhydrous sodium acetate, 16.1 g. (0.1 mole) of 2-nitrobutyl acetate, 30 ml. of water and 300 ml. of methanol, was stirred at $34-36^{\circ}$ for 22 hr. At the end of this time the methanol was removed *in vacuo* and the residual material was extracted with ether. Evaporation of the solvent yielded 12.1 g. of a semi-solid. This hygroscopic material was placed on a clay plate and kept under vacuum for 2 days. After this treatment it was found that only 6.0 g. (27% yield) of a solid, m.p. 86-89° could be scraped off the plate. Recrystallization from chloroform afforded 2-hydroxymethyl-2,4-dinitro-1-hexanol, m.p. 101-102°.

Anal. Calcd. for $C_7H_{14}N_2O_6$: C, 37.84; H, 6.31; N, 12.61. Found: C, 37.64; H, 6.28; N, 12.42.

Ethyl 2-carbethoxy-4-nitrohexanoate. In a 300-ml. three necked flask equipped with a stirrer, thermometer, and condenser with a drying tube was placed 4.6 g. (0.2 g.-atom) of sodium metal in 30 ml. of absolute ethanol. After ethoxide formation was complete, 32.03 g. (0.2 mole) of diethyl malonate and 8.2 g. (0.1 mole) of sodium acetate were added. After salt formation was complete, 16.1 g. (0.1 mole) of 2-nitrobutyl acetate dissolved in 30 ml. of absolute ethanol was added dropwise over a period of 30 min. The reaction mixture was kept at 53-55° for 24 hr., cooled to 0-5°, 7.2 g. (0.12 mole) of glacial acetic acid added all at once and the mixture stirred for 2 more hr. The solvent was removed in vacuo and the product separated from the sodium acetate by trituration with small portions of ether. Evaporation of the ether and vacuum distillation of the residual oil yielded 13.7 g. (52% yield) of product, b.p. 115-122° at 1-1.5 mm. Redistillation afforded ethyl 2carbethoxy-4-nitrohexanoate, b.p. 101° at 0.17 mm., $n_{\rm D}^{20.0}$ 1.4403.

Anal. Calcd. for $C_{11}H_{1,9}NO_2$: C, 50.56; H, 7.33; N, 5.36. Found: C, 50.45; H, 7.10; N, 5.51.

5,8-Diaza-3,5,8,10-tetranitrododecane. A stirred solution of 4.1 g. (0.1 mole) of 98% assay sodium hydroxide in 35 ml. of water was cooled to $0-2^{\circ}$ and 7.5 g. (0.05 mole) of ethylenedinitramine was added all at once. Then, 8.2 g. (0.1 mole) of anhydrous sodium acetate was added, and the mixture was allowed to stir until salt formation was complete. At

this time, 16.1 g. (0.1 mole) of 2-nitrobutyl acetate dissolved in 100 ml. of methanol was added all at once. Stirring for 22 hr. at 35-38°, cooling to room temperature and filtering gave 14.3 g. (81% yield) of a solid with a melting range of 122-124°.

Separation of the diastereoisomers was accomplished by dissolving the solid in hot methanol and cooling. The high melting isomer crystallized preferentially. Subsequent recrystallizations from methanol yielded a white solid, m.p. 131-132°.

Anal. Caled. for C₁₀H₂₀O₈N₆: C, 34.09; H, 5.72; N, 23.86. Found: C, 33.87; H, 5.70; N, 23.70.

Evaporation of the mother liquors gave the lower melting isomer, m.p. 100-101°.

Found for C10H20O8N6: C, 33.96; H, 5.78; N, 24.06

4-(2,4-Dinitrophenylnitramino)-2-butanone. In a 125-ml. Erlenmeyer flask were placed 4.56 g. (0.020 mole) of 2,4dinitrophenylnitramine, 2.0 g. (0.024 mole) of 85% azeotrope methyl vinyl ketone, 1 drop of 20% sodium hydroxide solution, and 60 ml. of 95% ethanol. The flask was stoppered and allowed to stay at room temperature (24-26°) for 96 hr. At this time, 2 drops of 3N hydrochloric acid was added to the reaction mixture and the solvent was then removed in vacuo. The resulting oil was triturated with several small portions of isopropyl ether. The undissolved portion crystallized after being shaken with n-propyl ether, yielding the expected ketone, m.p. 92-94°. Since attempts to find a solvent from which the material could be recrystallized were unsuccessful, its 2,4-dinitrophenylhydrazone derivative was prepared. This compound was purified by recrystallization from acetonitrile, m.p. 167-168° dec.

Anal. Calcd. for C₁₆H₁₄N₈O₁₀: C, 40.16; H, 2.92; N, 23.43. Found: C, 40.31; H, 2.93; N, 23.23.

2,4-Dinitrophenylnitramine from 4-(2,4-dinitrophenylnitramino)-2-butanone by the reversal of the Michael addition. When 1.0 g. of 4-(2,4-dinitrophenylnitramino)-2-butanone was added to a solution of 0.16 g. of sodium hydroxide dissolved in 10 ml. of water which was cooled to 10-15°, there was immediately noticeable the characteristic odor of methyl vinyl ketone as the compound dissolved. The reaction mixture was allowed to come to room temperature, and the methyl vinyl ketone was removed in vacuo. Acidification of the reaction mixture with 3N hydrochloric acid yielded 0.5 g. of solid which on recrystallization from carbon tetrachloride melted at 82-84°. The infrared spectrum of this material and that of authentic 2,4-dinitrophenylnitramine were identical.

1-Methoxy-2-nitrobutane. A stirred solution of 8.2 g. (0.1 mole) anhydrous sodium acetate in 35 ml. of water and 70 ml. of methanol was heated to 40° and 16.1 g. (0.1 mole) of 2-nitrobutyl acetate was added all at once. The temperature was maintained at 35-40° for 16 hr., the methanol removed in vacuo, the aqueous residue extracted with small portions of ether and the solvent removed in vacuo. The remaining liquid was vacuum distilled yielding 4.5 g. (34%) yield) of product, b.p. 70-72° at about 8.5 mm. Redistillation gave 1-methoxy-2-nitrobutane, b.p. 61° at 4.6 mm., $n_{D}^{20.0}$ 1.4203.

Anal. Caled. for C₅H₁₁NO₃: C, 45.11; H, 8.27; N, 10.55. Found: C, 44.92; H, 8 14; N, 10.50.

2,3-Dimethyl-2,4-dinitropentane. A mixture of 12.2 g. (0.3 mole) of 98% assay sodium hydroxide and 26.7 g. (0.3 mole) of 2-nitropropane was stirred in a solvent mixture, consisting of 40 ml. of water and 180 ml. of t-butyl alcohol, until salt formation was complete. Then 16.1 g. (0.1 mole) of 3-nitro-2-butyl acetate was added all at once and the reaction mixture was heated to 41-43° for 17 hr. It was then cooled to 20° and 13.0 g. of glacial acetic acid was added all at once. After 3 hr., the t-butyl alcohol was removed in vacuo and the residual aqueous layer was extracted with several portions of ether. Evaporation of the ether and vacuum distillation of the residual oil, afforded 13.6 g. or 71% yield of 2,3-dim $h_{1/2}$,4-dinitropentane, b.p. 80° at $0.5 \text{ mm.}, n_{\rm D}^{20} 1.4560.$

Anal. Caled. for C₇H₁₄O₄N₂: C, 44.20; H, 7.42; N, 14.73. Found: C, 44.47; H, 7.60; N, 14.94.

4,7-Diaza-3,8-dimethyl-2,4,7,9-tetranitrodecane. To a stirred solution of 4.04 g. (0.1 mole) of 98% assay sodium hydroxide in 45 ml. of water and 170 ml. of t-butyl alcohol were added 7.5 g. (0.05 mole) of ethylenedinitramine and 8.2 g. (0.1 mole) of anhydrous sodium acetate at $0-5^{\circ}$. After salt formation was complete, the reaction mixture was allowed to come to room temperature and 16.1 g. (0.1 mole) of 3-nitro-2-butyl acetate was added all at once. The mixture was heated to $39-41^{\circ}$ for 48 hr., the *t*-butyl alcohol was removed in vacuo and the water was decanted leaving an oily solid residue. It solidified after being shaken with a small portion of 95% ethanol, which had been cooled to 0°. Recrystallization from methanol gave 3.7 g. (21% yield) of product, m.p. 120-122°. Subsequent recrystallization from methanol and Norite yielded 4,7-diaza-3,8-dimethyl-

2,4,7,9-tetranitrodecane, m.p. 124.5-125.5°. Anal. Calcd. for C₁₀H₂₀N₆O₈: C, 34.09; H, 5.72; N, 23.86. Found: C, 34.16; H, 5.91; N, 24.04.

2,9-Dimethyl-2,4,7,9-tetranitrodecane. To a solution of 2.44 g. (0.06 mole) of 98% sodium hydroxide in 85 ml. of methanol and 20 ml. of water were added 5.34 g. (0.06 mole) of 2nitropropane and 4.92 g. (0.06 mole) of anhydrous sodium acetate at 0-5°. After salt formation was complete, 8.76 g. (0.03 mole) of 1,6-diacetoxy-2,5-dinitrohexane was added all at once. The reaction mixture was then heated to 34° and maintained there for 16 hr. Cooling, filtering, washing the precipitate with water and drying gave 10.3 g. (98% yield) of product m.p. 170-175° dec.

Separation of the diastereoisomers was accomplished by recrystallizing from benzene. One of the isomers, m.p. 193-194° dec. crystallized out of the benzene solution.

Anal. Calcd. for C12H22N4O8: C, 41.14; H, 6.28; N, 16.00. Found: C, 41.16; H, 6.49; N, 16.04.

Evaporation of the filtrate and recrystallization from a mixture of benzene and cyclohexane yielded the second isomer, m.p. 161-163°

Found for $C_{12}H_{22}N_4O_8$: C, 41.14; H, 6.52; N, 15 87. 3,3,5,8,10,10-Hexanitrododecane. To a solution of 4.9 g. (0.12 mole) of 98% assay sodium hydroxide in 75 ml. of water which was cooled to 0-5°, was added 8.04 g. (0.06 mole) of 1,1-dinitropropane. After salt formation was complete, 3.6 g. (0.06 mole) of glacial acetic acid was added slowly at 10°. Then a slurry of 8.76 g. (0.03 mole) of 1,6diacetoxy-2,5-dinitrohexane in 50 ml. of methanol was added all at once. The temperature was raised to 50° and maintained there for 16 hr. The reaction mixture was then cooled and filtered, yielding 12.5 g. (94% yield) of product, m.p. 146-148°. Recrystallization of this material from glacial acetic acid, and cleaning with Norite, gave 3,3,5,8,10,10hexanitrododecane, m.p. 158-159°. Anal. Calcd. for C₁₂H₂₀N₆O₁₂: C, 32.72; H, 4.54; N, 19.09.

Found: C, 32.51; H, 4.66; N, 18.92.

5,12-Diaza-5,7,10,12-tetranitrohexadecane. To a stirred solution of 0.81 g. (0.02 mole) of 98% assay sodium hydroxide in 10 ml. of water and 70 ml. of methanol were added 1.64 g. (0.02 mole) of anhydrous sodium acetate and 2.36 g. (0.02 mole) of 1-nitroaminobutane at $0-5^{\circ}$. The reaction was allowed to come to room temperature, and after salt formation was complete, 2.92 g. (0.01 mole) of 1,6diacetoxy-2,5-dinitrohexane was added all at once. The reaction was run at 24° for 15 hr. and then at 38-40° for 7 hr. more. Cooling in an ice bath gave 3.6 g. (88% yield) of product, m.p. 118-121° dec. One of the diastereoisomers was removed by triturating the product with hot isopropyl ether. Subsequent cooling of the ether and filtration yielded a white powder, m.p. 135-137° dec. Several more recrystallizations from isopropyl ether yielded the analytical sample, m.p. 139-140° dec. Infrared spectra of the crude product, analytical sample and the residue remaining after trituration were all very similar indicating that the crude material obtained (m.p. 118-121° dec.) from the reaction consisted entirely of diastereoisomeric material.

Anal. Calcd. for C14H23N6O8: C, 41.17; H, 6.91; N, 20.58. Found: C, 40.94; H, 6.83; N, 20.29.

5-Methyl-5-nitro-2-hexanone. To a solution of 8.16 g. (0.2 mole) of 98% assay sodium hydroxide in 60 ml. of methanol and 40 ml. of water were added 17.8 g. (0.2 mole) of 2nitropropane and 16.4 g. (0.2 mole) of anhydrous sodium acetate at 0-5°. After salt formation was complete, 26.0 g. (0.2 mole) of 3-ketobutyl acetate was added dropwise over a 15-min. period. The temperature was raised to 40-45° and maintained there for 20 hr. The methanol was then removed in vacuo and the residual material extracted with small portions of ether. Removing the solvent in vacuo and distilling gave 29.4 g. (92% yield) of 5-methyl-5-nitro-2-hexanone, b.p. 88-91° at 2 mm., $n_D^{20.°}$ 1.4450, lit. value,¹⁴ n^{20.6} 1.4444.

The 2,4-dinitrophenylhydrazone derivative melted at 130.5-131.5°, lit. value, 14 m.p. 130.5-131.5°.

5-Nitro-2-heptanone. To a stirred solution of 12.24 g. (0.3 mole) of 98% assay sodium hydroxide in 60 ml. methanol and 30 ml. of water which was cooled to 0-5°, were added 26.7 g. (0.3 mole) of 1-nitropropane and 24.6 g. (0.3 mole)

of anhydrous sodium acetate. After salt formation was complete, the temperature was raised to 35° and 39.0 g. (0.3 mole) of 3-ketobutyl acetate dissolved in 60 ml. of methanol was added dropwise over a 45-min. period. The temperature was then increased to 40-45° and maintained there for approximately 17 hr. Removing the solvent *in vacuo*, extracting with ether, evaporating the solvent and distilling the remaining oil, gave 34.4 g. (72% yield) of product, b.p. 100-105° at 5 mm. Redistillation afforded 5-nitro-2heptanone, b.p. 102° at 4.8 mm., n_D^{20} 1.4410.

Anal. Caled. for C7H13NO3: C, 52.83; H, 8.17; N, 8.80. Found: C, 52.86; H, 8.35; N, 8.82.

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LAFAYETTE, IND.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Diels-Alder Reactions with Nitro Olefins Generated In Situ¹

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Nitro olefins generated in situ from the corresponding 2-nitroalkyl acetates with sodium acetate react readily in the Diels-Alder reaction with cyclopentadiene in hydroxylic and nonhydroxylic solvents, and with anthracene in nonhydroxylic solvents.

The Diels-Alder reaction of nitro olefins with suitable dienes has been employed for many years, without any substantial improvement in the original procedure of Alder and co-workers.² Thus, the addition of nitro olefins to dienes has been effected generally either at elevated temperatures and pressures^{3,4} with or without solvents or in high boiling solvents at atmospheric pressure.^{5,6} Several workers have carried out these reactions at approximately room temperature,⁷⁻⁹ but even here, as in the former cases, the nitro olefins had to be prepared and purified separately. The nitro olefins are usually prepared from the corresponding alcohols by dehydration or by dehydroacetylating

the corresponding nitroalkyl acetates.¹⁰ In both procedures the old fin is removed from the reaction medium by distillation, and purified by rectification. Generally, the back temperatures employed in the preparation and purification leads to some decomposition of the nitro olefin.

It was pollulated that this difficulty could be overcome to a large extent if the olefins were generated in situ. Since it had been found that 2nitroalkyl acetates could be converted readily to nitro olefins under mild conditions,¹⁰ it was decided to employ these esters directly as the source of nitro olefins in the Diels-Alder reaction. The results of these experiments are listed in Table I.

J ccently,¹¹ 2,2-dinitroethanol was employed disculy in a Diels-Alder reaction. Dehydration in situ to 1,1-dinitroethene was achieved on adding 2.2 -finitroethanol to a refluxing solution of cyclopentadiene in chlorobenzene. Also, Kaplan and Shechter¹² have prepared 4-nitrocyclohexene from 1,3-lutadiene and nitroethylene which was generated in situ from 2-nitroethyl acetate and catalytic amounts of sodium acetate at 95-105° or

^{(1) (}a) From the Ph.D. Thesis of Robert Miller, Purdue University, September 1958. (b) Much of the work described in this paper was presented at the fall, 1959, ACS meeting in Atlantic City, N. J.

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