

methoxide ion on 3,5-dinitrobenzonitrile.^{20,24} The failure to observe formation of a transient species by either pmr or calorimetric probes in the reaction of methoxide ion with **16** is also consistent with this reactivity and stability pattern. In the symmetrical anisole **16**, attack is directed to the 1 position (*para* to nitro) to yield the 1,1 complex **4** as both the kinetic and thermodynamic product of the reaction. From these and our preceding studies,¹ it is clear that the same substitutional factors which determine the relative stabilities of the thermodynamically stable 1,1 complexes also determine the occurrence and position of attack in the formation of 1,3 complexes.

(34) M. I. Foreman and R. Foster, *Can. J. Chem.*, **47**, 729 (1969).

Registry No.—**4**, 12384-95-1; **5**, 12384-96-2; **6**, 22433-89-2; **7**, 22433-90-5; **10**, 22487-60-1; **11**, 22433-91-6; **13**, 22433-92-7; **14**, 22433-93-8; **15**, 22414-19-3; **16**, 22433-95-0; **18**, 12244-75-6; **19**, 12384-97-3; sodium methoxide, 124-41-4.

Acknowledgment.—This study was supported in part by grants from the U. S. Atomic Energy Commission and the Research Corporation (to J. W. L.). A portion of the pmr studies was carried out with instrumentation provided by a grant (FR 00292-03) from the National Institutes of Health. One of us (J. W. L.) gratefully acknowledges the advice and assistance of Mr. Otto Prater in the construction of the calorimeter.

Oxidation of Nitronates with Persulfate and with Silver Ions

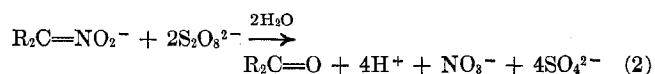
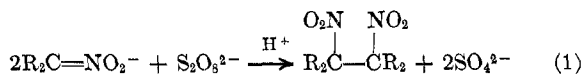
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Received June 6, 1969

Sodium or ammonium persulfates convert salts of primary nitro compounds into secondary vicinal dinitro compounds ($R_2CHNO_2CHNO_2R$) and aldehydes. Silver ion catalyzes the oxidation-reduction reactions, and advantageous specific procedures using buffers and heterogeneous extractants are described for effecting oxidative dimerization. Experimental methods have been developed which minimize transformation of the oxidative dimers to conjugated nitro olefins and their addition products. Salts of phenylnitromethane, 1-nitropropane, 1-nitrobutane, and 2-methyl-1-nitropropane are converted by persulfates into their corresponding vicinal dinitro derivatives. In the absence of an extractant, ammonium persulfate oxidizes sodium phenylmethanenitronate to *cis*- α -nitrostilbene, α,β,γ -triphenyl- α -nitropropene, 3,4,5-triphenylisoxazoline oxide, and 3,4,5-triphenylisoxazole, along with benzaldehyde. Sodium 1-phenyl-1-ethanenitronate, sodium 9-fluorenenitronate, and sodium 1-(1-cyclohexenyl)-1-ethanenitronate, secondary nitronates having conjugating unsaturated centers, are converted effectively into acetophenone, fluorenone, and 1-cyclohexenyl methyl ketone, respectively. Potassium 1-nitropentane-1-nitronate and ammonium persulfate yield pentanoic acid and pentanamide. Various mechanisms for oxidation of nitronates by persulfates have been considered. An effective method for oxidizing secondary nitronates to tertiary vicinal dinitro compounds ($R_2CNO_2CNO_2R_2$) by reaction with equivalent quantities of silver nitrate in aqueous dimethyl sulfoxide or acetonitrile has been developed. 9-Nitrofluorene, 1-phenyl-1-nitroethane, nitrocyclohexane, and 2-nitropropane have thus been oxidized advantageously to 9,9'-dinitro-9,9'-bifluorenyl, 2,3-dinitro-2,3-diphenylbutanes, 1,1'-dinitrobicyclohexyl, and 2,3-dimethyl-2,3-dinitrobutane. Oxidative dimerization of silver salts of primary nitro compounds to secondary vicinal dinitro compounds is complicated by competitive oxidative nitration of the silver nitronates by silver nitrite to primary geminal dinitro alkanes.

Salts of secondary nitro compounds are oxidized by persulfates in the pH range of 9.5–7.0 at 0–5° to vicinal tertiary dinitro compounds (eq 1) and ketones (eq 2).¹



Thus alkaline solutions of 2-nitropropane, 2-nitrobutane, and nitrocyclohexane, respectively, with ammonium or sodium persulfates yield 2,3-dimethyl-2,3-dinitrobutane (**1**, 51–62%) and acetone (8–27%), 3,4-dimethyl-3,4-dinitrohexane² (**3**, 37%) and 2-butanone (48%), and 1,1'-dinitrobicyclohexyl (**2**, 14–30%) and



(1) H. Shechter and R. B. Kaplan, *J. Amer. Chem. Soc.*, **75**, 3980 (1953).
 (2) The stereochemistry of the 3,4-dimethyl-3,4-dinitrohexane is not known.

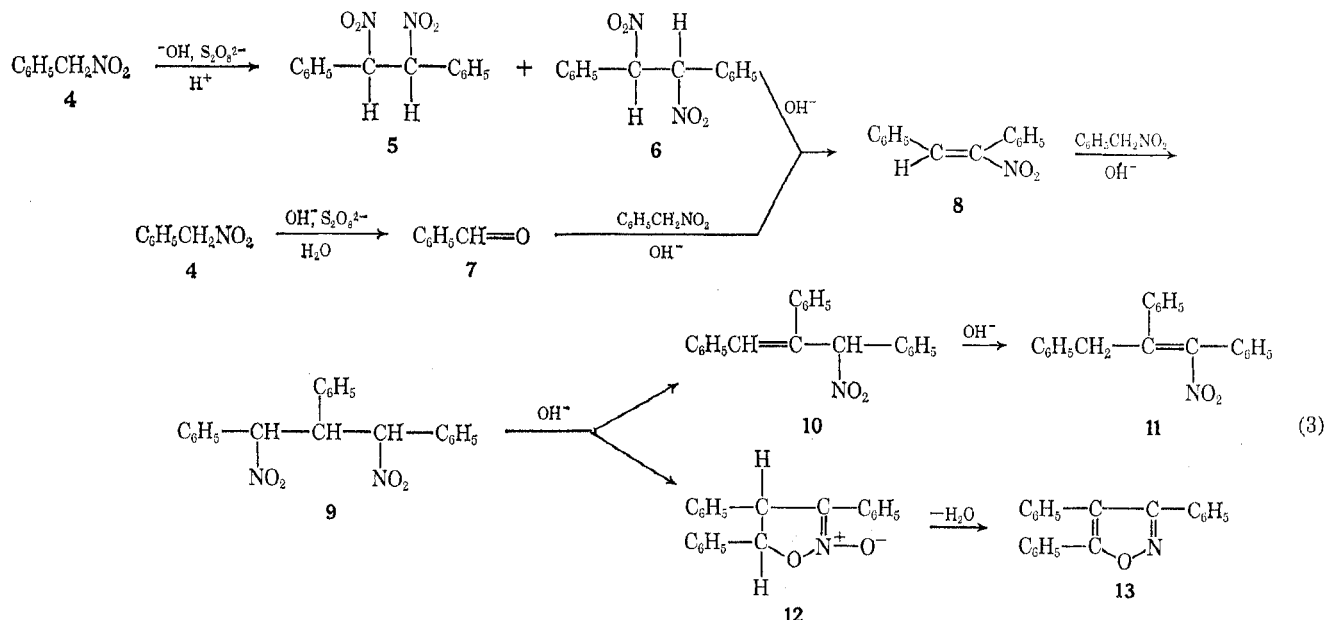
cyclohexanone (67%). Oxidation of salts of primary nitro compounds by persulfates has been limited to nitroethane, which results ultimately in 3,4,5-trimethylisoxazole (**3**, ca. 25%),¹ and to phenylnitromethane² (**4**), which gives *meso*- (**5**, 5%) and *dl*- (**6**, 33%) 1,2-dinitro-1,2-diphenylethanes along with benzaldehyde (**7**).

The present investigation was initiated to determine the reactions of persulfates with salts of primary nitroalkanes, unsaturated primary and secondary nitro compounds, and 1,1-dinitro alkanes. The study was expanded to include the catalytic effects of silver ion on oxidation of salts of primary and secondary nitro compounds with persulfates. These efforts led to investigation of the actions of stoichiometric quantities of silver ion on representative alkane nitronates and to development of an advantageous method for converting silver salts of secondary nitro alkanes into their vicinal oxidative dimers.

Oxidation of phenylnitromethane (**4**) by ammonium

(3) (a) A. Dornow and K. Fust, *Chem. Ber.*, **90**, 1774 (1957). (b) Reference 3a describes the oxidative dimers of **4** as α - and β -1,2-dinitro-1,2-diphenylethanes. The α and β oxidative dimers are **5** and **6**, respectively. The stereochemistry of **6** is established upon its partial resolution by less than 1 equiv of brucine: H. Shechter, J. J. Gardikes, and A. H. Pagano, *J. Amer. Chem. Soc.*, **81**, 5420 (1959).

persulfate in aqueous sodium hydroxide at 0–5° in 20 hr over the pH range of 11.7–6.0 yields benzaldehyde (7, 23%), *cis*- α -nitrostilbene (8, 58%),⁴ α,β,δ -triphenyl- α -nitropropene (11, 2.0%), 3,4,5-triphenylisoxazoline oxide (12, 1.3%), 3,4,5-triphenylisoxazole (13, 2.4%), and regenerated 4 (12%). Under the lengthy alkaline oxidative conditions, 8, 11, 12, and 13 are apparently derived from 5 and 6 or from 7 and 4 by sequences as shown in eq 3.^{5,6} To control the system so that satis-

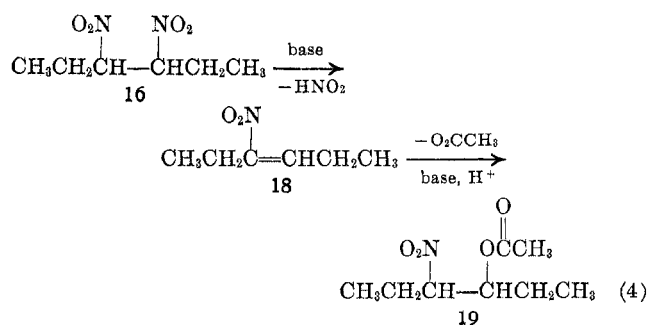


factory yields of the initial oxidation products could be obtained, the reactions were effected in the presence of heterogeneous extractants (chloroform or benzene) and the pH was controlled at 9.7–7.0 by use of sodium acetate as a buffer. Salts of 4 are thus oxidized by excess ammonium persulfate at various ratios of oxidant to nitro compound (Table I) to 5 (10–18%) and 6 (34–65%) along with 7 (12–16%), 12 (0.4%), 13 (0.4–2.6%), benzoic acid (14, 1.0–7.8%), and benzamide (15, 0.4–2.5%). Under the conditions of the persulfate oxidations, using chloroform as a heterogeneous extractant, neither 5 nor 6 isomerizes and their conversions into 8 and subsequent products are minimal. In the absence of the extractant, 5 and 6 are converted essentially quantitatively into 8 by aqueous sodium acetate or methanolic piperidine; reaction of 6 with 30% aqueous sodium hydroxide at 90–100° yields 13.

Oxidations of alkaline solutions of other primary nitro compounds with buffered persulfate ion in the presence of chloroform were effected as with 4. Sodium 1-propanenitronate and sodium persulfate give 3,4-dinitrohexanes (16, *ca.* 41%),⁷ propionaldehyde (17, 45–59%), 3-nitro-3-hexene (18, 2%), 4-acetoxy-3-nitrohexane (19, 3%), and 1-nitropropane (20). Similarly,

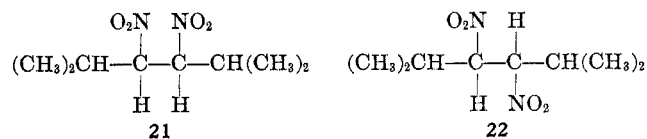
sodium 1-butanenitronate yields isomeric 4,5-dinitrooctanes (12%, stereochemistry unknown), butyraldehyde (18–27%), 4-nitro-4-octene (32%), and 5-acetoxy-4-nitrooctane. Oxidation of the 1-butanenitronate anion with ammonium persulfate results in butyramide (4%) and butyric acid (12%), along with the previous products.⁸ It is apparent that the 3-nitro-3-hexene (18) and the 4-nitro-4-octene obtained in the persulfate oxidations of 1-propanenitronate and

1-butanenitronate ions, respectively, are derived from the oxidative dimers, 3,4-dinitrohexane (16, eq 4) and



4,5-dinitrooctane, by base-catalyzed elimination of nitrous acid. Nucleophilic addition of acetate ion to the conjugated nitro alkenes in the protonic environment results in the formation of vicinal nitroacetates (eq 4).

Oxidation of sodium 2-methyl-1-propanenitronate, a relatively hindered nitronate, results in *meso*- (21) and *dl*-2,5-dimethyl-3,4-dinitrohexanes (22) (10%), iso-



(8) (a) A blank experiment with sodium 1-butanenitronate in which ammonium persulfate is omitted results in recovery of 99% of the initial 1-nitrobutane and only 1% as butyraldehyde (as its 2,4-dinitrophenylhydrazone). It is concluded that the oxidizing agent is necessary to produce significant amounts of carbonyl compounds from nitronates and that the yield of aldehyde from Nef reaction^{9b} in competition with that from persulfate oxidation is very small. (b) W. E. Noland, *Chem. Rev.*, **55**, 137 (1955).

(4) The stereochemistry of 8 (the phenyl groups are *cis*) has been assigned by J. P. Freeman and T. E. Stevens, *J. Org. Chem.*, **23**, 136 (1958).

(5) Conversions of 4 and 7 into 11, 12, and 13 have been studied by (a) F. Heim, *Chem. Ber.*, **44**, 2016 (1911); (b) E. P. Kohler and G. R. Barrett, *J. Amer. Chem. Soc.*, **46**, 2105 (1924); (c) D. E. Worrall, *ibid.*, **57**, 2299 (1935); (d) P. Ruggli and B. Hegedus, *Helv. Chim. Acta*, **22**, 405 (1939); (e) K. Rorig, *J. Org. Chem.*, **51**, 391 (1950); (f) A. Dornow and A. Frese, *Justus Liebigs Ann. Chem.*, **578**, 122 (1952); (g) A. T. Nielsen and T. G. Archibald, *Tetrahedron Lett.*, 3375 (1968).

(6) Oxidation of nitroethane to 8 by alkaline persulfate presumably follows a course analogous with that of 4.

(7) The isomeric 3,4-dinitrohexanes (16) could not be separated readily, and thus their stereochemistry was not determined.

TABLE I
 REACTION OF SODIUM PHENYLMETHANENITRONATE WITH AMMONIUM PERSULFATE (Eq 3)

[C ₆ H ₅ CH=NO ₂ Na], mol	[(NH ₄) ₂ S ₂ O ₈], mol	Temp, °C	Time, ^a hr	Yield, ^b %								
				5	6	7	12	13	14	15	4 ^c	
0.1	0.2 ^d	0-10	3.5	15.5	41.5	11.6	0.4	2.6	1.0			6.0
0.25	0.5 ^d	-5 to -10	6.0	9.5	34.2	16.3		0.4	7.8			7.3
0.1	0.2 ^d	12-15	0.37	18.5	44.0	15.0	0.4	2.5	1.3	0.4		5.6
0.095	0.285 ^d	10-20	1.0	10.7	65.0	16.3	0.4	2.3	1.9	2.5		6.4

^a Time elapsed between pH ca. 11 to 6.5; the reaction mixtures were then analyzed. ^b Yields are based on sodium phenylmethanenitronate consumed. ^c Recovery, per cent, of 4. ^d Ammonium persulfate was added to the alkaline solution of 4.

TABLE II

UNCATALYZED OR SILVER ION CATALYZED REACTIONS OF SODIUM 1-PROPANENITRONATE^a WITH PERSULFATES

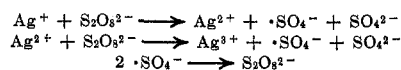
[C ₃ H ₇ NO ₂ Na], ^a mol	[S ₂ O ₈ ²⁻], ^{b,c} mol	Temp, °C	Time, min	Yield, %		
				16 ^{d,e}	17 ^f	20 ^{g,h}
0.3	0.9 ⁱ	10-20	90 ^{j,k}	30 ^l	24	10
0.3	0.9 ^{m,n}	10-20	60 ^{j,k}	50 ^l	40	3.1
0.3	0.9 ⁱ	0-5	390	27	25	11
0.3	0.9 ^{m,n}	0-5	240	23	58	5.3
0.3	0.9 ^o	10-20	90 ^{j,k}	18 ^l	48	12
0.3	0.9 ^{n,p}	10-20	240	41 ^l	46	4.8
0.3	0.9 ^q	10-20	15 ^{j,k}	45	29	17

^a Sodium 1-propanenitronate. ^b Persulfates. ^c The persulfate reagents were added to sodium 1-propanenitronate. ^d 3,4-Dinitrohexanes. ^e Yields based on 20 consumed. ^f Propionaldehyde, isolated as its 2,4-dinitrophenylhydrazone. ^g 1-Nitropropane. ^h Recovery of 20. ⁱ Sodium persulfate (Becco Chemical Division, Food Machinery and Chemical Corp.) catalyzed with aqueous 10% silver nitrate (10 ml, 5.9 × 10⁻³ mol). ^j Time elapsed between pH ca. 11 to pH ca. 6.5 when reaction mixtures were worked up. ^k At the same temperature, catalyzed Becco sodium persulfate did not decrease the reaction time as much as catalyzed Eimer and Amend sodium persulfate. ^l Yields for oxidative dimers were lower with catalyzed or uncatalyzed Becco sodium persulfate than with catalyzed or uncatalyzed Eimer and Amend sodium persulfate. ^m Sodium persulfate (Eimer and Amend) catalyzed with aqueous 10% silver nitrate (10 ml, 5.9 × 10⁻³ mol). ⁿ In all cases Eimer and Amend sodium persulfate was less soluble than Becco persulfate. ^o Sodium persulfate (Becco) uncatalyzed. ^p Sodium persulfate (Eimer and Amend) uncatalyzed. ^q Ammonium persulfate (J. T. Baker) catalyzed with aqueous 10% silver nitrate (7.7 ml, 4.5 × 10⁻³ mol).

butyraldehyde (20%), and 4-acetoxy-2,5-dimethyl-3-nitrohexanes (15%), along with regenerated 2-methyl-1-nitropropane. The stereochemistry of oxidative dimerization in this system is similar to that for 4 in that 22 (the *dl* isomers) is formed in greater yield than is 21 (the *meso* isomer, the ratio of 22/21 is 4.5:1). The stereochemical assignments for the isomers are made on the basis that *l*-brucine effects elimination of nitrous acid from *l*-2,5-dimethyl-3,4-dinitrohexane to form 2,5-dimethyl-3-nitro-3-hexene at a greater rate than from the *d* isomer.

Since oxidative dimerizations of alkane nitronates and particularly α -aryl alkane nitronates such as from 4 occur so slowly, a study was made of the influence of small proportions of silver ion (the mole ratio of Ag⁺ to RCH=NO₂⁻ is less than 1:60) on the oxidations.⁹ Oxidative dimerizations of 1-propanenitronate, 1-butanenitronate, 2-methyl-1-propanenitronate, and phenylmethanenitronate ions are greatly accelerated by silver ion. Reaction times were reduced by more than 80% in most cases (from 1-7 hr to 0.25-1 hr).

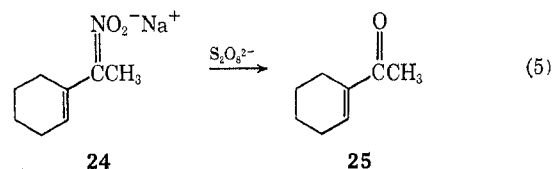
(9) Monopositive silver ion is oxidized by persulfates to dipositive and tripositive silver, possibly according to the following equations; in the presence



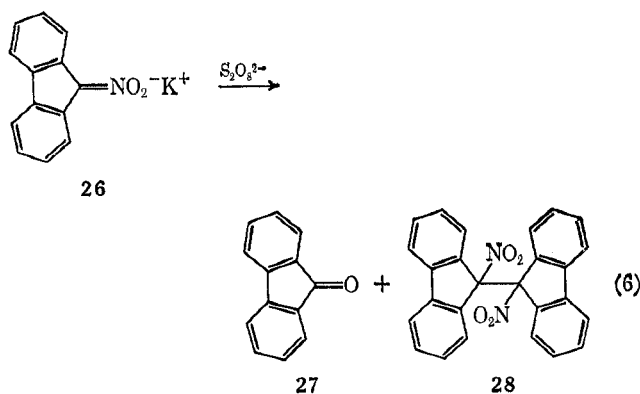
of reducing agents, tripositive and possibly dipositive silver ions are converted rapidly into monopositive silver and the oxidized form of the reducing agent. For discussion of this system and variants thereof, see D. M. Yost, *J. Amer. Chem. Soc.*, **48**, 152 (1926), and C. E. Bawn and D. Margerison, *Trans. Faraday Soc.*, **51**, 925 (1955).

The products and yields resulting from the silver-catalyzed method are essentially identical with those obtained in the absence of catalyst. The slightly improved yields with silver ion as catalyst are attributed more to improved techniques in isolation of the products than to any effect by silver ion. The results for uncatalyzed and for silver ion catalyzed reactions of sodium 1-propanenitronate with persulfates are summarized in Table II.

Oxidations of secondary alkane nitronates having a conjugating aryl group or carbon-carbon double bond were also effected with persulfates. Reactions of sodium 1-phenyl-1-ethanenitronate (23) and of sodium 1-(1-cyclohexenyl)-1-ethanenitronate (24), respectively, give acetophenone (70-72%) and 1-cyclohexenyl methyl ketone (25, 61-66%, eq 5). No oxidative dimers could

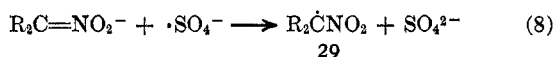
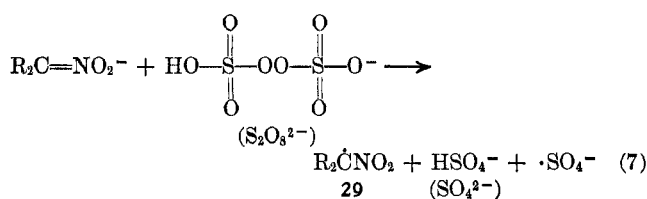


be isolated in either case. Transformation of 24 to 25 by persulfate indicates that the oxidation method may be of general value for converting unsaturated nitronates into their corresponding unsaturated carbonyl derivatives. From potassium 9-fluorenenitronate (26) the major product is fluorenone (27, 72%); the oxidative dimer 28 (13%) is also obtained (eq 6).

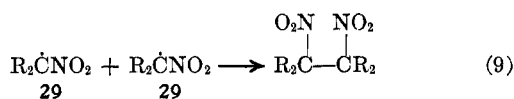


There are no simple observable correlations between the effects of structure of primary and secondary nitronates and the major products obtained in their oxidation with persulfates; each compound has its own disciplines of oxidation. For preparative purposes it is advantageous to effect oxidation of secondary rather than primary nitronates, because formation and isolation of vicinal tertiary dinitro compounds are not complicated by products derived from or after base-catalyzed elimination of nitrous acid, as in the case of vicinal secondary dinitro compounds. It is clear also that conversion of primary and secondary nitronates into aldehydes (and acids) and ketones is enhanced at elevated temperatures and in dilute solution. It will also be seen that oxidation of primary nitronates by persulfates is more efficient for preparing vicinal secondary dinitro alkanes than is decomposition of silver salts of primary nitro compounds.

The detailed mechanisms of reactions of mononitronates with persulfates are not known. Oxidation of salts of mononitro compounds apparently involves transfer of one electron to hydropersulfate and/or persulfate ion and to sulfate radical ions, as in eq 7 and 8.



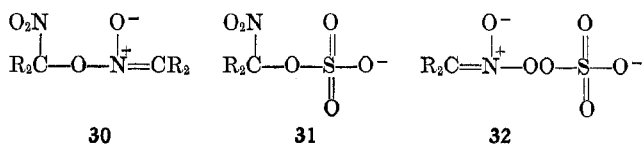
The nitroalkyl radicals (29) possibly dimerize to vicinal dinitro compounds (eq 9) and the isomeric α -nitro alkyl



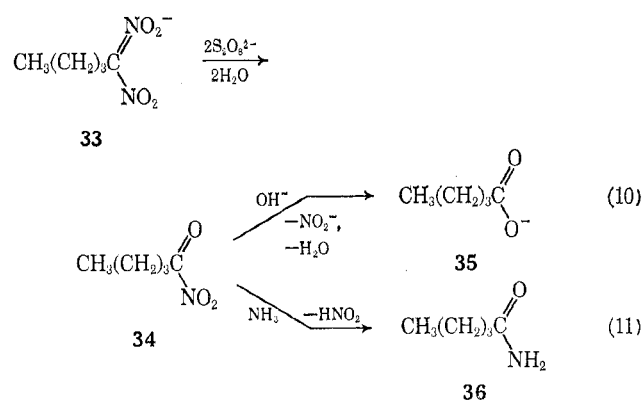
alkane nitronates (30, nitronic esters) or pair with sulfate radical ions. Hydrolysis of 30, 31, and 32 thus can give the carbonyl product, nitrous acid, and the parent mononitro compound,¹⁰ displacement of 30, 31,

(10) There are other routes by which nitro alkyl radicals (29) can give vicinal dimers and carbonyl compounds which fit the present facts. Of particular note are possible reactions of nitro alkyl radicals and/or sulfate radical anions with nitronate ions by carbon and/or oxygen alkylation to give intermediate nitroxyl radical anions such as $\text{R}_2\text{C}(\text{NO}_2)\text{CR}_2(\text{NO}_2)^{\cdot-}$, $\text{R}_2\text{C}=\text{NO}_2\text{CR}_2(\text{NO}_2)^{\cdot-}$, $-\text{O}_2\text{SO}_2\text{CR}_2(\text{NO}_2)^{\cdot-}$, and $-\text{O}_2\text{SO}_2\text{N}(\text{O}^-)\text{CR}_2$, which are then oxidized to vicinal dinitro compounds, 30, 31, and 32. The radical

and 32 by alkane nitronate may result in vicinal dinitro compounds.



The possible oxidation of 1-nitro alkane nitronates [$\text{RC}(\text{NO}_2)=\text{NO}_2^-$] by persulfates to their corresponding tetranitro compounds has been investigated. Exposure of the potassium salt of phenyldinitromethane to persulfate ion for 12 hr results in recovery of ca. 90% of the initial materials. In the oxidation of potassium 1-nitropentane-1-nitronate (33) with ammonium persulfate, 5,5,6,6-tetranitrodecane is not obtained; pentanoic acid (35, 35%) and pentanamide (36, 55%) are formed. The interesting transformations of 33 to 35 and 36 are explainable on the assumption that 34 undergoes nucleophilic reaction with hydroxide ion and with ammonia (eq 10 and 11).



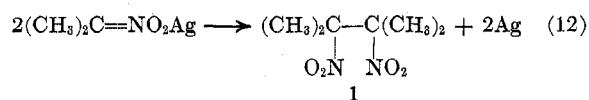
The results of oxidation of nitronates with persulfates, the catalytic effects of silver ion on such systems, and previous knowledge of oxidative nitration of nitronates and nitrite ion to geminal dinitro compounds by silver ion¹¹ have led to study of decomposition of silver salts of mononitro and 1,1-dinitro compounds in homogeneous solution as a possible improved method for preparing vicinal dinitro derivatives. Silver salts of primary nitronates have been previously reported to decompose in heterogeneous media to silver and the corresponding vicinal secondary dinitro compounds.¹² Thus silver salts of nitroethane and 1-nitropentane, respectively, decompose heterogeneously in water to 2,3-dinitrobutane and 5,6-dinitrodecane and silver in unspecified yields.^{12a} Similarly, silver phenylmethane nitronate in benzene slowly gives 1,2-dinitro-1,2-diphenylethane and silver.^{12b} In previous work¹ from this laboratory, aqueous mixtures of silver nitrate and sodium 2-propanenitronate have been observed to convert impractically into acetone (30%), 2,3-dimethyl-2,3-dinitrobutane (11%), and 2-nitropropane (ca. 30%).

anions $\text{R}_2\text{C}(\text{NO}_2)\text{CR}_2(\text{NO}_2)^{\cdot-}$ have been proposed as intermediates by G. A. Russell and W. C. Danen [*J. Amer. Chem. Soc.*, **88**, 5663 (1966)] in conversion of the 2-propanenitronate ion by 2-halo-2-nitropropanes into 2,3-dimethyl-2,3-dinitrobutane.

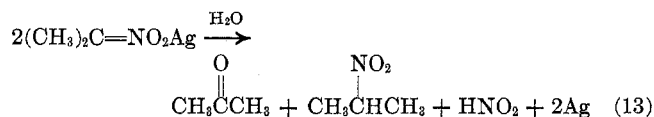
(11) R. B. Kaplan and H. Shechter, *J. Amer. Chem. Soc.*, **83**, 3535 (1961).

(12) (a) A. Angeli and L. Alessandri, *Atti Accad. Naz. Lincei, Rend., Cl. Fis. Mat. Nat.*, **191**, 784 (1910); (b) R. L. Shriner and G. B. Brown, *J. Org. Chem.*, **2**, 376 (1937).

It has now been found that, upon addition of concentrated solutions of sodium 2-propanenitronate at 30–32° to silver nitrate dissolved in acetonitrile or, preferably, dimethyl sulfoxide containing small proportions of water,¹³ silver 2-propanenitronate is formed, which decomposes, possible *via* the complex ion $(R_2C=NO_2)_2-Ag^-Ag^+$, to silver and **1** (61–84%, eq 12). Acetone



(8–20%), 2-nitropropane (6–23%), and nitrous acid are also formed (eq 13). In this system dimethyl sul-



foxide and, to a considerable extent, acetonitrile dissolve silver 2-propanenitronate and decomposition occurs quickly to give **1** in markedly improved conversions compared with previous heterogeneous methods. With either dimethyl sulfoxide or acetonitrile as solvent, silver 2-propanenitronate decomposes essentially completely at *ca.* 30° in the dark in less than 0.5 hr. In either solvent conversion of silver 2-propanenitronate (Table III) into **1** is increased and conversion into acetone is lowered as the temperature is raised from –10 to 33°. Decomposition of sodium 2-propanenitronate and silver nitrate to products is considerably faster in water–dimethyl sulfoxide than in methanol–dimethyl sulfoxide (5 hr). Silver 2-propanenitronate is photosensitive; upon exposure to light in acetonitrile, its conversion into acetone is enhanced.

TABLE III
DECOMPOSITION OF SILVER 2-PROPANENITRONATE

Solvent (ml)	Temp, °C	Time, ^a hr	Yield, %		
			1 ^b	C ₃ H ₆ O ^{b,c}	C ₃ H ₇ NO ₂ ^d
CH ₃ CN (350)	–10 to –5	17.0	10	51	12
CH ₃ CN (350)	0–5	17.0	34	31	19
CH ₃ CN (300)	30–32	5.0	66	20	16
CH ₃ CN (400)	30–32	0.5	61	39	11
CH ₃ CN (400)	80°	1.0	53	23	28
DMSO (150)	0–5	12.0	39	20	30
DMSO (150)	30–32	5.0	61	19	23
DMSO (350)	32–34	5.0	77 ^f	13	6.0
DMSO (350)	30–31	4.0	77	8	6.0
H ₂ O (170)	0–5	12.0	20	49	31

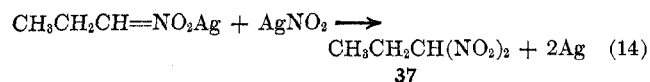
^a Total storage time of the reaction mixture. Reaction at 30° was essentially complete in 0.5 hr. ^b Yield based on 2-nitropropane not recovered. ^c Acetone, isolated as its 2,4-dinitrophenylhydrazone. ^d Recovered 2-nitropropane. ^e The reaction mixture was refluxed. ^f Yields of **1** as high as 84% have been obtained under these conditions.

Silver salts of other secondary nitro compounds decompose rapidly in water–dimethyl sulfoxide to oxidative dimers in good yields. On the basis of the secondary nitronates studied, the method is reliable and of general advantage for preparing vicinal tertiary dinitro compounds. Thus silver 9-fluorenenitronate, cyclohexanenitronate, and 1-phenyl-1-ethanenitronate,

(13) Although there are experimental features which make acetonitrile more desirable than dimethyl sulfoxide as a solvent in these oxidations (see Experimental Section), dimethyl sulfoxide is preferred because higher yields of vicinal oxidative dimers are obtained.

respectively, give 9,9'-dinitro-9,9'-bifluorenyl (**28**, 60%) and fluorenone (**27**, 33%), 1,1'-dinitrobicyclohexyl (**2**, 49%) and cyclohexanone (40%), and isomeric 2,3-dinitro-2,3-diphenylbutanes (63%) and acetophenone.

Decompositions of silver 1-propanenitronate, a primary nitronate, were effected homogeneously in dimethyl sulfoxide or acetonitrile as above for secondary nitronates and heterogeneously in water as described previously.¹ In all experiments the yields of oxidative dimers and propionaldehyde are low, and the products are more complex than those from silver salts of secondary nitro compounds. Decomposition of silver 1-propanenitronate thus yields 3,4-dinitrohexanes (**16**, 6–23%) and propionaldehyde (**17**, 6–12%); 1-nitropropane (**20**), 1,1-dinitropropane (**37**, 10–22%), and 3-nitro-3-hexene (**18**, trace) are also formed.¹⁴ With water–acetonitrile as solvent, **16** is not obtained; the products are 4-nitro-3-hexanol (22–28%), **37** (17–22%), **17** (6%), and **20**. Silver 2-methyl-1-propanenitronate in water–dimethyl sulfoxide decomposes very inefficiently to *dl*-2,5-dimethyl-3,4-dinitrohexane (**22**); the major reactions lead to 2-methyl-1,1-dinitropropane (32%) and isobutyraldehyde (18%) and regeneration of 2-methyl-1-nitropropane. Decomposition of such silver primary nitronates is not a satisfactory synthetic method for preparing vicinal secondary dinitro alkanes. It is apparent that oxidative decomposition of these silver alkane nitronates leads in part to silver nitrite, and the silver 1-alkane nitronates undergo oxidative nitration with silver nitrite to give 1,1-dinitro alkanes (as in eq 14) in competition with oxidative dimerization



to vicinal secondary dinitro compounds. Silver phenylmethanenitronate, however, does not undergo extensive decomposition to silver nitrite and subsequent oxidative nitration to phenyldinitromethane (2%) under the above conditions. Its principal products are *dl*-1,2-dinitro-1,2-diphenylethane (**6**, 35%), *cis*- (**8**) and *trans*- α -nitrostilbene (32%), and benzaldehyde (**7**, 18%).¹⁵

Possible thermolysis of silver nitronates was extended to 1,1-dinitro compounds. Reaction of the potassium salt of 1,1-dinitroethane with silver nitrate in dimethyl sulfoxide does not result in oxidative decomposition. Even after 7 days at 45°, silver is not precipitated from a homogeneous solution of silver 1-nitroethanenitronate in dimethyl sulfoxide in light. Silver salts of 1,1-dinitro alkanes are much more stable than those of mononitro compounds. Additional methods for oxidizing 1-nitro alkane nitronates are being investigated.

Experimental Section

Reagents.—Ammonium persulfate (J. T. Baker, ARG, 99.1%) was used the most extensively as the persulfate oxidant. Occasionally, sodium persulfate (Eimer and Amend, assay unknown) and potassium persulfate (Matheson Coleman and Bell, RG, 98%) were used. Technical 1-nitropropane, 2-nitropropane,

(14) As the reaction temperature is increased, conversion into **16** decreases even further.

(15) No attempt was made to maximize conversion into oxidative dimers in this system. *meso*-1,2-dinitro-1,2-diphenylethane (**5**) was not obtained; it, along with **6**, might have undergone conversion into **8** and *trans*- α -nitrostilbene in the present experiments.

and 1-nitrobutane were washed with aqueous sodium bicarbonate (10%) and rectified over boric acid before use. 2-Methyl-1-nitropropane,^{16a} 1-nitro-1-phenylethane,^{16b} 1-(1-cyclohexenyl)-1-nitroethane,^{16c} potassium 9-fluorenenitronate,^{16d} 1,1-dinitroethane,¹¹ 1,1-dinitropentane,¹¹ and phenyldinitromethane^{16e} were prepared by adaptation of known procedures.

Technical acetonitrile and dimethyl sulfoxide were used as solvents for the oxidations with silver nitrate. Acetonitrile has the advantage over dimethyl sulfoxide in that it is more easily removed, the products are cleaner, and lower reaction temperatures can be used. Dimethyl sulfoxide is superior, however, with respect to yields.

Sodium Phenylcyanomethanenitronate.¹⁷—A mixture of phenylacetone (234 g, 2.0 mol) and amyl nitrate (373 g, 2.8 mol, Ethyl Corp., Baton Rouge, La.) at 0° was added over a 1-hr period to a well-stirred solution of sodium (4.6 g, 2.0 g-atom) in absolute ethanol (600 ml) at 4–10°. The mixture was stirred for 1 hr at 5° and stored in ice-salt for 24 hr. The precipitate was filtered and washed with ethyl ether. After the combined ether-ethanol filtrate had been vacuum evaporated to dryness, the sodium phenylcyanomethanenitronate was triturated with ether, filtered, and washed with ether, yield 360 g (98%) of white material.

Phenylnitromethane (4).¹⁷—Sodium phenylcyanomethanenitronate (360 g, 1.96 mol) was added in small portions over a 1-hr period to a stirred, refluxing solution of sodium hydroxide (300 g, 7.5 mol) in water (1000 ml). Copious evolution of ammonia occurred after addition of the sodium salt. The mixture was boiled for 2.5 hr and cooled to 30°, and ice (600 g) was added. The vigorously stirred mixture was acidified at 0–10° with concentrated hydrochloric acid (825 ml) and extracted with ethyl ether. The combined ether extracts were washed with cold aqueous saturated sodium bicarbonate, ice-water containing a few drops of hydrochloric acid, and ice-water. The ether solution was dried (Na₂SO₄), concentrated at reduced pressure, and distilled twice to obtain 4: yield 195–206 g (71–75%); bp 76–79° (2 mm); *n*_D²⁰ 1.5287; strong ir absorption at 6.4 μ (C–NO₂), none for C=O or C–ONO. *Caution:* fuming of 4 was experienced in initial distillation.

Homogeneous Reaction of Sodium Phenylmethanenitronate with Ammonium Persulfate.—Ammonium persulfate (15.7 g, 0.069 mol) in water (55 ml) adjusted to pH 8 by 10% aqueous sodium hydroxide was added dropwise to stirred 4 (19.0 g, 0.138 mol) in water (100 ml)—sodium hydroxide (8.1 g, 0.202 mol, pH 11.7) at <10°. Within 15 min a yellow-white solid precipitated. The pH of the reaction mixture was 9.3 upon addition of the oxidizer, remained at 8–9 for 10 hr, and changed gradually and stabilized at 6.0–6.3 during the next 10 hr.

The mixture was filtered and the solid was washed with water and dried. Addition of ethyl ether and petroleum ether to the solid gave yellow *cis*-α-nitrostilbene (8), yield 8.0 g (58.4%), mp 73–74° (from ethanol), no depression by authentic 8. Concentration of the filtrate gave yellow α,β,γ-triphenyl-α-nitropropene (11), yield 0.25 g (1.9%), mp 101–103° (from ethanol) (lit.¹⁸ mp 102–103°).

Anal. Calcd for C₂₁H₁₇NO₂: C, 80.01; H, 5.39; N, 4.47. Found: C, 80.04; H, 5.50; N, 4.50.

The alkaline filtrate and the aqueous washes were cooled, acidified to pH 4.5 with aqueous urea-acetic acid, and continuously extracted with ethyl ether. The ether extract was washed with water, 5% aqueous sodium bicarbonate, hydrochloric acid (0.1 N), and water, dried (Na₂SO₄), filtered, and evaporated.

The aqueous filtrate and washings were acidified further with hydrochloric acid. An aliquot of this solution, upon reaction with excess 2,4-dinitrophenylhydrazine reagent, gave benzaldehyde 2,4-dinitrophenylhydrazone (mp 235.5–236.5°, no depression by authentic sample) corresponding to 4.8% benzaldehyde (7, 0.0059 mol) in the combined solution.

Evaporation of the ether extract yielded an oil, from which separated white 3,4,5-triphenylisoxazole (13), yield 0.29 g

(2.4%), mp 210–212°, no depression by authentic 13. Distillation of the residue gave 7, yield 2.40 g (18.5%), characterized as its semicarbazone, mp 220–221°, and 4, yield 2.2 g (11.6%), bp 82–84° (2–3 mm), *n*_D²⁰ 1.5323, ir absorption essentially identical with that of initial 4. Crystallization of the distillation residue from petroleum ether yielded white 3,4,5-triphenylisoxazole oxide (12), yield 0.17 g (1.3%), mp 161–162.5°, no depression by authentic 12.

Heterogeneous Reaction of Sodium Phenylmethanenitronate with Ammonium Persulfate.¹⁹—A solution of ammonium persulfate (65 g, 0.285 mol), sodium acetate (41.2 g, 0.5 mol), and water (150 ml) was added rapidly at 10–20° to a stirred mixture of phenylnitromethane (4, 13.02 g, 0.095 mol), water (65 ml), sodium hydroxide (5.5 g, 0.138 mol), and chloroform (70 ml). The pH dropped from 9.1 to 6.8 over a 1-hr period. The mixture was filtered, washed with water, and air dried to give white *meso*-1,2-dinitro-1,2-diphenylethane (5), yield 1.28 g (10.7%), mp 239° (lit.³ mp 235–237°).

The aqueous layer was extracted with chloroform. Concentration of the chloroform extracts and addition of ethyl ether gave white *dl*-1,2-dinitro-1,2-diphenylethane (6), yield 7.07 g, mp 150–152°, no depression by authentic 6.

Concentration of the ethereal filtrate gave a residue (4.58 g) which at 0° precipitated 12, yield 0.03 g (0.35%), mp 162–164° (from ethanol). An aliquot of the residue was converted into benzaldehyde semicarbazone, mp 222–223°; the derivative corresponds to 0.052 g (16.3%) of 7 in the residue. A second aliquot (ca. 0.11 g) was dissolved in aqueous sodium hydroxide (0.1 N, 75 ml); analysis of a 10-ml sample diluted to 1000 ml at 290 nm (pure sodium phenylmethanenitronate has an extinction coefficient of 20,000 at 291 nm) revealed that 6.4% 4 (0.83 g, 6.1 × 10⁻³ mol) was present. A third aliquot (0.5 g) in benzene-Skellysolve B was chromatographed on silicic acid using Skellysolve B (10 ml) as prewash and 10% ethyl ether-Skellysolve B (75 ml) as developer. The top band, on elution with ethyl ether, gave benzamide (15), mp 127–129°, corresponding to 0.21 g (2.5%) in the residue. The lower band gave 6, mp 145–146°, corresponding to 0.69 g in the residue. Crystallization of the residue from ethanol resulted in 13, yield 0.19 g (2.5%), mp 215°.

Evaporation of the aqueous extract and trituration of the residue with ethyl ether gave, upon removal of solvent, benzoic acid (14), mp 121°.

Conversion of *meso*-1,2-Dinitro-1,2-diphenylethane (5) by Sodium Acetate into *cis*-α-Nitrostilbene (8).—Water was added to 5 (0.20 g, 7.4 × 10⁻⁴ mol) in hot methanol (100 ml) until the solution became near-cloudy. Sodium acetate (0.061 g, 7.4 × 10⁻⁴ mol) was then added and the mixture was refluxed for 10 min. After standing for several hours, the solution was extracted with ethyl ether. The ether extract, after drying (MgSO₄) and vacuum evaporation, gave 8, yield 0.16 g (97%), mp 69–70.5°, no depression by authentic 8.

Conversion of *dl*-1,2-Dinitro-1,2-diphenylethane (6) by Sodium Acetate into *cis*-α-Nitrostilbene (8).—A mixture of sodium acetate (0.061 g, 7.4 × 10⁻⁴ mol), 6 (0.20 g, 7.4 × 10⁻⁴ mol), and methanol (20 ml) containing a few drops of water was refluxed for 10 min. The mixture was kept at 20–25° for 1 hr; 8, yield 0.08 g, mp 71–72.5°, precipitated during this period. The alcoholic solution was extracted with ethyl ether. The combined ether extracts were dried (MgSO₄) and evaporated. The yellow residue (0.09 g) was dissolved in benzene (3 ml) and chromatographed on silicic acid using Skellysolve B as prewash and 10% ethyl ether-Skellysolve B as developer (35 ml). The yellow band was eluted with ethyl ether. The eluent was dried and evaporated, giving additional 8, yield 0.07 g (91%), mp 69–70.5°.

Conversion of *dl*-1,2-Dinitro-1,2-diphenylethane (6) by Sodium Hydroxide into 3,4,5-Triphenylisoxazole (13).—Reaction of 6 (2.0 g, 0.0074 mol) with aqueous 30% sodium hydroxide (50 ml) at 80–90° for 4 hr gave a solid which was washed with water and a little ethanol and recrystallized from ethanol-acetic acid to give white 13, yield 0.5 g (63%), mp 213–215°, no depression by authentic 13.

Reaction of Sodium 1-Propanenitronate with Sodium Persulfate Catalyzed by Silver Ion.—This experiment is a prototype of that for oxidation of 1-propanenitronate, as summarized in Table II.

(16) (a) N. Kornblum, H. O. Larson, R. K. Blackwood, D. D. Mooberry, E. P. Oliveto, and G. F. Graham, *J. Amer. Chem. Soc.*, **78**, 1497 (1956); (b) N. Kornblum, R. A. Smiley, R. K. Blackwood, and D. C. Iffland, *ibid.*, **77**, 6269 (1955); (c) H. Fraser and G. F. Kon, *J. Chem. Soc.*, 604 (1934); (d) W. Wislicenus and M. Waldmuller, *Chem. Ber.*, **41**, 3338 (1908); (e) L. F. Fieser and W. E. Doering, *J. Amer. Chem. Soc.*, **68**, 2252 (1946).

(17) This is a significantly improved procedure over that of A. H. Blatt, "Organic Syntheses," Coll. Vol. II, 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1943, p 512.

(18) F. Heim, *Chem. Ber.*, **44**, 2022 (1911).

(19) This experiment is a prototype of those in Table I.

Sodium persulfate (205 g, 0.9 mol) and sodium acetate (123 g, 1.5 mol) in water (500 ml) and then 10% aqueous silver nitrate (5.9×10^{-3} mol) were added to a stirred mixture of 1-nitropropane (20, 26.7 g, 0.3 mol), 10% aqueous sodium hydroxide (150 ml), and chloroform (500 ml) at 10–20°. After 1 hr the pH of the mixture was 6.7. The silver deposited and the aqueous and chloroform layers were separated. The aqueous portion (A) was extracted with chloroform. The chloroform extracts were washed with 5% aqueous sodium bicarbonate and dilute hydrochloric acid, dried (MgSO_4), and distilled to give distillate B and residue C. The aqueous washings D were acidified.

Extract A was steam distilled into D. An aliquot of this solution, when treated with excess 2,4-dinitrophenylhydrazine, gave propionaldehyde 2,4-dinitrophenylhydrazone, mp 156–158° from ethanol, no depression by authentic sample, corresponding to 5.8 g of propionaldehyde (17) in A–D. Rectification of B and the most volatile component of C gave additional 17, 0.35 g, analyzed as its 2,4-dinitrophenylhydrazone, and 20: yield 0.83 g (3.1%), bp 49–53° (50 mm); n_D^{20} 1.4016–1.4020 (lit.²⁰ n_D^{20} 1.4015). The total conversion into 17 was 40%.²¹

Residue C, on distillation, gave (1) a mixture (1.26 g) of 4-acetoxy-3-nitrohexane (19) and 3-nitro-3-hexene (18), bp 52–69° (10 mm), n_D^{20} 1.4382–1.4555, and (2) 3,4-dinitrohexanes (16), yield 5.46 g (49.5%) of pale yellow liquid, bp 50–54° (0.3 mm), n_D^{20} 1.4512. Fraction 1 was separable by chromatography or by distillation to (1) 18, yield 0.3 g (1.6%), a pale yellow lachrymator, bp 62–65° (10 mm), n_D^{20} 1.4580 [authentic 18 from 19 and sodium acetate, bp 66–66.5° (10 mm), n_D^{20} 1.4580]; and (2) 19, yield 0.75 g (2.7%), a colorless liquid, bp 90–93° (10 mm), n_D^{20} 1.4347 (the chromatographic and the spectral properties are essentially identical with those of authentic 19).

Fraction 2 was distilled into various fractions of 19: bp 67° (1.3 mm); mp ca. 27°; n_D^{20} 1.4431.

Anal. Calcd for $\text{C}_8\text{H}_{12}\text{N}_2\text{O}_4$: C, 40.91; H, 6.83; N, 15.85. Found: C, 40.72; H, 6.97; N, 15.37.

The structure of 16 was confirmed upon its reaction (1.0 g, 5.68×10^{-3} mol) with aqueous sodium hydroxide (6.1×10^{-3} mol) for 45 min, extraction of a subsequent ethereal solution with dilute hydrochloric acid, work-up, and vacuum distillation to 18: yield 0.62 g (85%); n_D^{20} 1.4575; ir 6.6 and 7.5 ($\text{C}=\text{CNO}_2$) and 6.0μ ($\text{C}=\text{C}$); its properties are essentially identical with those of authentic 18.

Reaction of Sodium 1-Butanenitronate with Ammonium Persulfate Catalyzed by Silver Ion.—Oxidation of a heterogeneous mixture of 1-nitrobutane (27 g, 0.26 mol) in aqueous 10% sodium hydroxide (130 ml) and chloroform (450 ml) at 10–20° was effected at pH ca. 11.0 upon addition of ammonium persulfate (178 g, 0.78 mol), sodium acetate (107 g, 1.3 mol) in water (300 ml), and aqueous silver nitrate (4.3×10^{-3} mol). The reaction mixture was handled essentially identically with those from sodium 1-propanenitronate and sodium persulfate. The following materials were obtained: (1) butyraldehyde, yield 4.25 g (27%), as its 2,4-dinitrophenylhydrazone, mp 121–122°, no depression by an authentic sample; (2) 1-nitrobutane, yield 4.3 g (16%), bp 76–77° (67 mm), n_D^{20} 1.4106 (lit.²⁰ n_D^{20} 1.4112); (3) 5-acetoxy-4-nitrooctane, yield 0.44 g (ca. 2%), contaminated slightly with 4-nitro-4-octene, bp 64° (2 mm), n_D^{20} 1.4457; (4) 4-nitro-4-octene, yield 5.63 g (32%), pale yellow lachrymator, bp 66–68° (2 mm), n_D^{20} 1.4590–1.4597 [lit.²⁰ bp 93° (10 mm), n_D^{20} 1.4593], ir 6.6 and 7.5 ($\text{C}=\text{CNO}_2$) and 6.0μ ($\text{C}=\text{C}$); and (5) 4,5-dinitrooctanes, yield 2.70 g (12%), yellow oil, bp 85–87° (0.5 mm), n_D^{20} 1.4517, ir 6.4 and 7.5 μ (CNO_2). The dinitrooctanes were contaminated with some 4-nitro-4-octene as a result of decomposition during distillation.

Anal. Calcd for $\text{C}_8\text{H}_{16}\text{N}_2\text{O}_4$: C, 47.05; H, 7.85; N, 13.71. Found: C, 47.52; H, 7.47; N, 13.86.

Reaction of Sodium 2-Methyl-1-propanenitronate and Ammonium Persulfate Catalyzed by Silver Ion.—Aqueous silver nitrate (4.5×10^{-3} mol) was added to a mixture of 2-methyl-1-nitropropane (30.9 g, 0.3 mol), 10% aqueous sodium hydroxide (150 ml), ammonium persulfate (205 g, 0.9 mol), sodium acetate (123 g, 1.5 mol), chloroform (500 ml), and water (300 ml) at 10°. After 1 hr the chloroform solution was washed with 5% sodium bicarbonate, dilute hydrochloric acid, and water.

(20) H. B. Hass and E. F. Riley, *Chem. Rev.*, **32**, 373 (1943).

(21) In all experiments in which aldehydes or ketones were analyzed as precipitated 2,4-dinitrophenylhydrazones, the data were corrected to include losses of the derivatives owing to their solubilities under the experimental conditions.

Analysis of the combined aqueous extracts and an aliquot of the chloroform solution by reaction with 2,4-dinitrophenylhydrazine (mp 179.5°, no depression by an authentic sample) showed formation of isobutyraldehyde in 38% yield. Distillation of the chloroform solution gave (1) 2-methyl-1-nitropropane, yield 8.4 g (27%), bp 65–67° (60 mm), n_D^{20} 1.4080, identical with initial material; (2) 4-acetoxy-2,5-dimethyl-3-nitrohexane, yield 3.7 g (15%), bp 64–68° (0.5 mm), n_D^{20} 1.4389, essentially identical with authentic material; and (3) a residue which solidified on cooling. Addition of ethyl and petroleum ether to the semisolid gave white, unstable *dl*-2,5-dimethyl-3,4-dinitrohexane (22), yield 3.0 g (13%), mp 123–124°, upon recrystallization from Skellysolve B and acetone.

Anal. Calcd for $\text{C}_8\text{H}_{16}\text{N}_2\text{O}_4$: C, 47.05; H, 7.88; N, 13.71. Found: C, 47.56; H, 7.67; N, 13.63.

Evaporation and recrystallization of the residue gave *meso*-2,5-dimethyl-3,4-dinitrohexane (21), yield 0.82 g (4%), mp 80–83°.

Anal. Calcd for $\text{C}_8\text{H}_{16}\text{N}_2\text{O}_4$: C, 47.05; H, 7.88; N, 13.71. Found: C, 47.54; H, 7.65; N, 13.62.

Partial Resolution of *dl*-2,5-Dimethyl-3,4-dinitrohexane (22).—A solution of 22 (0.80 g, 3.92×10^{-3} mol) and *l*-brucine (0.52 g, 1.31×10^{-3} mol) in benzene (80 ml) was stored at 25° for 5 hr. The mixture was washed with water, hydrochloric acid (0.05 *N*), and saturated aqueous sodium chloride, dried (MgSO_4), and concentrated *in vacuo* to give a yellow-white solid: yield 0.76 g; mp 120°; $[\alpha]_D^{20}$ 1.4° (α 0.17°, c 6.0, l = 2 dm).

Additional *l*-brucine (0.5 g) was added to the solid in benzene (80 ml) and the mixture was refluxed for 1 hr. The solution on treatment as above yielded a yellow semisolid (0.26 g). Addition of petroleum ether gave a white solid: mp 115–118° after recrystallization from Skellysolve B–acetone; mixture melting point with 22, no depression; ir almost identical with 22; $[\alpha]_D^{20}$ 11° (α 0.74°, c 3.3, l = 2 dm).

The above procedure with 21 gave no optical rotation in the recovered material.

2,5-Dimethyl-3-nitro-3-hexene.—Isobutyraldehyde (42 g, 0.585 mol), 2-methyl-1-nitropropane (61 g, 0.59 mol), aqueous 10 *N* sodium hydroxide (8 ml), and 95% ethanol were stirred for 72 hr at 30–38°. The mixture was acidified with hydrochloric acid, neutralized, washed, and vacuum distilled to give 2,5-dimethyl-4-nitro-3-hexanol: yield 25.6 g (49%); bp 94–97° (10 mm); n_D^{20} 1.4486; ir 6.4 and 7.2 (NO_2) and 2.9μ (OH).

2,5-Dimethyl-4-nitro-3-hexanol (25.6 g, 0.144 mol), acetic anhydride (16 g, 0.154 mol), and sulfuric acid (0.5 ml) were stirred at 40–70° for 2.5 hr and then distilled to yield 4-acetoxy-2,5-dimethyl-3-nitrohexane: yield 21.7 g (73%); bp 86–87° (2–2.5 mm); n_D^{20} 1.4387; ir 6.4 and 7.2 (CNO_2) and 5.7 and 8.1 μ (CO_2).

4-Acetoxy-2,5-dimethyl-3-nitrohexane (22 g, 0.101 mol) and anhydrous sodium acetate (12.0 g) were heated slowly at 115° (15 mm). The product that distilled at 70–80° (15 mm) was dissolved in ethyl ether, washed with aqueous 5% sodium bicarbonate, dilute hydrochloric acid, and water, dried (MgSO_4), and fractionated to give 2,5-dimethyl-3-nitro-3-hexene: yield 10.0 g (64%); bp 74–76° (10 mm); n_D^{20} 1.4506; ir 6.6 and 7.4 ($\text{C}=\text{CNO}_2$) and 6.0μ ($\text{C}=\text{C}$).

Anal. Calcd for $\text{C}_8\text{H}_{16}\text{NO}_2$: C, 61.12; H, 9.62; N, 8.79. Found: C, 61.28; H, 9.94; N, 8.51.

Reaction of Sodium 1-Phenyl-1-ethanenitronate (23) with Ammonium Persulfate.—Ammonium persulfate (30.6 g, 0.134 mol) and sodium acetate trihydrate (45.5 g, 0.335 mol) in water (100 ml) was added to 1-nitro-1-phenylethane (30 g, 0.067 mol) and sodium hydroxide (3.35 g, 0.0837 mol) in water (32 ml) at 0–5°. After 7 hr (pH change of ca. 11 to 6.5) the aqueous layer was extracted with chloroform and ethyl ether. The organic extracts were washed with 5% sodium bicarbonate, dilute hydrochloric acid, and water, dried (MgSO_4), and distilled to give (1) acetophenone, yield 4.96 g (71%), bp 34–36° (0.3 mm), n_D^{20} 1.5328–1.5334, identified as its 2,4-dinitrophenylhydrazone, mp 253–254° (from ethanol), no depression by an authentic sample; and (2) 1-nitro-1-phenylethane, yield ca. 1.0 g (10%), bp 53° (0.3 mm), n_D^{20} 1.5214, spectral and chromatographic properties identical with initial material.

Oxidation of Sodium 1-(1-Cyclohexenyl)-1-ethanenitronate (24) with Ammonium Persulfate Catalyzed by Silver Ion.—On addition of ammonium persulfate (43 g, 0.19 mol) and sodium acetate trihydrate (43.5 g, 0.32 mol) in water (60 ml) to 1-(1-cyclohexenyl)-1-nitroethane (10 g, 0.0645 mol) in 10% sodium hydroxide (33 ml) and chloroform (50 ml) at 9°, the pH changed from 11.6 to 8.7. Aqueous 10% silver nitrate (1.5 ml) was then

introduced; in 1 hr the pH was *ca.* 6.0. The aqueous layer was extracted with chloroform and with ethyl ether. The organic extracts were concentrated *in vacuo*. An aliquot of the concentrate dissolved in methanol, on addition to 2,4-dinitrophenylhydrazine, gave 1-cyclohexenyl methyl ketone 2,4-dinitrophenylhydrazone, mp (from ethanol) 205–207°, no depression by an authentic sample,²² corresponding to a yield (4.5 g) of 1-cyclohexenyl methyl ketone of 66%.

The remainder of the concentrate was stirred with excess 10% sodium hydroxide at 0° and extracted with ethyl ether. The ether extract was washed with saturated sodium chloride containing a few drops of hydrochloric acid, dried (MgSO₄), and distilled, yielding 1-cyclohexenyl methyl ketone: bp 58–59° (2.5 mm); *n*_D²⁰ 1.4861 (lit.²³ *n*_D²⁰ 1.4881); *ir* 5.8 (C=C) and 6.0 μ (C=C).

The basic, aqueous layer, after acidification with acetic acid-urea-water at 0–5°, was extracted with ethyl ether. The ether extract, after having been washed with 5% sodium bicarbonate and saturated aqueous sodium chloride containing a trace of hydrochloric acid, dried (MgSO₄), and distilled, resulted in 1-(1-cyclohexenyl)-1-nitroethane, yield 1.5 g, (15%), bp 75–79° (2.5 mm), identical with initial material.

Reaction of Potassium 9-Fluorenenitronate (26) with Potassium Persulfate.—Potassium persulfate (10.8 g, 0.04 mol), water (250 ml), and a few drops of aqueous 10% potassium hydroxide were added to a stirred, heterogeneous mixture of 26 (5.0 g, 0.02 mol), water (60 ml), benzene (60 ml), and sufficient aqueous potassium hydroxide to bring the pH to *ca.* 9.0. Aqueous potassium hydroxide was added periodically to maintain the pH at 8–9.5 at 20–30°. After 4 hr, the pH of the mixture was raised to pH *ca.* 12.0 by addition of potassium hydroxide and the benzene layer was separated. The aqueous layer was extracted with benzene and ethyl ether. The organic extracts were dried (MgSO₄) and concentrated. Addition of benzene and petroleum ether gave 9,9'-dinitro-9,9'-bifluorenyl (28), yield 0.55 g (13%), mp 181–182° (from benzene-petroleum ether), no depression by an authentic sample. Concentration of the filtrate and cooling yielded fluorenone, yield 2.6 g (72%), mp 82–83°, no depression by an authentic sample.

Reaction of Sodium 1-Nitropentane-1-nitronate (33) with Ammonium Persulfate.—Ammonium persulfate (98 g, 0.428 mol) in water (144 ml) was added to 1,1-dinitropentane (18.5 g, 0.144 mol) in aqueous 10% sodium hydroxide (63 ml). The mixture was warmed to 30–40° for 8.5 hr, heated to 53–55° (the pH dropped to 5.3), cooled, and acidified with dilute hydrochloric acid to pH *ca.* 1.5.

The aqueous layer was extracted with ethyl ether. The residue obtained, upon evaporation of the organic extracts, was triturated with ethyl ether and Skellysolve F and cooled. Valeramide separated, yield 2.28 g, mp 104–105°, no depression by an authentic sample.

The ethyl ether-Skellysolve F filtrate was evaporated and distilled to give a volatile fraction, yield 4.54 g, bp 75–90° (10 mm), and a residue. Addition of Skellysolve F to the residue precipitated additional valeramide, yield 1.55 g, mp 104–105°; the valeramide produced in this experiment totaled 55%. The distillate exhibited strong infrared absorption at 3.0–3.5 (CO₂H) and 6.3 μ [C(NO₂)₂]. An aliquot (10 ml) of the distillate (0.1643 g) in 0.1 N sodium hydroxide (100 ml) was diluted to 1000 ml and analyzed at 226 and 386 μ . The aliquot corresponds to 4.47 g of 1,1-dinitropentane (24.5% recovery) in the distillate. The valeric acid, as determined by difference, totaled 1.07 g (35%).

The aqueous layer was evaporated and the residue was triturated with ethyl ether. The ether extract, on evaporation, yielded a residue which gave strong absorption for a carboxyl group and which, when refluxed with thionyl chloride and then poured into cold ammonia, gave valeramide, mp 104–105°, no depression by an authentic sample.

Reaction of Sodium 2-Propanenitronate with Silver Nitrate.—A series of decompositions of silver 2-propanenitronate were effected (Table III) under differing conditions of temperature and time using dimethyl sulfoxide-water or acetonitrile-water as solvents. All oxidations were conducted as follows.

Sodium hydroxide (5.92 g, 0.148 mol), water (35 ml), and 2-nitropropane (13.4 g, 0.15 mol) were added rapidly to silver

nitrate (25.5 g, 0.15 mol) in either dimethyl sulfoxide or acetonitrile and stirred for the time indicated.

After the reaction was complete, the silver was filtered. Water (0.5–1.5 l.) was added to the filtrate and the mixture was cooled to 0–5°. 2,3-Dimethyl-2,3-dinitrobutane (1) was filtered, washed with water, and dried. An aliquot of the filtrate was dissolved in 2,4-dinitrophenylhydrazine reagent. The remaining aqueous filtrate was acidified with acetic acid-water-urea at 0° and extracted with ethyl ether. The ether extract was washed with water, aqueous sodium bicarbonate, and dilute sulfuric acid, dried (MgSO₄), and concentrated. The oily residue was dissolved in minimal ethyl ether, a large quantity of Skellysolve F was added, and additional 1 was filtered. The ethereal filtrate was concentrated and the 2-nitropropane recovered was distilled.

Reaction of Potassium Cyclohexanenitronate with Silver Nitrate.—A solution of nitrocyclohexane (12.9 g, 0.1 mol), potassium hydroxide (5.6 g, 0.1 mol), and water (40 ml) was added rapidly to a stirred mixture of silver nitrate (17.0 g, 0.1 mol) in dimethyl sulfoxide (400 ml) at 30°. After 5.5 hr, the silver was filtered and washed with warm chloroform. Water (*ca.* 1.5 l.) was added to the combined filtrate. The filtrate was extracted with chloroform and ethyl ether and analyzed for cyclohexanone via precipitation of its 2,4-dinitrophenylhydrazone.

Concentration of the organic extracts *in vacuo* gave a viscous residue and 1,1'-dinitrobicyclohexyl (2). Ethyl ether (10 ml and Skellysolve B (100 ml) were added and 2 (3.50 g) was filtered. The filtrate was washed with water, dried (MgSO₄), filtered, and cooled to 0°; additional 2 (1.03 g) precipitated, overall yield 49%, mp 217–221.5°, no depression by authentic 2.

The various filtrates after separation of 2 were concentrated and analyzed for cyclohexanone as its 2,4-dinitrophenylhydrazone and for regenerated nitrocyclohexane (3.48 g, 27%) by difference. The overall yield of cyclohexanone was 40%.

Reaction of Sodium 1-Phenyl-1-ethanenitronate with Silver Nitrate.—A solution of 1-nitro-1-phenylethane (13.8 g, 0.091 mol) and potassium hydroxide (5.04 g, 0.090 mol) in water (40 ml) was added to silver nitrate (15.6 g, 0.092 mol) in dimethyl sulfoxide (400 ml) at 20–35°. After 4 hr the silver was filtered; water (*ca.* 1 l.) was added to the filtrate. The solution was extracted with chloroform and with ethyl ether at 0°. The silver was washed with warm chloroform. The extracts were washed with water, dried (MgSO₄), and concentrated *in vacuo*. When ethyl ether and Skellysolve B were added to the residue, the solution was stored at 0°, and the precipitate was filtered, white 2,3-dinitro-2,3-diphenylbutane (3.0 g) was obtained, mp 140–141° (from ethanol-water), *ir* 6.45 μ (CNO₂).

Anal. Calcd for C₁₆H₁₆N₂O₄: C, 63.99; H, 5.37; N, 9.32. Found: C, 64.34; H, 5.56; N, 9.08.

The ethereal filtrate, on vacuum distillation, gave a mixture of acetophenone and 1-nitro-1-phenylethane, yield 5.53 g, bp 32–58° (*ca.* 0.2 mm), and a residue (3.78 g) which crystallized on addition of ethanol or ethyl ether to give white 2,3-dinitro-2,3-diphenylbutane, mp 150° (from ethanol-water), *ir* 6.45 μ (CNO₂). The melting point of a mixture of the two isomeric forms of 2,3-dinitro-2,3-diphenylbutane was 100–180°. ²⁴

Anal. Calcd for C₁₆H₁₆N₂O₄: C, 63.99; H, 5.37; N, 9.32. Found: C, 63.62; H, 5.30; N, 9.17.

An aliquot of the distillation product was added to methanol and the mixture was dissolved in excess 2,4-dinitrophenylhydrazine solution. The acetophenone 2,4-dinitrophenylhydrazone was isolated, mp 250°, no depression by an authentic sample, and corresponds to 2.66 g of acetophenone in the distillate. The remainder of the distillate was 1-nitro-1-phenylethane (2.87 g, 21%). An aliquot of the initial aqueous layer and the aqueous washings gave additional acetophenone 2,4-dinitrophenylhydrazone. The total acetophenone obtained corresponded to 40% conversion of 1-nitro-1-phenylethane.

Reaction of Potassium 9-Fluorenenitronate with Silver Nitrate.—The silver, formed during a 4.5-hr period after addition of potassium 9-fluorenenitronate (10 g, 0.04 mol) in water (45 ml) to silver nitrate (7.7 g, 0.045 mol) in dimethyl sulfoxide (200 ml),

(24) Stereochemical assignments can possibly be made for the isomeric 2,3-dinitro-2,3-diphenylbutanes on the basis of their melting points. Using the generalization (R. Stern, Abstracts, 131st National Meeting of the American Chemical Society, Miami, Fla., Apr 1957, No. 5-0)—of diastereoisomeric compounds containing two identically substituted acyclic centers of asymmetry, the *meso* modification will have the higher melting point than either the racemic or the optically active epimer provided that it is centrosymmetrical—thus the 2,3-dinitro-2,3-diphenylbutane having the melting point of 150° would be assigned as the *meso* isomer.

(22) W. H. Linnell and C. C. Shen, *J. Pharm. Pharmacol.*, **2**, 13 (1950).

(23) L. Ruzicka, D. R. Koolhaas, and A. H. Wind, *Helv. Chim. Acta*, **14**, 1157 (1931).

was filtered and washed with hot benzene. Water (ca. 1 l.) was added to the dimethyl sulfoxide-water filtrate and the resulting aqueous solution was extracted with benzene. The combined organic extracts were washed with saturated sodium chloride, dried (MgSO₄), and concentrated *in vacuo*. Addition of ethyl ether and petroleum ether to the semisolid and concentration of the mixture gave 9,9'-dinitro-9,9'-bifluorenyl (28), yield 5.45 g, mp 181–182°, no depression by authentic 28. Concentration, cooling, and filtration of the benzene-ethyl ether-petroleum ether filtrate gave fluorenone (27), yield 2.38 g (33%), mp 82–83°, no depression by authentic 27. Reaction of the final filtrate with hydroxylamine hydrochloride resulted in formation of fluorenone oxime, yield 0.23 g (3%), mp 194–195° (from chloroform-petroleum ether), no depression by an authentic sample.

Reaction of Sodium 1-Propanenitronate with Silver Nitrate.—The results of the following experiment are typical of those of a series for silver 1-propanenitronate in dimethyl sulfoxide-water, acetonitrile-water, and water.

A solution of sodium hydroxide (11.9 g, 0.209 mol), water (45 ml), and 1-nitropropane (20, 26.7 g, 0.3 mol) was added to silver nitrate (51 g, 0.3 mol) in dimethyl sulfoxide (375 ml)-methanol (45 ml)²⁵ at 0–5°. After 5 hr the silver was filtered. Water (ca. 1.6 l.), ethyl ether, and hydrochloric acid were added to the filtrate (pH ca. 1.5) at ca. 10° and the mixture was separated. The ether extract was washed with water, dried, and concentrated to give distillate A and residue B. The aqueous extract and washings were acidified.

Residue B was distilled to give (1) highly volatile products; (2) 20,²⁶ yield 4.7 g (19%); (3) 1,1-dinitropropane²⁶ (37), yield

(25) The methanol was added to lower the freezing point of the dimethyl sulfoxide.

(26) Identified by comparison with authentic samples.

5.7 g (17%), bp 58–60° (4–4.5 mm), *n*_D²⁰ 1.4360, ir 6.3 μ [(NO₂)₂]; (4) 4-nitro-3-hexanol²⁶ containing a small amount of 3-nitro-3-hexene, yield 2.6 g (14%), bp 85–88° (4–4.5 mm), *n*_D²⁰ 1.4458; and (5) 3,4-dinitrohexanes²⁶ (16), yield 4.0 g (18%), bp ca. 106° (4–4.5 mm), *n*_D²⁰ 1.4510. The volatile products were combined with distillate A and analyzed for propionaldehyde (17) as its 2,4-dinitrophenylhydrazone. The 1-nitropropane converted into 17 amounted to 10%.

Registry No.—Sodium phenylcyanomethanenitronate, 12385-04-5; sodium phenylmethanenitronate, 12321-46-9; ammonium persulfate, 7727-54-0; sodium 1-propanenitronate, 12384-98-4; sodium persulfate, 7775-27-1; sodium 1-butanenitronate, 12385-00-1; sodium 2-methyl-1-propanenitronate 12385-01-2; 2,5-dimethyl-4-nitro-3-hexanol, 22482-65-1; 4-acetoxy-2,5-dimethyl-3-nitrohexane, 22482-66-2; 2,5-dimethyl-3-nitro-3-hexene, 22482-67-3; potassium persulfate, 7727-21-1; sodium 2-propanenitronate, 12384-99-5; silver nitrate, 7761-88-8; potassium cyclohexanenitronate 12385-03-4; 2,3-dinitro-2,3-diphenylbutane, 22479-37-4; *meso*-2,3-dinitro-2,3-diphenylbutane, 22486-14-2; 4, 622-42-4; 16, 22482-64-0; 21, 22485-93-4; 22, 22485-94-5; 23, 12385-05-6; 24, 12385-06-7; 26, 12385-07-8; 33, 12385-02-3.

Acknowledgment.—We are pleased to acknowledge support of this research by the Office of Naval Research.

Arylation by Aromatic Nitro Compounds at High Temperatures.

VIII. Reactions of Nitrobenzene and Nitrobenzene-*d*₅ with Cyclohexane at 600°

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Received May 27, 1969

Nitrobenzene and cyclohexane at 600° give benzene, biphenyl, phenol, ethylene, propylene, and butadiene as major products. Minor products are ethylbenzene, styrene, β-methylstyrene, allylbenzene, indene, and naphthalene; these are formed by reaction of olefins derived from cyclohexane with phenyl radicals derived from nitrobenzene. Only a small amount of benzene comes from cyclohexane; dehydrogenation is mainly to cyclohexene. Phenyl radical prefers to abstract hydrogen from cyclohexane rather than add to the aromatic ring of benzene by a ratio of 16:1. The products from cycloheptane and cyclooctane are similar to those from cyclohexane; cyclopentane differs mainly in giving almost no products derived from a C₄ fragment.

Nitrobenzene decomposes above 400° to phenyl radical and NO₂.² In the presence of aromatic compounds, even of such a completely substituted benzene derivative as hexafluorobenzene, phenyl radical adds to the aromatic system to give biphenyls as the major products.³ Hydrogen abstraction is a minor process; nitrobenzene with toluene gives mainly methylbiphenyl isomers, rather than benzene and biphenyl.⁴

It was of interest, therefore, to study the behavior of nitrobenzene with compounds that contain only abstractable hydrogens and no carbon-carbon double bonds. This article describes the reactions of nitrobenzene and nitrobenzene-*d*₅ with cyclohexane, and of

nitrobenzene with cyclopentane, cycloheptane, and cyclooctane.

Experimental Section

Reactions were run in a Vycor tube filled with Vycor chips in an electric furnace maintained at 600 ± 1° under pure, dry nitrogen with contact times of 14–22 sec. The vapors were condensed in a flask at 0°; the uncondensed effluent gases were passed through a series of three traps containing bromine in chloroform at 0°. The condensates were distilled to recover unreacted material, and the residues were analyzed by gas chromatography, mass spectrometry, and directly coupled gas chromatography-mass spectrometry.⁵ The brominated products were analyzed by gas chromatography.

Gas chromatographic-mass spectral analysis was used not only to identify chromatographically separated components of product mixtures but also to determine the isotopic composition of such components from reactions with nitrobenzene-*d*₅. For the latter purpose, variation of the isotopic distribution over the

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