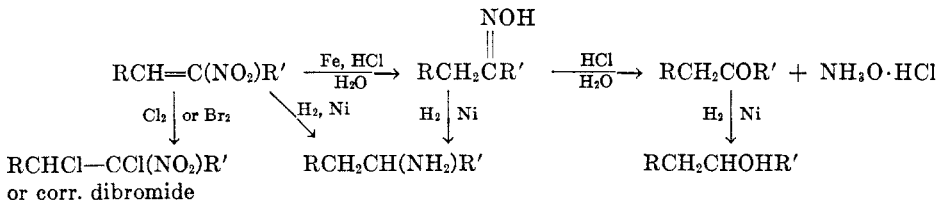
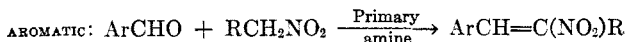
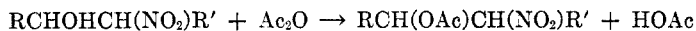
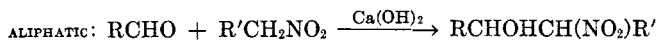


NITRO ALKENE DERIVATIVES¹

H. B. HASS,² A. G. SUSIE,³ AND R. L. HEIDER⁴

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The relatively recent enhancement of the availability of the lower nitro alkanes (1) and of the nitro alcohols (2) led to the present investigation of the nitro alkenes and their derivatives. The latter are easy to synthesize in good yields and have proved to be intermediates for the facile production of higher ketones, alcohols, amines, oximes, and dihalo nitro alkanes. The highly active double bond of the nitro alkene molecule and the ease of reduction of the nitro group open the way to further syntheses still to be investigated. The accompanying diagram indicates the generic relationships involved.



EXPERIMENTAL

The nitro alcohols and their acetate esters were obtained in good yields using the technique of Vanderbilt and Hass (2).

The purely aliphatic nitro alkenes were produced by a slight modification of the procedure of Schmidt and Rutz (3). One mole of sodium carbonate is added to a solution of two moles of nitroalkyl acetate dissolved in 200 ml. of anhydrous benzene and refluxed in a round-bottom flask for six hours. The flask is cooled and the product decanted from solids. The residue (sodium acetate) is extracted with benzene, dissolved in water, and further extracted with small portions of benzene. The benzene solution is dried over K_2CO_3 , the benzene distilled and the nitro alkene remaining is purified by distillation, usually at 10 mm., through a Podbielniak column. The nitro alkenes prepared in this way are shown in Table I.

If the aldehyde contains a formyl group attached to an aromatic nucleus the nitro alkene may be synthesized by the method of Knoevenagel and Walter (4) in a single step. This is illustrated in the preparation of *1-phenyl-2-nitropropene*. One mole each of benzaldehyde and nitroethane, 5 ml. of *n*-butylamine, and 100 ml. of absolute ethanol were refluxed

¹ Abstracted from the doctoral theses of Mr. Susie and Mr. Heider.

² Present address: General Aniline and Film Corp., 230 Park Ave., N. Y.

³ Present address: Marbon Corporation, Gary, Indiana.

⁴ Present address: Monsanto Chemical Company, Dayton, Ohio.

TABLE I
 PHYSICAL CONSTANTS OF THE NITRO ALKENES

NITRO ALKENE	BOILING POINT °C. (MM.)	REFRACTIVE INDEX AT 25°	d_4^{25}	CARBON, %	
				Calc'd	Found
2-Nitropropene.....	57.0 (100)	1.4105	1.0559	41.38	41.10
2-Nitro-2-butene.....	70.4 (30)	1.4584	1.0429	47.48	47.44
2-Nitro-2-hexene.....	82.3 (10)	1.4572	0.9824	55.77	55.74
3-Nitro-2-pentene.....	57.8 (10)	1.4590	1.0069	52.14	52.05
3-Nitro-3-heptene.....	84.4 (10)	1.4580	0.9625	58.70	58.60
3-Nitro-2-hexene.....	72.0 (10)	1.4572	.9833	55.77	55.70
4-Nitro-4-octene.....	93.0 (10)	1.4593	.9484	61.10	61.10
4-Methyl-3-nitro-2-pentene.....	64.0 (10)	1.4530		55.77	55.40
2-Methyl-3-nitro-3-heptene.....	85.5 (10)	1.4537		61.10	60.00
2-Nitro-1-butene ^a	60.5 (50)				
2-Nitro-1-pentene ^a	58.0 (20)				

^a The other physical constants of 2-nitro-1-butene and 2-nitro-1-pentene were not determined.

 TABLE II
 PREPARATION OF ARYL NITRO ALKENES

ARYL NITRO ALKENES	CON- VER- SION, %	YIELD, %	B.P., °C. (MM.)	SP. GR.	REFR. INDEX	ANALYSES			
						Calc'd		Found	
						C, %	H, %	C, %	H, %
1-Phenyl-2-nitropropene (4)	65 64	85 86.5	(m.p., 65)						
1-Phenyl-2-nitro-1-butene	70		125-129 (10) 121 (6) (m.p., 12)	1.1064 $\frac{25}{4}$	(25°) 1.5832	67.80	—	67.42	—
1-Phenyl-2-nitro-1-pentene	65-70		108-109 (3) 133-135 (6)	1.083 $\frac{25}{5}$	n_D^{25} 1.5706	69.13	6.81	68.93	6.90
1-Furyl-2-nitropropene		85-90	(m.p., 48-49)			54.91	4.61	55.05	4.65
1-Furyl-2-nitro-1-butene (6)	70		130-131 (13) 124-125 (10)						
1-Furyl-2-nitro-1-pentene (6)			136-137 (13)						
1-Anisyl-2-nitro-1-butene	35-40	90	(m.p., 56)			63.75	6.32	63.71	6.18
1-Anisyl-2-nitro-1-pentene	35-40	90	(m.p., 35-36)			65.14	6.84	65.35	6.42

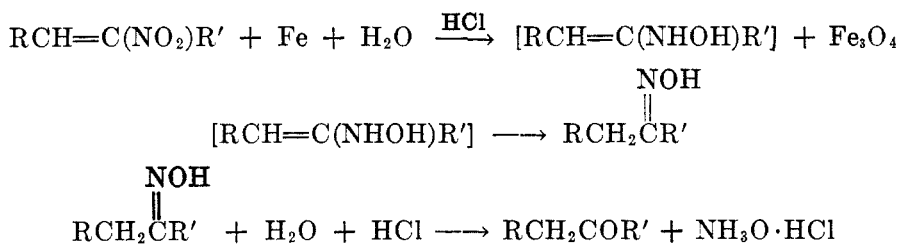
for 8 hours in a 1000-ml. round-bottom flask. When the contents were cooled and stirred a heavy, yellow, crystalline mass formed immediately. After recrystallization from absolute ethanol the product weighed 105 g. (conversion 64% of theory, yield 86.5%) with m.p. 65°.

Table II contains a list of nitro alkenes prepared thus. The method failed with ω -nitrostyrene, a poor yield of 2-nitro-1,3-diphenyl-1,3-propanediol being obtained instead. It

also failed with vanillin and nitroethane, 1-nitropropane, and 1-nitrobutane because of tar formation and with dinitroneopentane and benzaldehyde for the same reason.

REDUCTION OF NITRO ALKENES

Although nitro alkenes had been reduced by means of aluminum amalgam (5), zinc and acetic acid (5, 9) and Raney nickel and hydrogen (8), apparently no one prior to the present authors had studied the effect of cast iron turnings and dilute hydrochloric acid, which is the preferred procedure for the reduction of aromatic nitro compounds. This method proved to give good yields of either ketone or ketoxime depending upon the amount of hydrochloric acid used. The following steps are indicated.



EXPERIMENTAL

One-tenth of a mole of nitro alkene, 0.72 gram-atom (40 g.) of 40 mesh cast iron turnings, 75-100 ml. of distilled water, and 0.1 g. of ferric chloride were placed in a 500-ml. round-bottom, three-neck flask equipped with a graduated dropping-funnel, a mercury-seal stirrer, and a reflux condenser. Fifteen ml. of conc'd HCl was added dropwise for 5 to 6 hours and the temperature of the surrounding oil-bath maintained between 85 and 95°. The reaction mixture was then basified with 25% NaOH solution and distilled with steam. The distillate was extracted several times with ether, the ether distilled, and the residue rectified through a Podbielniak column at reduced pressure.

Table III indicates experiments on the reduction of 1-phenyl-2-nitropropene.

Table IV indicates the nitro alkenes reduced with iron and acid.

Table V indicates the oximes prepared either directly by reduction of nitro alkenes or by the action of hydroxylamine on ketones so prepared.

Table VI indicates the amines made by reducing the corresponding oximes with Raney nickel and hydrogen. The procedure used was as follows: A Parr hydrogenation bomb was charged with 0.04-0.06 mole of ketoxime, 6-10 g. of Raney nickel, and 75 ml. of absolute ethanol. Hydrogen was run in until the pressure was 1000-2000 p.s.i. and reduction proceeded readily at room temperature for 3-5 hours. The ethanol was distilled from the amine and this was rectified in a small modified Podbielniak column. If the hydrochloride was a crystalline solid, the amine was identified by conversion to the hydrochloride and titration with standard silver nitrate using dichlorofluorescein as an indicator.

Table VII indicates the secondary alcohols made by catalytic hydrogenation of the corresponding ketones. The procedure used was as follows: A solution of 100-150 ml. of absolute ethanol and 0.05-0.20 mole of ketone was placed in a Parr hydrogenation bomb, and freshly prepared Raney nickel (8 g. of Raney nickel per 0.1 mole of ketone) was washed into the bomb with absolute ethanol. The autoclave was then sealed and hydrogen added until the pressure was 1400-2000 p.s.i. The surrounding rocking cradle was then heated to a temperature of 125-150°, except in the case of furylacetone which was reduced at room temperature, and the rocking device started. The reduction was allowed to proceed for 5-6 hours and the contents of the bomb were washed with absolute ethanol into a beaker and the catalyst

TABLE III
SUMMARY OF EXPERIMENTS ON REDUCTION WITH IRON AND HYDROCHLORIC ACID

EXPT. NO.	MOLAR RATIO		ML./MOLE ALKENE		PRODUCT, % CONVERSION TO	
	Fe/Alkene	HCl/Alkene	Water	Solvent	Phenyl-propanone	Oxide of Phenyl propanone
101	2	0	500	0	—	20.1
102	2	0.06	500	0	5.2	49.0
103	2	0	500	0	0	0
104	2	0.10	500	0	11.3	32.5
105	2	.232	500	0	24.6	27.4
106	2	.464	500	0	36.5	23.1
108	2	0	500	0	3.7	23.8
109	2	0.06	500	0	3.7	45.0
110	2	.06	0	500 ^a	0	0
111	1	.06	500	0	trace	34.6
112	2	.06	250	500 ^a	10.5	62.6
113	2	.06	250	500 ^b	0	0
114	2	.06	250	250 ^a	10.7	45.6
116	2	.06	250	250 ^b	0	0
117	1	.06	250	250 ^b	0	0
123	2	.06	250	250 ^c	9.9	64.2
127	2	.06	250	500 ^c	9.7	63.0
128	2	1.392	500	0	41.1	20.2
129	2	1.74	500	0	56.0	13.4
130	2	1.74	1000	500 ^c	41.0	30.2
131	2	1.74	1000	500 ^b	18.7	40.3
II 4	7.15	1.74	750	0	75	0
RXY 24	7.15	1.97	670	0	77	0
132	2.5	2.00	500	0	44.7	20.2
136	2.5	0.52	500	0	10.5	37.5

^a CH₃OH. ^b C₆H₆. ^c C₂H₅OH.

TABLE IV
REDUCTION OF NITRO ALKENES WITH IRON AND HCL

REDUCTION OF	PRODUCT, YIELD, %	B.P., °C. (MM.)	SP. GR. 25°/25°	n _D ²⁰	ANALYSES			
					Calc'd		Found	
					C, %	H, %	C, %	H, %
1-Phenyl-2-nitro-propene	Phenylacetone, 75-77	215-216						
1-Phenyl-2-nitro-1-butene	1-Phenyl-2-butanone, 68	101-102 (10)						
1-Phenyl-2-nitro-1-pentene	1-Phenyl-2-pentanone, 45-50	107 (10)						
1-Furyl-2-nitro-propene	Furylacetone, 35-40	179-180						
1-Furyl-2-nitro-1-butene ^a	1-Furyl-2-butanone, 65-70	76 (11-12) 99 (27)	1.032	1.4680	69.55	7.29	69.45	7.40
1-Furyl-2-nitro-1-pentene	1-Furyl-2-pentanone, 64	95 (15)	0.999	1.4629	71.02	7.95	70.95	8.03
1-Anisyl-2-nitro-1-butene	1-Anisyl-2-butanone, 60	132 (5)	1.039	1.5101	74.14	7.92	74.33	7.92
1-Anisyl-2-nitro-1-pentene ^b	1-Anisyl-2-pentanone, 60-62	120-122 (3)	1.025	1.5120	74.99	8.39	74.92	8.12

^a 1-Furyl-2-alkanones, colorless liquids with peculiar odors, tend to become reddish brown on standing. ^b 1-Anisyl-2-alkanones are colorless liquids, stable on standing, and have characteristic, pleasant odors.

filtered from the solution. Most of the ethanol distilled from the reduction products and purification of the secondary alcohol was effected by distillation through a modified Podbielniak column under reduced pressure.

If nitro alkenes are reduced directly with Raney nickel and hydrogen, saturated amines are obtained in a single step. The reduction of 3-nitro-2-pentene in this way using 1-butanol as solvent gave a 55% yield of 3-pentylamine, identified by boiling point and m.p. of hydrochloride [217.5° (Literature, 216°)]. Some ammonium chloride was formed simultaneously.

TABLE V
PREPARATION OF OXIMES

OXIME	B.P., °C. (MM.)	SP. GR. 25°/25°	n_D^{25}	ANALYSES			
				Calc'd		Found	
				C, %	H, %	C, %	H, %
1-Phenyl-2-propanone oxime (60-65%) plus 8-12% 1-phenyl-2-propanone, from reduction of 1-phenyl-2-nitropropene	99 (2) (m.p., 68-70)						
1-Phenyl-2-butanone oxime	117-118 (2)	1.036	1.5363	73.60	8.03	74.00	7.88
1-Phenyl-2-pentanone oxime	116 (1-2)	1.017	1.5292	74.54	8.53	74.47	8.54
1-Furyl-2-propanone oxime (7)	95 (5)						
1-Furyl-2-butanone oxime	119-120 (10)	1.082	1.4980	62.72	7.23	62.82	6.83
1-Furyl-2-pentanone oxime	118 (4)	1.054	1.4935	64.66	7.84	64.66	7.92
1-Anisyl-2-butanone oxime	(m.p., 75)			68.38	7.83	68.00	7.97
1-Anisyl-2-pentanone oxime	ca. 135 (1-2) (m.p., 58-59)			69.51	8.27	69.49	8.18

TABLE VI
PREPARATION OF AMINES

Compound reduced.....	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
Ketoxime, mole.....	0.058	0.05	0.065	0.05	0.05	0.057	0.042	0.041
Raney nickel, grams.....	8	8	10	6	10	10	10	10
Ethanol, ml.....	150	75	150	75	125	125	125	100
Initial H pressure, p.s.i.....	1800	810	1900	1900	1440	1900	1240	1240
Time of reduction, hours....	2	4-5	5	3	5	5½	5	5
Temperature, °C.....	80	Room	Room	Room	Room	Room	Room	Room
Yield of amine, %.....	55	75	70	90	50	60	40	70

- | | |
|--------------------------------|--------------------------------|
| (1) 1-Phenyl-2-propanone oxime | (5) 1-Furyl-2-butanone oxime |
| (2) 1-Phenyl-2-butanone oxime | (6) 1-Furyl-2-pentanone oxime |
| (3) 1-Phenyl-2-pentanone oxime | (7) 1-Anisyl-2-butanone oxime |
| (4) 1-Furyl-2-propanone oxime | (8) 1-Anisyl-2-pentanone oxime |

Table VIII indicates the dihalides formed by addition of chlorine or bromine to various nitro alkenes. Nitro alkenes add the halogens readily giving the dihalide derivatives. These are stable, high-boiling liquids which possess an odor much milder than that of the parent nitro alkene. The dichlorides were prepared by absorbing the mole-equivalent of chlorine in a carbon tetrachloride-nitro alkene solution. The following method was employed in the preparation of the dibromides of nitro alkenes.

Two-tenths mole of bromine dissolved in 75 ml. of carbon tetrachloride was added slowly to a solution of two-tenths mole of 3-nitro-2-pentene in 25 ml. of carbon tetrachloride. The

solution was shaken vigorously and kept cool during the addition of bromine. At the end of the addition the solution had a pronounced bromine color. After standing for one day the unreacted bromine was extracted with 5% sodium hydroxide solution. The oily layer was washed with water and dried over calcium chloride. The dried sample was analyzed by distillation on a modified Podbielniak column. The dibromide fraction was collected between 98–101°/10 mm. The purified 2,3-dibromo-3-nitropentene had b.p. 100°/10 mm. Yield, 87.5%.

The dibromides of 3-nitro-3-heptene and 4-nitro-4-octene decomposed slightly upon distillation, giving off hydrogen bromide. The dichloride of 3-nitro-3-heptene, however, was quite stable at its boiling point.

TABLE VII
PREPARATION OF *sec*-ALCOHOLS

Compound reduced.....	(1)	(2)	(3)	(4)	(5)	(6)
Ketone, mole.....	0.20	0.20	0.043	0.157	0.10	0.048
Raney nickel, grams.....	15	15	6	8	8	4
Ethanol, ml.....	150	150	100	100	100	100
Initial H pressure, p.s.i.....	1800	1800	1900	1400	1600	1620
Time of reduction, hours.....	5	5	5	6	6	6
Temperature, °C.....	140	90	150	Room	125	125
Yield of <i>sec</i> -alcohol, %.....	95	80	60	55+	83+	80+

(1) Phenylacetone

(4) Furylacetone

(2) 1-Phenyl-2-butanone

(5) 1-Furyl-2-butanone

(3) 1-Phenyl-2-pentanone

(6) 1-Furyl-2-pentanone

+ Represents yield of tetrahydrofuryl-*sec*-alcohol.

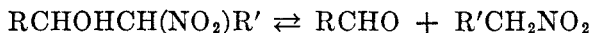
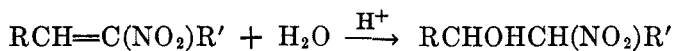
TABLE VIII
PHYSICAL CONSTANTS OF THE DIHALIDES

COMPOUND	B.P., °C. (10 MM.)	RE-FRACTIVE INDEX (25°)	d_4^{25}	HALOGEN, %	
				Calc'd	Found
1,2-Dibromo-2-nitrobutane.....	98.4	1.5217	1.9151	61.27	61.37
2,3-Dibromo-2-nitrobutane.....	60.0 (m.p.)			61.27	61.15
2,3-Dibromo-3-nitropentane.....	102.8	1.5169	1.8097	58.14	58.12
2,3-Dibromo-2-nitrohexane.....	113.0	1.5112		55.32	55.15
2,3-Dibromo-3-nitrohexane.....	111.8	1.5101	1.7057	55.32	55.37
3,4-Dibromo-3-nitroheptane.....	115.5	1.5062		52.76	51.78
4,5-Dibromo-4-nitrooctane.....	122–124	1.5018		50.44	49.90
2,3-Dichloro-3-nitropentane.....	69.4	1.4621		38.12	37.85
2,3-Dichloro-2-nitrohexane.....	89.6	1.4617	1.2170	35.46	35.53
3,4-Dichloro-3-nitroheptane.....	90.5	1.4630	1.1916	33.14	33.25

The halogen content of the dihalides was determined by the Carius sealed-tube method. Ten new dihalides of nitro alkenes are reported in Table VIII.

Hydrolysis of Nitro Alkenes

It was found that the nitro alkenes dissolve readily in sulfuric acid (3:1, H₂SO₄:H₂O by volume) with decomposition. In all cases the nitro alkene was cleaved at the double bond with the simultaneous formation of an aldehyde fragment. This may be interpreted as follows:



Polymerization of nitro alkenes. All nitro alkenes polymerize with more or less rapidity. For this reason they should be used promptly after synthesis. The polymerization products are black, viscous materials readily soluble in acetone and benzene.

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WEST LAFAYETTE, INDIANA

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