acid solution was decanted from the residual zinc, concentrated to a small volume, and cooled, giving 0.05 g. (69%) of benzylhydroxyquinolone, m.p. and mixed m.p.  $218-219^{\circ}$ .

Reaction of 1-methyl-3-benzyl-3-bromo-2,4(1H,3H)quinolindione with base. To a solution of 0.5 g. of potassium hydroxide in 12 ml. of methanol was added 0.2 g. of 1-methyl-3benzyl-3-bromo-2,4(1H,3H)quinolindione, and the reaction heated 2 hr. at reflux. The clear yellow solution was cooled, diluted with water, extracted with methylene chloride, and the aqueous layer acidified with acetic acid to give a white solid. Recrystallization from aqueous acetic acid gave 0.07 g. (45%) of 1-methyl-3-benzyl-4-hydroxy-2-quinolone, m.p. and mixed m.p. 216-218°. After 6 hr. in refluxing aqueous methanol, the bromo compound was recovered unchanged.

CLEMSON, S. C.

### [CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

# **Preparation of 1,1,1-Trichloro-3-nitro-2-alkenes**<sup>1</sup>

# G. BRYANT BACHMAN AND NORMAN W. STANDISH<sup>2</sup>

#### Received July 20, 1960

The condensation of chloral with nitro paraffins has been found to take place in the vapor phase at 360° in the presence of a magnesium sulfate-amine catalyst. Formaldehyde has also been found to condense satisfactorily with nitro paraffins under similar conditions but not a variety of other carbonyl compounds. In both cases the corresponding nitro alcohols are formed as well as the expected nitro olefins.

Nitro olefins with the general structure  $CCl_3CH=$ CRNO<sub>2</sub> were desired for other studies contemplated in this laboratory. A logical approach to these compounds appeared to lie in the condensation of chloral with nitro paraffins according to reactions (1) and (2). The first of these reactions has been reported

 $CCl_{3}CHO + RCH_{2}NO_{2} \longrightarrow CCl_{3}CHOHCHRNO_{2} \quad (1)$  $CCl_{3}CHOHCHRNO_{2} \longrightarrow CCl_{3}CH=CRNO_{2} + H_{2}O \quad (2)$ 

for R=H by Chattaway and Witherington<sup>3</sup> and for R=CH<sub>3</sub> by Chattaway, Dewitt, and Parkes.<sup>4</sup> These reactions were carried out by condensing chloral with the corresponding nitro paraffins in the liquid phase using sodium sulfite or potassium carbonate as catalysts. The second reaction was studied for R=H by Irving and Fuller<sup>5</sup> who treated this trichloronitro alcohol with phosphorus pentoxide at elevated temperatures.

It occurred to us that chloral might be caused to condense with nitro paraffins directly, and nitro olefins obtained in one step, by operating in the vapor phase over a suitable catalyst. A search of the literature revealed a patent by Hasche<sup>6</sup> claiming a similar vapor phase condensation between nitro paraffins and formaldehyde using a variety of inorganic acids and salts as catalysts. Unfortunately the patent discloses no data on yields or purity of the products. Accordingly, it was decided to re-examine this method as a preliminary step in achieving the desired syntheses.

Studies with formaldehyde and nitropropane indicated that the catalysts recommended by Hasche give only traces of 2-nitro-1-butene. Hence, a number of other substances were tested, and it was found that a combination of magnesium sulfate and amines was considerably more effective than any other catalyst. Neither the magnesium sulfate nor the amines alone gave more than a few per cent of nitro olefins while together they gave up to 40% conversion. Next an attempt was made to determine the type of amine which worked best. It was found that ammonia and primary amines were ineffective, secondary amines were moderately effective, and low molecular weight tertiary amines (C<sub>3</sub> to C<sub>6</sub>) were best.

The condensation conversions are highly dependent upon the concentration of amine catalyst in the reaction mixture and on the temperature of the reaction zone. The effective range of concentration found for triethylamine was 0.10 to 1.00 mole per cent with optimum results being obtained at about 0.23 mole per cent. Similarly the effective range of temperature in the reactor was 200° to 390° with optimum conversions being obtained at about 290-350°.

In all of the above runs 2-nitro-1-butanol was also formed. The principal factor affecting the nitro alcohol-nitro olefin ratio was the amine concentration with higher concentrations of amine favoring higher ratios of alcohol. Optimum conversions (ca. 45%) to 2-nitro-1-butanol were obtained with 2.0-4.0 mole per cent of triethylamine.

Application of the above information to the synthesis of nitro olefins from other primary nitro paraffins than 1-nitropropane showed that 1nitrobutane gave similar conversions while nitroethane gave much poorer conversions to nitro

<sup>(1)</sup> Abstracted in part from a dissertation submitted by Norman W. Standish to the Graduate School of Purdue University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, January 1960.

<sup>(2)</sup> Commercial Solvents Corporation Research Assistant. Present address: The Standard Oil Company of Ohio, Cleveland, Ohio.

<sup>(3)</sup> F. Chattaway and D. Witherington, J. Chem. Soc., 1178 (1935).

<sup>(4)</sup> F. Chattaway, J. Dewitt, and G. Parkes, J. Chem. Soc., 1294 (1936).

<sup>(5)</sup> H. Irving and H. Fuller, J. Chem. Soc., 1989 (1948).

<sup>(6)</sup> R. L. Hasche, U. S. Pat. 2,298,375 (Oct. 13, 1938).

Com- pound	M.P.	B.P. (mm.)	n <sup>20</sup>	$d_{\bullet}^{20}$	Formula	Calcd.	Found			
CCl <sub>3</sub> CHOHCHNO <sub>2</sub> R										
$R = H^{a}$	41.2	93-94(1)	<u> </u>		$C_{3}H_{4}NCl_{3}O_{3}$	C 17.28	17.28			
						H 1.93 N 6.72	1.75 6.47			
CH.		121 - 123(7)	1 5015	1 566	C.H.NCLO	C = 21.60	21.83			
0113		121 120(1)	1.0010	1.000	0411811 01303	H = 2.72	2.91			
						N 6.23	6.48			
$C_2H_5$		111-112(2)	1.4958	1.488	$C_5H_8NCl_3O_3$	C 25.98	25.87			
						H 3.41 N 5.02	3.17 5.79			
C.H.		123(3)	1 4901	1 416	CeH10NChO2	C 28.77	28.73			
03117		120 (0)	1.1001		0011101.01303	H 4.02	3.82			
						N 5.59	5.78			
CCl <sub>3</sub> CH(OCC	)CH <sub>3</sub> )CHNO <sub>2</sub> R				C II NOLO					
$R = H^{\circ}$	59-60	${190-192}$	1 4708	1 441	CH-NCLO					
C.H.	<u> </u>	120-123(2) 110(3)	1 4745	1 392	C7H19NCl3O4	C 30.17	30.44			
Ciging		110(0)	1.1110	1.001	0,11,101,01,004	H 3.62	3.81			
						N 5.03	5.17			
$C_{3}H_{7}$	_	105(2)	1.4713	1.348	$C_8H_{12}NCl_3O_4$	C 32.13	31.95			
						H 4.14	3.82			
CCLCH-CN	IO B					19 4.00	0.07			
$R = H^{o}$		62-65(1)	1.5128	1.549	$C_3H_2NCl_3O_2$	C 18.92	19.03			
						H 1.07	1.32			
						N 7.36	7.52			
$CH_3$		45-47 (2)	1.5139	1.483	$C_4H_4NCI_3O_2$	U 23.50 H 1.03	23.81			
						N 6.85	$\frac{2.13}{7.21}$			
C <sub>2</sub> H <sub>5</sub>		68 - 70(2)	1.5020	1.401	$C_5H_6NCl_3O_2$	C 27.49	27.17			
- 20					· · ·	H 2.76	2.79			
						N  6.41	6.23			
$C_{3}H_{7}$	—	78-82(3)	1.4960	1.319	$C_6H_8NCl_3O_2$	C 31.00	$\frac{31.21}{2.20}$			
						$\frac{11}{N}$ $\frac{3.47}{6.02}$	6.12			
CCl <sub>s</sub> CH(NH)	NHC <sub>6</sub> H <sub>5</sub> )CHNO <sub>2</sub> R						0.12			
R = H	119-120		<u> </u>		$\mathrm{C_9H_{10}N_3Cl_3O_2}$	C 36.19	36.04			
						H 3.38	3.51			
CH	109 104				C. H. N.CLO.	N 14.07	13.82			
$OH_3$	120-124			_	010111210301302	H 3.87	3.89			
						N 13.44	13.48			
$C_2H_5$	115 - 116		—		$\mathrm{C_{11}H_{14}N_{3}Cl_{3}O_{2}}$	C 40.45	40.13			
						H 4.32	4.30			
O II	00 00 F				C H N CLO	N 12.87	12.69			
$C_3H_7$	00-00.0				$O_{12}\Pi_{16}N_{3}O_{13}O_{2}$	H 42.31	42.30			
N 12.34 1										
CCl <sub>3</sub> CH(NHC <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> )CHNO <sub>2</sub> R										
R = H	61-62	—			$C_{10}H_{12}N_2Cl_3O_2$		—			
C.H.	105-106	_	_		$C_{11}H_{14}N_2OI_3O_2$ $C_{10}H_{14}N_2OI_3O_2$					
$C_3H_7$	80-81				$C_{13}H_{18}N_2Cl_3O_9$					
- ••										

TABLE I Physical Properties of Chloral-Nitroparaffin Reaction Products

<sup>a</sup> See Ref. 3, m.p. 45–46°. <sup>b</sup> See Ref. 4, b.p. 115° (2 mm.), n [sic.] 1.5040. <sup>c</sup> See Ref. 3, m.p. 61–62°. <sup>d</sup> See Ref. 4, b.p. 125° (2 mm.), n [sic.] 1.4790. <sup>e</sup> F. Bower and H. Burkett, J. Am. Chem. Soc., 75, 1082 (1953), b.p. 88–89° (16 mm.),  $n_D^{21}$  1.5162,  $d_4^{20}$  1.5695.

olefins and nitromethane gave only tars. Substitution of other aldehydes and ketones for formaldehyde gave uniformly unsuccessful results except for chloral. Only traces of nitro olefins and nitro alcohols were obtained using acetaldehyde, acetone, 2-butanone, cyclopentanone, cyclohexanone, and benzaldehyde. The failures with ketones were apparently not the result of self condensations of the carbonyl compounds with themselves, but rather the result of their lower reactivities. Most of the carbonyl compound used was recovered unchanged from the reaction mixture except in the case of acetaldehyde which gave tars, and of benzaldehyde which gave benzoic acid.

No detailed study was made to determine whether better results could be obtained with

	Product, Conversion, %								
		One Step Vapor Phase							
	Alcohol	Acetate Ester	Olefin Ester Pyrolysis		Method <sup>1</sup>				
Reactants			Phthalate	Acetate	Olefin	Alcohol			
Formaldehyde						······································			
Nitromethane	62*		67°(42)		0	0			
Nitroethane	63*		66°(42)	85.	15	9			
1-Nitropropane	920	90-95°	37 (31)	90 (75)	40	Ő			
1-Nitrobutane	85'		30 (26)		35	9			
Chloral			(		•••	-			
Nitromethane	80	95 (76)	9(7)	23 (18)	Trace	49			
Nitroethane	65	80 (68)	17 (15)	29(20)	9	26			
1-Nitropropane	42	80 (34)	11 (5)	31(11)	4	37			
1-Nitrobutane	32	85 (24)	5 (2)	0 (0)	Ō	44			

TABLE II Comparison of Various Methods of Producing Nitro Olefins and Nitro Alcohols

• W. E. Noland and P. J. Hartman, J. Am. Chem. Soc., 76, 3227 (1954). • B. M. Vanderbilt, Ph.D. thesis, Purdue University (1937). • See Ref. 11. • The figures in parenthesis represent overall conversions from starting nitro paraffins. • See Ref. 12. • Under optimum conditions for formation of nitro olefins.

these carbonyl compounds by altering the conditions of the reaction except in the case of acetone and nitromethane. In spite of wide variations in temperature, and catalyst concentration, no increase in conversion was obtained. The failure of benzaldehyde to yield significant amounts of nitro olefin with nitroethane is astonishing since good yields (ca. 76%)<sup>7</sup> of 1-phenyl-2-nitro-1-propene are obtained from these reactants in the liquid phase.

Chloral reacted in the vapor phase with nitro paraffins to give the corresponding trichloronitro olefins and substantial amounts of trichloronitro alcohols (Table I). In order to obtain maximum conversions to trichloronitro olefins which were poor at best, it was necessary to use a reaction temperature of 360°, and an amine concentration of 0.91 mole per cent. The amine concentration did not appear to be a factor influencing the olefin/ alcohol product ratio in marked contrast to the condensations with formaldehyde. The conversions to olefins and alcohols reached a maximum at the same concentration of amine.

*Product analysis.* Nitro olefins resulting from the condensation of primary nitro paraffins with formaldehyde boil very close to the starting nitro paraffins (within 2 to  $7^{\circ}$ ), and are consequently difficult to isolate in a pure form from the reaction mixture. Hence the nitro olefin content in the product was determined by a refractive index measurement on a narrow-boiling range fraction obtained by distillation. This was compared with a curve obtained by plotting the refractive index against the composition of mixtures of the pure nitro paraffins with the pure corresponding nitro olefins obtained by other methods (see below). This method of analysis was checked by another method which involved isolation of the nitro olefin-toluidine addition product. While not as quantitative, this method gave results sufficiently

near to those obtained by the refractive index method to indicate the probable reliability of the latter method. As the nitro alcohols boil much higher than either the corresponding nitro paraffins or nitro olefins, they could be isolated quantitatively and their yields determined by weighing. The nitro olefins and nitro alcohols obtained by condensation with chloral and other carbonyl compounds also boil in ranges which made their separation by fractional distillation of the reaction mixtures feasible.

Comparison with other methods. Although the conversions to trichloro nitro olefins by the onestep vapor phase method are not as high as might be desired they compare fairly well with the overall yields obtained by other two or three step methods (Table II), and they are much less time consuming.

#### EXPERIMENTAL

Reactor. A  $1.6 \times 122$  cm. pyrex glass tube, heated electrically, and filled with catalyst was supported in a vertical position. It was equipped at the top with a dropping funnel whose contents could be stirred continuously with a motor stirrer, and at the bottom with a 1-l., two necked receiving flask immersed in an ice bath and attached through its second neck to an upright water condenser.

Preparation of catalysts. The catalysts were generally supported on crushed tile<sup>8</sup> (about 14 mesh). Water-soluble catalysts were applied by soaking the tile in their aqueous solutions and evaporating to dryness. Water-insoluble catalysts were applied by soaking the catalyst support in an aqueous solution of a soluble compound of the metal ion and then in a solution of the proper precipitating agent. Catalysts prepared in this manner gave the following conversions of nitropropane to 2-nitro-1-butene; aluminum phosphate, 0.5%; barium sulfate, 0.4%; calcium phosphate, 0.7%; calcium sulfate, 1.3%; magnesium borate, 1.5%; magnesium phosphate, 0.3%; magnesium sulfate, 11.6%; and zinc sulfate, 6.0%. Calcium chloride, cobaltous chloride, cupric chloride, lithium sulfate, and silver nitrate gave no nitro olefin.

(8) "Suntile" supplied by the Cambridge Tile Co,. Cincinnati, Ohio, proved quite satisfactory.

<sup>(7)</sup> K. Knoevenagel and L. Walter, Ber., 37, 4503 (1904).

Procedure. Formaldehyde was generally used in 37% aqueous solution (Formalin) while chloral was used as its hydrate. The nitroalkane, carbonyl compound, and amine were mixed and added to the dropping funnel. Although triethylamine was usually employed, a number of other amines were tested. Thus, the following amines gave the indicated optimum conversion of 1-nitropropane to 2-nitro-1-butene: n-butylamine, 3.1%; diethylamine, 7.0%; piperidine, 11.6%; benzyltrimethylammonium hydroxide, 13.8%; pyridine, 3.6%; triethylamine, 18.0%; (all the above using 0.45 mole per cent of amine), and triethylamine, 40.2%; trimethylamine, 38.0%; tributylamine, 3.2%; tribenzyl-amine, 9.2% (using 0.23 mole per cent of amine). With tertiary amines warming occurred and the mixtures became homogeneous. With other amines the mixture usually remained heterogeneous and had to be stirred continuously throughout the run. With the reactor at the proper internal temperature as measured by a thermocouple the reactants were added dropwise at a rate of about 1 mole of nitroalkane per 20 min. At the end of the run the product was removed from the receiver, mixed with 200 cc. of ether, the mixture washed successively with 10% hydrochloric acid, saturated aqueous sodium bicarbonate solution, and water, and dried over sodium sulfate and fractionally distilled, eventually under vacuum. The fraction boiling in the nitro alkane-nitro olefin range was collected and weighed and its refractive index determined. From these data were calculated the per cent conversions. In the cases of the formaldehyde condensation products, a 5.0-g. aliquot of the fraction was dissolved in a solution containing 5.4 g. of p-toluidine in 20 ml. of 95% ethanol cooled to 0°. The mixture became warm and turned red in color. It was heated for 10 min. on a steam bath and allowed to stand overnight. The yellow crystals which formed were dried and weighed and then recrystallized from ethanol to obtain an accurate melting point. The conversions to these derivatives of the nitro olefins varied with the percentage of the nitro olefin present

in the product mixture and averaged about 70% in a typical mixture containing 85% nitro olefin.

In the cases of the chloral condensation products a 0.02 mole equivalent of the nitro olefin fraction was dissolved in 25 ml. of 95% ethanol, heated to boiling, and phenylhydrazine, 1.8 g. (0.02 mole), added dropwise. The solution turned red in a few seconds. Water was added dropwise until the solution became faintly cloudy and the mixture was allowed to cool. The yellow crystals obtained were dried, weighed, and recrystallized from ethanol to obtain an accurate melting point. The conversions to these derivatives of the trichloronitro olefins were as follows: propene, 99%; butene, 99%; pentene, 79%; hexene, 51%. All of the chloral condensation products gave a positive test<sup>9</sup> for the  $-CCl_3$  group.

Nitro alcohols and their acetate esters. The nitro alcohols and esters prepared in the liquid phase were obtained by published procedures.<sup>10</sup>

Nitro olefins. (a) By dehydration of nitro alcohols with phthalic anhydride. The procedure of Buckley and Scaife<sup>11</sup> gave good results in all cases except with 1,1,1-trichloro-3nitro-2-hexanol. In this case a small yield of the olefin was obtained by dehydration with phosphorous pentoxide.<sup>6</sup>

(b) By pyrolysis of the acetate esters. The procedure of Gold<sup>12</sup> gave good results except again in the case of 1,1,1-trichloro-3-nitro-2-hexyl acetate which gave no nitro olefin.

## LAFAYETTE, IND.

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[CONTRIBUTION FROM THE ORGANIC CHEMISTRY DEPARTMENT, RESEARCH DIVISION, ABBOTT LABORATORIES]

# Effect of Nuclear Substitution on the Reaction of Aromatic Amines with Ethylene Oxide

## MORRIS FREIFELDER AND GEORGE R. STONE

#### Received June 30, 1960

A study was made of the effect of nuclear substitution in aromatic amines on their reactivity with ethylene oxide. The steric effects of some ortho substituents are noted. Seventeen new N,N-bis(2-hydroxyethyl) aromatic amines are reported.

The need in this laboratory for some N,N-bis-(2-hydroxyethyl)anilines gave us the opportunity to observe the effect of nuclear substitution on the reaction of aromatic amines with ethylene oxide. Our interest had been aroused by the work of Ross<sup>1</sup> who reported successful reactions with o-, m- and p-toluidine and o- and p-anisidine at 90° for sixteen hours He found it necessary to raise the temperature to 150° to get bis substitution with p-chloroaniline, but reported failure with both oand m-chloroaniline at this temperature. As a result of these reactions and those of other aromatic amines in his work, he suggested that bishydroxy-

The reported values of the base strength of the chloroanilines,<sup>2</sup> showing that p-chloroaniline is the strongest base of the group and o-chloroaniline the weakest base, seem to support Ross' premise.

Using base strength as a criterion of reactivity, the observed values of o-anisidine and o-phenetidine<sup>3</sup> would suggest little difference in reaction of these compounds with ethylene oxide. From a study of molecular models, however, it appeared that steric effects would be a factor.

ethylation was dependent on the basicity of the aromatic amine.

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