

procedure of Kloetzel, *et al.*,⁹ and the lithium tri-*tert*-butoxy aluminum hydride¹⁰ as described by Brown and Subba Rao.

Reduction of 2,5-Diacetoxybenzoyl Chloride.—In a 3-neck flask, fitted with stirrer, dropping funnel, a low temperature thermometer, and a gas outlet tube attached to a drying tube containing anhydrous calcium sulfate, was placed 16.5 g. of acid chloride (0.064 mole) and 50 ml. of anhydrous diglyme (dimethyl ether of diethylene glycol). The flask was immersed in an insulated beaker containing a Dry Ice-trichloroethylene mixture and cooled to -70° . Lithium tri-*tert*-butoxy aluminum hydride (17.0 g.) in 100 ml. of anhydrous diglyme was added slowly over a 1–2 hr. period avoiding any major rise in temperature. The reaction mixture was then allowed to come to room temperature and to stand overnight. After standing, the contents of the flask were poured into an ice-water mixture, and the yellowish, gelatinous hydroxide filtered off. The hydroxide was washed with ethyl alcohol which was added to the filtrate. The filtrate was distilled, adding water if necessary, until 425 ml. of distillate were collected. The remaining solution was filtered and allowed to stand in the refrigerator. About 1.2–1.3 g. of crude aldehyde crystallized extraction of the mother liquors with ether followed by evaporation yielded an additional 0.6–0.9 g. of material. Yield 1.8–2.2 g.; 15–19%. Recrystallization from aqueous ethanol gave material melting at 79 – 80° (uncorr.). The aldehyde was identified by comparison of infrared curves of material synthesized by an independent route.¹¹ A melting point of an admixture of the aldehydes showed no depression.

Acknowledgment.—This work was supported in part by Grant A-5776 from the National Institutes of Health.

(9) M. Kloetzel, R. Dayton, and B. Abadir, *J. Org. Chem.*, **20**, 38 (1955).

(10) Also available from Metal Hydrides Inc., Beverly, Mass.

(11) J. Lambooy, *J. Am. Chem. Soc.*, **76**, 133 (1954).

The Chlorination of 1-Nitroalkanes

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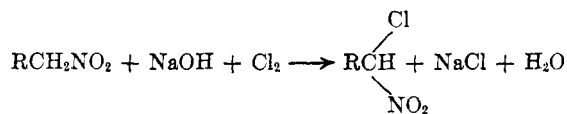
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There has been essentially no work reported in the literature on the chlorination of 1-nitroalkanes to give the 1-chloro-1-nitro derivatives. Henry¹ briefly mentions the preparation of chloronitroethane by the reaction of chlorine and nitroethane in potassium hydroxide. His product was isolated by distillation and could have been the 1,1-dichloro derivative or a mixture of the 1-chloro and the 1,1-dichloro derivatives, since they both boil at essentially the same temperature. More recently some physical studies were made on 1-chloro-1-nitroethane by Hurdes and Smyth,² but no mention was made as to the method of preparation of this compound. The preparation of monohalogenitromethanes by aqueous chlorination of the alkali metal salt has been reported by Tindall.³

(1) L. Henry, *Chem. Zentr.*, **1**, 192 (1898).

(2) E. C. Hurdes and C. P. Smyth, *J. Am. Chem. Soc.*, **64**, 2829 (1942).

It has now been found in our laboratories that 1-nitroparaffins can be chlorinated to give only the monochloro derivative in very high yield.



Preparation of only the monochloro derivative is particularly important with nitroethane, because 1-chloro- and 1,1-dichloro-1-nitroethane boil at about the same temperatures (124 – 126°) and cannot be separated by fractional distillation. Most of the work that will be discussed in this note was done with nitroethane.

1-Chloro-1-nitroethane was prepared in conversions up to 95% by controlled chlorination of nitroethane in aqueous base. The effects of variables on this reaction are discussed below.

Agitation.—In a stirred, three-necked flask, conversions to the monochloro compound of 20–40% were obtained. When stirring was eliminated, conversions of 65% were obtained and the product came out of solution as a lower layer. In the apparatus described below, the chlorine was bubbled through a solution of nitroethane in base and the product was removed as it formed. Under these conditions, up to 95% conversions of nitroethane to 1-chloro-1-nitroethane were obtained.

Temperature.—The chlorination reaction is very exothermic and, if the heat of reaction is not removed, the only organic products are acetic acid and acetaldehyde. At 15 – 20° , conversions to 1-chloro-1-nitroethane of 60–70% were obtained. At 0 – 5° , 90–95% conversions to the monochloro derivative were obtained.

Basicity.—Stoichiometric amounts of base were most satisfactory for high conversions. With 100% excess base, no monochloro derivative was recovered. The monochloro product dissolves in any excess base and undergoes various side reactions. Excess sodium chloride was added to the reaction solution to decrease the solubility of the monochloro derivatives in the aqueous phase.

Time.—The reaction is almost instantaneous and is controlled by the rate of chlorine addition which is, in turn, controlled by the efficiency of heat removal. The yield of monochloro derivative decreases markedly with the length of time the product is in contact with the reaction mixture.

Mechanism.—The reaction is a noncatalytic ionic chlorination of the *aci*-form of the nitro compound. As shown in Table I, experiment 7, the first product is exclusively 1-chloro-1-nitroethane. As the reaction proceeds, secondary reactions begin to occur. The first of these seems to be the exchange between the sodium salts of nitroethane and chloronitroethane (excess base, if present, reacts similarly),

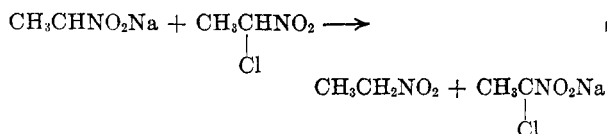
(3) J. B. Tindall, U.S. Patent 2,309,806 (1943).

TABLE I
CHLORINATIONS

Experiment No.	Nitroethane, g.	Cl ₂ , g.	NaOH, g.	H ₂ O, g.	NaCl, g.	Time, hr.	Temp., °C.	Crude product, g.	Conversions, ^a %	Remarks
1	90	78	40	250	..	3	15	94.5	20	Stirred reactor
2	90	78	49	250	..	3	15	102	65	No stirring
3	75	78	43	250	..	7	^b	58	0	
4	75	78	40	280	30	1.7	0-5	107	94.5	Special chlorinator
5	89 ^c	78	40	280	30	1.8	0	96.5	78	Special chlorinator
6	60 ^d	50	40	300	30	1.0	0	80.1	80	Special chlorinator
7	75	78	40	280	30	1.0	0	101.7	93	Samples taken during run ^e

^a To monochloro derivatives. ^b Not controlled. ^c 2-Nitropropane. ^d 1-Nitropropane. ^e CNE = 1-Chloro-1-nitroethane; DCNE = 1,1-Dichloro-1-nitroethane; NE = Nitroethane; see table below.

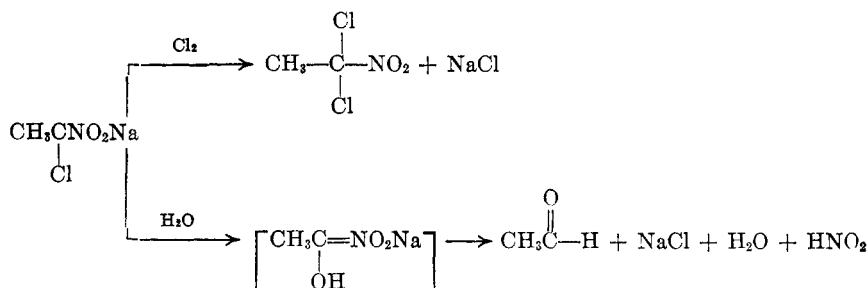
Time, min.	Wt., g.	% CNE	% DCNE	% NE
12	8.1	99.4	...	0.6
19	11.9	99.28
25	8.3	99.0	0.3	.7
30	7.5	99.0	.4	.6
36	7.4	99.0	.3	.7
47	10.7	98.4	.7	.8
55	7.9	97.8	.9	.9



The sodium salt of chloronitroethane will then react with more chlorine or be hydrolyzed.

The hydrolysis of 1-chloro-1-nitroethane was studied by Hawthorne and Strahm,⁴ who obtained acetic acid and nitrous oxide as products. In the

78 g. of nitroethane (99.8% from fractionation of an Eastman Organic Chemistry, Inc., product) in 140 ml. of water. When the nitroethane was dissolved, the solution was placed in the chlorinator and cooled to temperature. A measured amount of chlorine was added during 1-2 hr. The product came out of solution in droplets which settled to the bottom of the apparatus. This essentially pure 1-chloro-1-nitroethane was periodically removed. Chlorine was completely absorbed until all of the nitroethane had been consumed, whereupon the reaction solution became acid and chlorine escaped from the top of the reactor. The product was analyzed by infrared spectroscopy and gas chromatography.



present work, both acetic acid and acetaldehyde were isolated. The exchange reaction occurs more readily if there is agitation, and the amount increases with temperature and time. The parallel increase in amounts of nitroethane and 1,1-dichloro-1-nitroethane in the products with time substantiates the conclusion that exchange is occurring.

Experimental

Examples of typical experiments are shown in Table I. The procedure which gives the highest yields is described below.

A special chlorinator was used, consisting of a 12-in. jacketed glass column 2 in. in diameter fitted with a stopcock at the bottom, a fritted glass chlorine inlet 1 in. from the bottom, and a thermometer and reflux condenser.

A solution of 40 g. of sodium hydroxide in 140 ml. of water was added to a stirred and cooled (ice bath) suspension of

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Base-Catalyzed Rearrangement of Allylphenols and Haloallylphenols¹

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The base-catalyzed rearrangement of olefinic double bonds has been the subject of several recent publications,³⁻⁵ as well as that of some earlier

(4) M. F. Hawthorne and R. D. Strahm, *J. Am. Chem. Soc.*, **79**, 3471 (1957).