of 10% hydrochloric acid to adjust the pH to 3.0. The mixture was cooled to 10° and filtered to yield 11.5 g., m.p. 142–145°. Recrystallization from water gave a 62% recovery of I. The filtrate from the recrystallization yielded 2.0 g. (8%) of benzotriazole.

Reaction of I with benzoyl chloride in hydrochloric acid. A. At 20°. I (29.1 g., 0.19 mole) was mixed with 100 ml. of dioxane and the slurry was cooled to 12°. A 10% hydrochloric acid solution, 200 ml., and 42.2 g. of benzoyl chloride were added dropwise over a period of 45 min. at a 3:1 drop ratio, respectively, while the temperature was maintained at 20°. The mixture was stirred for an additional 15 min., filtered, and air dried to yield 34 g. of crude product. Recrystallization from ethyl acetate gave 17 g. (39%) of II, m.p. 112–113°, no depression on admixture with authentic material.

B. At 60°. I (14.6 g.) was dissolved in 150 ml. of dioxane by heating at 53°. The temperature was raised to 60° and 100 ml. of a 10% hydrochloric acid solution and 21.1 g. of benzoyl chloride were added over 1 hr. while maintaining this temperature. The solution was cooled to 30° while stirring for 1 hr. and partially concentrated by blowing air over the solution at 25°. The mixture was cooled to 5°, filtered, and the precipitate was air dried to yield 12 g. of crude material. Recrystallization from benzene gave 3.5 g. (19%) of benzoic acid, m.p. 121–123°. The filtrate from the reaction mixture was evaporated with air to yield crude I which was recrystallized from ethyl acetate.

Reaction of I with hydrochloric acid at 60°. A solution of 14.6 g. of I in 100 ml. of dioxane and 25 ml. of a 10% hydrochloric acid solution was heated for 2 hr. at 60°. The solution was cooled to 25° and air evaporated to yield 15 g. of crude I, recrystallized from ethyl acetate to yield 12 g. (82%) of I, m.p. 146–147°.

Reaction of I with benzoyl chloride. A mixture of 24.8 g. (0.17 mole) of I and 25.0 g. (0.17 mole) of benzoyl chloride was heated in an oil bath at 160° for 1 hr. The clear melt partially crystallized on cooling to room temperature. After the addition of 750 ml. of ether the mixture was stirred for 1 hr. in an ice bath. The ethereal solution was decanted and washed successively with aqueous solutions of sodium carbonate, hydrochloric acid, sodium bicarbonate, and water. After removal of the ether under vacuum the residue was recrystallized several times from an aqueous ethanol solution to yield 2.0 g. of IV, m.p. 191–192°. The residue, 15.0 g., from the original reaction mixture was washed as above to yield 10 g. of crude material which was recrystallized from ethyl acetate. A total of 5.5 g. (36% yield) of IV was obtained. On recrystallization from dilute ethanol the product had m.p. 191–193° (reported[5] m.p. 192–193°).

Anal. Calcd. for $C_{13}H_{10}N_6$: C, 62.39; H, 4.03; N, 33.48. Found: C, 62.45; H, 3.91; N, 33.43.

Reaction of I with benzoic anhydride. A mixture of 24.8 g. (0.17 mole) of I and 38 g. (0.17 mole) of purified benzoic anhydride was heated in an oil bath at 160° for 1 hr. The crude product was crystallized from dilute ethanol to yield 5.5 g. of product, m.p. 88–92°. Recrystallization from dilute ethanol gave 5.0 g. (24%) of III, m.p. 92–94°, no depression on admixture with the product from the Schotten-Baumann reaction at 20°, and benzoic acid.

Reaction of I with benzoic acid and p-toluenesulfonyl chloride. A solution of 10 g. (0.067 mole) of I in 50 ml. of pyridine was added slowly with stirring to a mixture of 23.6 g. (0.124 mole) of *p*-toluenesulfonyl chloride and 7.6 g. (0.062 mole) of benzoic acid in 100 ml. of pyridine. The temperature was maintained at 5–10° during the addition and for an additional 1.5 hr. The reaction mixture was poured into 3 volumes of ice water and the precipitated solid was filtered and air dried to yield 2.6 g. of III. The filtrate was concentrated by blowing air over the surface of the solution to yield an additional 1.0 g. of III, total 3.6 g. (21.4% yield). Acidification of the filtrate to pH 2 resulted in the precipitation of 3.15 g. (31.5%) of I.

When the reaction was carried out with 25.4 g. (0.134 mole) of *p*-toluenesulfonyl chloride and 8.1 g. (0.067 mole) of benzoic acid in 50 ml. of pyridine, a total of 4.7 g. (27.4% yield) of III was obtained.

Reaction of I with acetyl chloride in pyridine. A solution of 23.5 g. (0.3 mole) of acetyl chloride in 25 ml. of dioxane was added dropwise over 0.5 hr. to a solution of 29.1 g. of I in 100 ml. of dioxane and 31.6 g. (0.4 mole) of pyridine. The temperature was maintained at 20° during the addition and then the mixture was heated at 55° for 1 hr. The mixture was diluted with 750 ml. of ether and stirred for 0.5 hr. at 5° in an ice bath. The ethereal solution was decanted and washed successively with aqueous solutions of sodium carbonate, hydrochloric acid, sodium bicarbonate, and water. After drying over calcium chloride the ether was evaporated to yield 16.4 g. of crude product which was distilled and collected at 95–115° (0.5 mm.). A white solid (7.5 g., 24%) distilled first, followed by 6.5 g. of a clear liquid. The solid had m.p. 49–51° and on recrystallization had m.p. 50–51°.

Anal. Calcd. for $C_8H_7N_3O$: C, 59.63; H, 4.35; N, 26.09. Found: C, 59.42; H, 4.41; N, 25.87.

Redistillation of the liquid gave an additional 2.0 g. (total yield 30%) of *1-acetyl-1H-benzotriazole* and 3.0 g. (8%) of liquid, b.p. 112–120° (0.3 mm.). Analysis of the liquid fraction indicated the probable presence of the ester *1-acetoxymethyl-1H-benzotriazole.*

Anal. Calcd. for $C_9H_9N_3O_2$: C, 56.54; H, 4.71; N, 21.99. Found: C, 57.60; H, 4.50; N, 23.10.

Acknowledgment. The assistance of Daniel J. Kay and Karl Schmidt in portions of the experimental work is gratefully acknowledged.

NEW YORK, N. Y.

[CONTRIBUTION FROM E. I. DU PONT DE NEMOURS & CO., INC., EASTERN LABORATORY]

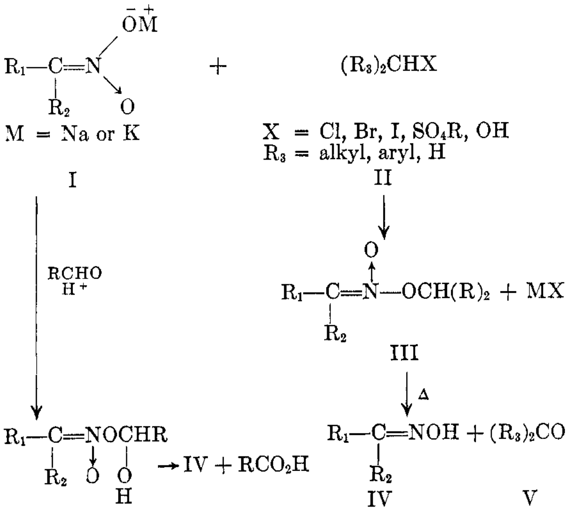
Reduction of Nitroparaffins by Alkylation. I. Aklylation with Trialkyl Oxonium Salts[1]

L. GUY DONARUMA[2]

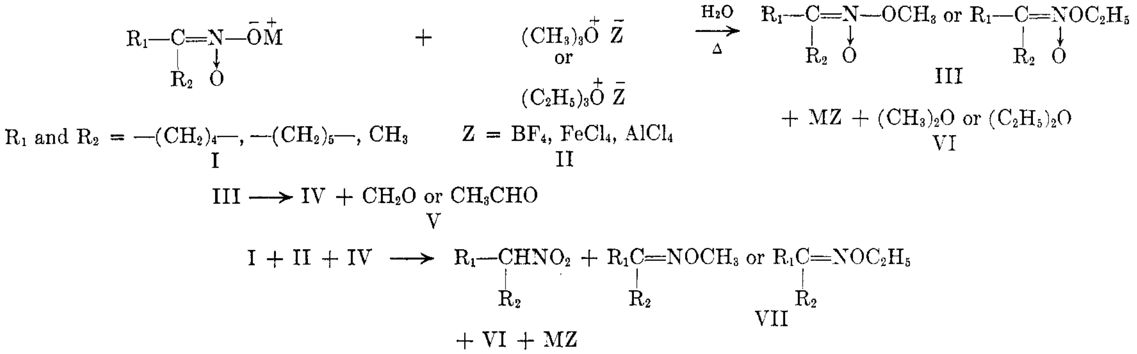
Received February 22, 1957

The reduction of the sodium *aci* salts of nitrocyclohexane, nitrocyclopentane, and 2-nitropropane by alkylation is described. The preparation of trialkyl oxonium salts is discussed. The preparation and certain reactions of some cyclohexanone oxime-*O*-alkyl ethers is described.

The oxygen alkylation of nitroparaffin *aci* salts (I) has been studied by various investigators.[3–6] The usual products of the reaction are an oxime (IV) and a carbonyl compound (V). The nature of the carbonyl compound (V) is determined by the constitution of the alkylating agent (II).[3-6]



We have studied the alkylation of nitroparaffin *aci* salts (I) with various types of alkylating agents. This initial report describes the reaction of nitronate salts with trialkyl oxonium salts (II)[7,8] to yield the oxime (IV) and oxime-*O*-alkyl ether (VII) corresponding to the nitroparaffin *aci* salt (I) employed, the ether (VI) from which the oxonium salt (II) was prepared,[7,8] and products characteristic of the oxonium salt anion. Listed in Table I are the data obtained by reacting three alkyl nitronate sodium salts (I) with various trialkyl oxonium salts (II).



The table shows data which indicate that certain nitronate salts (I) can be reduced to oximes (IV) in good yield by alkylation with trialkyl oxonium fluoborates (II). Oxime-*O*-alkyl ethers (VII) are formed as by-products. The yield of oxime ether (VII) can be increased by using an excess of the oxonium fluoborate (II) and excess base. The table also shows that triethyl oxonium fluoborate (II_a) is slightly superior to trimethyl oxonium fluoborate (II_d). The trimethyl oxonium salt (II_d) decomposes in water ten times faster[7,8] than the triethyl homolog (II_a):

$$(CH_3)_3\overset{+}{O}\,\overset{-}{B}F_4 + H_2O \rightarrow (CH_3)_2O + HBF_4 + CH_3OH$$

Therefore, in order to obtain high yields of oxime (IV) by alkylation with II_d it was necessary to decrease the amount of water in the reaction mixture by 50%.

The trialkyl oxonium tetrachloroferrates (II_b) and tetrachloroaluminates (II_c) were not good alkylating agents. The yields of cyclohexanone oxime and cyclohexanone oxime-*O*-ethyl ether from alkylation of sodium *aci* nitrocyclohexane with these oxonium salts were low. This may have been because of the regeneration of the nitroparaffin or the formation of iron and aluminum *aci* salts from the nitronate salt by ferric chloride or aluminum chloride generated from the oxonium salt (II_b or II_c) by alkylation or hydrolytic decomposition.

This explanation seems reasonable because the yield of products (IV and VII) increased as the amount of excess sodium hydroxide in the reaction mixture was increased. This might be expected because the excess alkali would prevent loss of I by regeneration to the nitroparaffin, would presumably precipitate more metal ions as hydroxides than as heavy metal *aci* salts, and leave more of the *aci* salt (I) available for alkylation.

The alkylation of the sodium *aci* salt of nitrocyclopentane with trimethyl oxonium fluoborate (II_d) did not proceed well. The yield of cyclopentanone oxime was only 42%. However, when the triethyl homolog (II_a) was used the yield increased to 86%. An explanation for this observation may be the surmise that in order for the intermediate nitronate ester (III) to decompose and form an aldehyde or ketone (V) and an oxime (IV), the nitrogen-

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(1) Portions of this material were disclosed in the specification of U. S. Patent **2,763,685.**

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(3) F. Arndt and J. D. Rose, *J. Chem. Soc.*, 1 (1935).

(4) K. Harman and K. Bauer (to Farbenfabriken Baeyer), German Patent **825,547** (Dec. 20, 1951).

(5) H. Welz and J. Weise (to Farbenfabriken Baeyer), German Appln. **F 1,054** (May 23, 1950).

(6) H. Welz (to Farbenfabriken Baeyer), German Appln. **F 1,053** (May 23, 1950).

(7) H. Meerwein, E. Battenberg, H. Gold, E. Pfeil and G. Willfang, *J. prakt. Chem.*, **154,** 83 (1940).

(8) H. Meerwein, G. Hing, P. Hofmann, E. Kroning. and E. Pfeil, *J. prakt. Chem.*, **147,** 257 (1937).

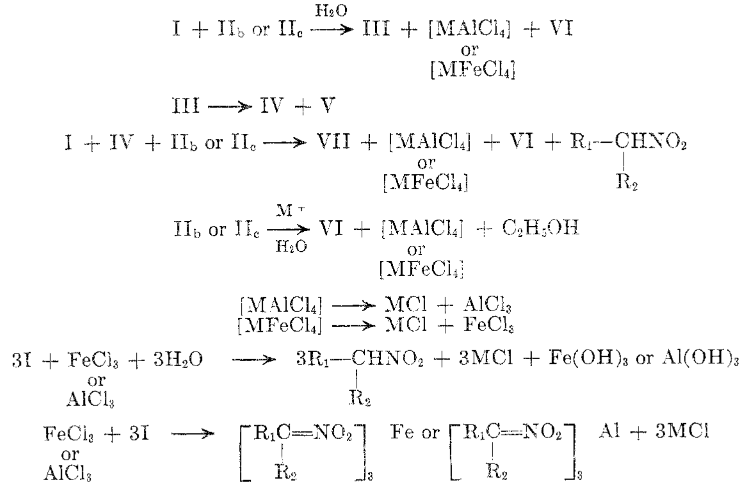
TABLE I

Reaction of *aci* Salts of Nitrocyclohexane, Nitrocyclopentane, and 2-Nitropropane with Various Oxonium Salts

Legend

Na(NCH) = Sodium *aci* nitrocyclohexane
K(NCH) = Potassium *aci* nitrocyclohexane
Na(NCP) = Sodium *aci* nitrocyclopentane
Na(2NP) = Sodium *aci* 2-nitropropane
CHO = Cyclohexanone oxime
CPO = Cyclopentanone oxime
(CHO)Me = Cyclohexanone oxime-*O*-methyl ether
(CHO)Et = Cyclohexanone oxime-*O*-ethyl ether
(CPO)Me = Cyclopentanone oxime-*O*-methyl ether
(CPO)Et = Cyclopentanone oxime-*O*-ethyl ether
II_a = Triethyl oxonium fluoborate; $(C_2H_5)_3O^+BF_4^-$
II_b = Triethyl oxonium tetrachloroferrate; $(C_2H_5)_3O^+FeCl_4^-$
II_c = Triethyl oxonium tetrachloroaluminate; $(C_2H_5)_3O^+AlCl_4^-$
II_d = Trimethyl oxonium fluoborate; $(CH_3)_3O^+BF_4^-$

aci Salt (I)	Oxonium Salt (II)	Temp., °C.	% Yield, Oxime (IV)	% Yield, Oxime Ether (VII)	Remarks
Na(NCH)	II_a	50–60	74, CHO	19, (CHO)Et	
Na(NCH)	II_a	50–60	79, CHO	12, (CHO)Et	
Na(NCH)	II_a	80–100	51, CHO	18, (CHO)Et	
Na(NCH)	II_a	25–30	52, CHO	7, (CHO)Et	
Na(NCH)	II_a	50–60	41, CHO	8, (CHO)Et	Absolute alcohol used as solvent
Na(NCH)	II_a	50–60	32, CHO	35, (CHO)Et	1 molar excess NaOH used with 0.5 molar excess II
Na(NCH)	II_b	50–60	5, CHO	9, (CHO)Et	
Na(NCH)	II_b	50–60	10, CHO	5, (CHO)Et	0.5 molar excess NaOH used
Na(NCH)	II_b	50–60	7, CHO	10, (CHO)Et	1.5 molar excess NaOH used
Na(NCH)	II_b	50–60	17, CHO	10, (CHO)Et	5 molar excess NaOH used
Na(NCH)	II_c	50–60	7, CHO	10, (CHO)Et	
Na(NCH)	II_c	50–60	5, CHO	8, (CHO)Et	
Na(NCH)	II_d	50–60	35, CHO	8, (CHO)Me	
K(NCH)	II_d	50–60	31, CHO	21, (CHO)Me	
Na(NCH)	II_d	50–60	66, CHO	13, (CHO)Me	*aci* salt concentration doubled over preceding reactions
Na(NCP)	II_a	60–70	86, CPO	5, (CPO)Et	
Na(NCP)	II_d	60–70	42, CPO	trace, (CPO)Me	*aci* salt concentration doubled over preceding reaction
Na(2-NP)	II_a	60–70	20, acetoxime		



$$\mathrm{I} + \mathrm{II_b}\ \text{or}\ \mathrm{II_c} \xrightarrow{H_2O} \mathrm{III} + [MAlCl_4]\ \text{or}\ [MFeCl_4] + \mathrm{VI}$$

$$\mathrm{III} \longrightarrow \mathrm{IV} + \mathrm{V}$$

$$\mathrm{I} + \mathrm{IV} + \mathrm{II_b}\ \text{or}\ \mathrm{II_c} \longrightarrow \mathrm{VII} + [MAlCl_4]\ \text{or}\ [MFeCl_4] + \mathrm{VI} + R_1\text{—}CH(R_2)NO_2$$

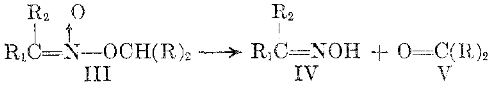
$$\mathrm{II_b}\ \text{or}\ \mathrm{II_c} \xrightarrow[H_2O]{M^+} \mathrm{VI} + [MAlCl_4]\ \text{or}\ [MFeCl_4] + C_2H_5OH$$

$$[MAlCl_4] \longrightarrow MCl + AlCl_3$$
$$[MFeCl_4] \longrightarrow MCl + FeCl_3$$

$$3\mathrm{I} + FeCl_3\ \text{or}\ AlCl_3 + 3H_2O \longrightarrow 3R_1\text{—}CH(R_2)NO_2 + 3MCl + Fe(OH)_3\ \text{or}\ Al(OH)_3$$

$$FeCl_3\ \text{or}\ AlCl_3 + 3\mathrm{I} \longrightarrow \left[R_1(R_2)C{=}NO_2\right]_3 Fe\ \text{or}\ \left[R_1(R_2)C{=}NO_2\right]_3 Al + 3MCl$$

oxygen bond should weaken to allow for the formation of specie(s) which might give rise to the products (IV and V). Examination of molecular models indicates that a cyclopentyl nitronate ester (III) derived from triethyl oxonium fluoborate (II_a) might be more unstable than a methyl nitronate ester due to more crowding of the ester portion of

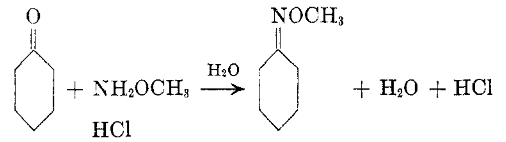


$$R_1(R_2)C{=}\overset{O}{\overset{\uparrow}{N}}\text{—}OCH(R)_2 \longrightarrow R_1(R_2)C{=}NOH + O{=}C(R)_2$$

III → IV + V

the molecule by the α-carbon atoms and their hydrogen substituents. This might tend to weaken the bond and facilitate the decomposition of the nitronate ester (III). Since the model of the ethyl ester exhibited more crowding than the model of the methyl ester, this rationalization might explain the difference in product yields obtained by the alkylation of sodium *aci* nitrocyclopentane with the two oxonium salts. Difficulties of this nature were not present in models of the cyclohexyl homologs. Construction of models of cyclohexyl nitronate methyl and ethyl esters indicates that spatial relationships between the nitronate ester group and the rest of the molecule are present which might aid in weakening the bonds necessary to form the products of the reaction.

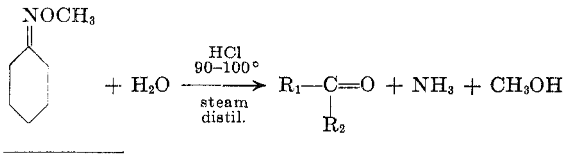
As stated earlier, oxime ethers (VII) are formed as by-products of the reaction. Some cyclohexanone oxime-*O*-alkyl ethers have been prepared previously by Hudlicky and Hokr[9] by alkylation of cyclohexanone oxime with dialkyl sulfates or alkyl halides. The properties of the cyclohexanone oxime-*O*-methyl and *O*-ethyl ethers (VII) obtained from the alkylation of nitronate salts of nitrocyclohexane were comparable with those formed by alkylation of cyclohexanone oxime. As a further means of proving the structure of the oxime ethers, cyclohexanone oxime-*O*-methyl ether was prepared by condensing cyclohexanone with methoxyamine hydrochloride.

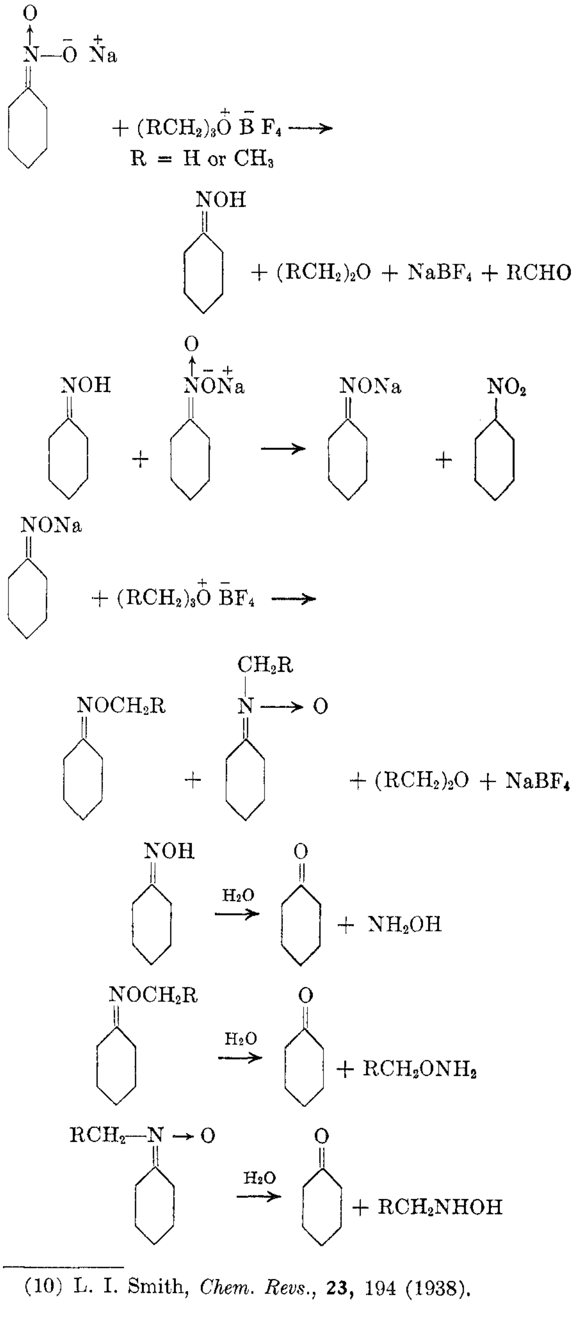


The infrared spectra of the *O*-methyl ethers prepared by the three methods were identical. The hydrobromide salts of the cyclohexanone oxime-*O*-methyl ether obtained from the nitronate salt (I) could be decomposed in water and titrated to give values of the neutral equivalent close to the theoretical value (211 observed; 208 calculated).

Cyclohexanone oxime-*O*-ethyl ether was characterized in a similar manner. Cyclopentanone oxime-*O*-alkyl ethers were present in reaction mixtures only in very small amounts. They were not characterized. However, the characteristic terpene-like odor of cycloalkanone oxime-*O*-alkyl ethers was always present.

The oxime-*O*-alkyl ethers (VII) appear to be very easily hydrolyzed by both acids and bases. It was possible to isolate cyclohexanone and ammonium chloride by hydrolysis of cyclohexanone oxime-*O*-methyl ether with hydrochloric acid. Samples of cyclohexanone oxime-*O*-methyl ether which were presumed to be pure showed an increase of carbonyl content (by infrared spectroscopy) upon standing. The removal of cyclohexanone from the crude cyclohexanone oxime-*O*-alkyl ethers (VII) obtained by distillation of the reaction mixtures was difficult. The ketone may have been present as a result of the hydrolytic decomposition of cyclohexanone oxime and/or one of its *O*-alkyl ethers or a cyclohexyl-*N*-alkyl nitrone.[10] Nitrones are known to be one of the products formed by the alkylation of oximes.[10]





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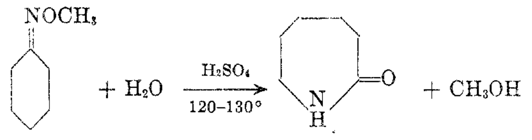
(9) M. Hudlicky and J. Hokr, *Collection Czechoslov. Chem Communs.*, **14**, 561 (1943).

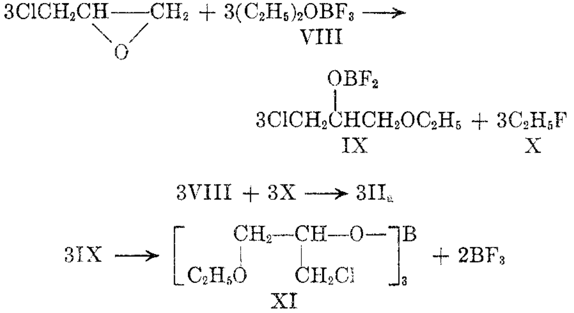
(10) L. I. Smith, *Chem. Revs.*, **23**, 194 (1938).

To purify a cyclohexanone oxime-*O*-alkyl ether it was necessary to wash the crude ether with a large excess of water prior to distillation.

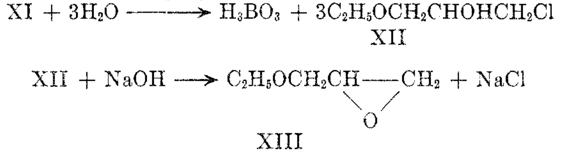
Cyclohexanone oxime-*O*-methyl ether was converted to ϵ-caprolactam by treatment with hot concentrated sulfuric acid.[9]



Meerwein[7,8] has described the preparation of oxonium salts (II) in some detail and formulated the reactions involved in the synthesis of triethyl oxonium fluoborate using epichlorohydrin as follows:



We were able to duplicate Meerweins[7,8] results. In addition, we were able to utilize the borate ester (XI) to prepare oxonium salts.



Epiethylin (XIII) could then be utilized in place of epichlorohydrin to prepare trialkyl oxonium salts.

EXPERIMENTAL

Oxonium salts (II). The oxonium salts used were prepared according to the directions of Meerwein.[7,8] The salts appeared to be stable for several months when stored under ether. The epoxide used to prepare the oxonium salts was epichlorohydrin except in the case where epiethylin (XIII) was prepared from by-products formed by using epichlorohydrin to prepare triethyl oxonium fluoborate.

Preparation of epiethylin (XIII). The preparation of 1.5 moles of triethyloxonium fluoborate from 140 g. (1.5 moles) of epichlorohydrin was carried out.[7,8] After removal of the oxonium salt by filtration, the ether was removed from the filtrate by distillation and the residue agitated with 100 ml. of saturated sodium carbonate solution and 100 ml. of water for 1 hr. At the end of this time, the mixture was extracted with ether and the extract washed with water and dried. The solvent was removed by distillation and the residue distilled under vacuum to yield 122 g. of 1-chloro-2-hydroxy-3-ethoxypropane (XII) (b.p.$_{14}$ 73°) and 22 g. of mixed borate esters (b.p.$_{10}$ 155°) derived from epichlorohydrin. Epiethylin was prepared from XII by the method of Flores-Gallardo and Pollard.[11] When epiethylin was employed to prepare triethyloxonium fluoborate (II$_a$) instead of epichlorohydrin, the yield of oxonium salt (II$_a$) was 80%.

Reaction of trialkyl oxonium salts (II) *with nitroparaffin aci salts* (I). The method can be best illustrated by describing the preparation of cyclohexanone oxime from sodium *aci* nitrocyclohexane. The departures from this procedure were by the addition of excess reagents (Table I) or where trimethyl oxonium fluoborate (II$_d$) was used as the alkylating agent and the quantity of water employed was reduced 50%.

Preparation of cyclohexanone oxime (IV). Twenty-five and eight-tenths grams (0.2 mole) of nitrocyclohexane was dissolved in 100 ml. of water containing 8.0 g. (0.2 mole) of sodium hydroxide by warming on a steam bath with good agitation. To this solution at 50–60° was added, in small portions, 38 g. (0.2 mole) of solid triethyl oxonium fluoborate (II$_a$). During the reaction, diethyl ether was liberated and refluxed very vigorously. When the addition was complete, the mixture was stirred 30 min. at 50°. The reaction mixture was cooled to room temperature and, if necessary, the *p*H was adjusted to 5. Enough sodium chloride was added to the reaction mixture to saturate the water and the mixture extracted with ether. The solvent was removed from the dry extract by distillation and the residue distilled under vacuum to yield 16.7 g. (74%) of cyclohexanone oxime (b.p.$_{10}$ 102°) and 5.4 g. (19%) of cyclohexanone oxime-*O*-ethyl ether (b.p.$_{10}$ 60°). The oxime ether was contaminated with small amounts of cyclohexanone. Cyclohexanone was also found in the cold trap. Fluoborate ion, which was present in the water, was isolated by precipitation as potassium fluoborate with potassium acetate.

The reaction products were characterized by comparison of their infrared spectra with the spectra of authentic specimens of the products.

Oxime-O-alkyl ethers (VII). For characterization purposes, cyclohexanone oxime-*O*-methyl ether and cyclohexanone oxime-*O*-ethyl ether were prepared by the method of Hudlicky and Hokr.[9]

In order to take the infrared spectra of the methyl and ethyl ethers, cyclohexanone had to be removed. This was accomplished by washing the ethers with water and drying the washed ethers with magnesium sulfate. The spectra of the *O*-methyl and *O*-ethyl cyclohexanone oxime ethers were then taken on a Perkin-Elmer Model 21 Spectrometer.

Condensation of cyclohexanone with methoxyamine. Twenty grams (0.24 mole) of methoxyamine hydrochloride was dissolved in 60 ml. of water. Twenty-grams (0.20 mole) of cyclohexanone was added to this solution dropwise with strong agitation. A water-insoluble liquid soon began forming in the reaction mixture. When the addition of cyclohexanone was complete, 80 ml. of 10% sodium hydroxide was added dropwise to the reaction mixture at 25°. The mixture was allowed to stir 30 min. at room temperature and extracted with ether. The extract was washed with water and dried. The solvent was removed from the extract by distillation to leave a residue of 24.2 g. (95%) of crude cyclohexanone oxime-*O*-methyl ether. The product was distilled under vacuum (b.p.$_{12}$ 50°). The product had an infrared spectrum identical with that of the cyclohexanone oxime-*O*-methyl ether prepared by the method of Hudlicky and Hokr[9] and to the material obtained by the reaction of sodium *aci* nitrocyclohexane with trimethyl oxonium fluoborate (II$_d$).

Preparation of ϵ-caprolactam from cyclohexanone oxime-O-methyl ether. Twenty-seven and six-tenths grams (0.22 mole) of cyclohexanone oxime-*O*-methyl ether was added slowly with stirring to 60 g. of 105% sulfuric acid. The temperature of the acid during the addition was held at 25° or below by external cooling. When the addition was com-

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[11] H. Flores-Gallardo and C. B. Pollard, *J. Org. Chem.*, 12, 831 (1947).

plete, the acid mixture was added with stirring to 30 g. of 105% sulfuric acid at 120–130°. The hot acid solution was then allowed to stir at 120° for 10 min. The mixture was cooled in an ice bath and neutralized with concentrated ammonia at a temperature of 25° or below. One hundred milliliters of chloroform was added to the neutral mixture. After agitation for 10 min., the mixture was filtered and the filter cake washed with chloroform. The organic layer was separated, the aqueous phase extracted with chloroform, and the combined chloroform solution dried. The solvent was removed from the extract by distillation to leave 18.5 g. of crude semi-solid ε-caprolactam. The crude lactam was distilled under vacuum to yield 17 g. (68%) of ε-caprolactam (b.p.$_{10}$ 138°). The infrared spectrum of the product was identical with the spectrum of an authentic sample of ε-caprolactam.

WILMINGTON, DEL.

[CONTRIBUTION FROM THE PIONEERING RESEARCH DIVISION, TEXTILE FIBERS DEPARTMENT,
E. I. DU PONT DE NEMOURS AND CO., INC.]

Some Reactions of 3,3-Bis(chloromethyl)oxetane

TOD W. CAMPBELL

Received January 2, 1957

The neopentyl type halides in bis(halomethyl)oxetanes are readily displaced by nucleophilic reagents. A number of such reactions have been studied, and the products characterized.

In comparison to the tremendous amount of research which has been devoted to a study of the chemistry of ethylene oxides, the chemistry of trimethylene oxides (oxetanes) has been overlooked under quite recently. Reviews of certain phases of earlier work have appeared[1] and in the past few years, a number of workers, notably Searles[2–8] have contributed to the field. In this paper some work carried out in these laboratories will be presented.

In general, the preparation of trimethylene oxides is carried out by removing the elements of HX from a 1,3-halohydrin, or better, a halohydrin acetate by treatment with alkali at elevated temperatures.[2,9–11] The yields may be poor because of competing elimination reactions, resulting in the formation of open chain, unsaturated derivatives.[2] If the central carbon atom is substituted with negative groups, for example with two chloromethyl groups,[12] the ring closure by alkali can be carried out at low temperatures, thus minimizing side reactions. A convenient source of an appropriately substituted trimethylene oxide which has been recognized[12] and exploited[13–15] recently is pentaerythritol. This inexpensive raw material reacts readily in glacial acetic acid with hydrogen chloride at elevated temperatures (ca. 160°) to give tris(chloromethyl) ethyl acetate in high yield:

$$C(CH_2OH)_4 + 3HCl + HOAc \xrightarrow[\text{solvent}]{\text{HOAc}} (ClCH_2)_3CCH_2OAc$$

The corresponding bromo derivative may be made in the same fashion.

Ring closure in refluxing methanol with two equivalents of alkali yields the trimethylene oxide easily, despite the fact that the halogen displaced during ring closure is of the neopentyl type.[16]

The product, 3,3-bis(chloromethyl)oxetane, is quite stable under normal conditions, although it is quite sensitive to acidic reagents, and under proper conditions can be converted to a high molecular weight polyether, as reported by several workers.[13,14,17,18] We find the halogen atoms are surprisingly reactive[19] considering that they are still nominally neopentyl halides. They can be displaced by a variety of nucleophilic reagents under mild conditions. This enhanced reactivity undoubtedly arises from the altered geometry of the

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[18] British Patent **723,777** assigned to Imperial Chemical Industries.

[19] Compare Ref. 14.