ianes and their anionic transformation to bicyclo[3.2.2]nonatriene and to two of its alkylated derivatives.

9-Bromobarbaralane[6] was obtained from the corresponding alcohol,[7] triphenylphosphine, and carbon tetrabromide[8] in 79% yield. 9-Chlorobarbaralane[9] was obtained both by the analogous use of carbon tetrachloride (61%) as well as by thionyl chloride treatment of bicyclo[3.2.2]nonatrien-4-ol (87%).

Most explicitly, Na-K-LiBr treatment of 9-chlorobarbaralene in 1,2-dimethoxyethane-d_{10} at −20° generated the deep green color and unmistakable ^{1}H NMR spectrum of lithium bicyclo[3.2.2]nonatrienide.[5a,10] Although contamination by (as much as 20%) bicyclo[3.2.2]nonatriene could not entirely be avoided, no more than 2% barbaralane[11a] was ever present. As expected, alcohol protonation of these anionic solutions provided only bicyclo[3.2.2]nonatriene (101% from methanol, 68% from *tert*-butyl alcohol, each contaminated by less than 1.3% barbaralane[11b]). Qualitatively similar results were also obtained: (a) in tetrahydrofuran solution, (b) employing the bromide rather than the chloride, or (c) with the chloride in tetrahydrofuran containing triethylamine.

4-Methylbicyclo[3.2.2]nonatriene[12] appeared also to be the exclusive methyl iodide alkylation product of such anionic solutions. The significantly more sluggish reaction of 9-chlorobarbaralane with *n*-butyllithium in refluxing ether[13] provided 75% of a 1:1 mixture of bicyclo[3.2.2]nonatriene and its 4-*n*-butyl derivative[14] after aqueous protonation.

The sense of reversible charge control (i.e., $\mathbf{2A} \underset{+}{\overset{-}{\rightleftharpoons}} \mathbf{2B}$) is of course consistent with qualitative theoretical descriptions of the bicyclo[3.2.2]nonatrienyl anion (bicycloaromatic) and cation (antibicycloaromatic).[3] The more quantitative treatments required by the 9-barbaralyl ions enhance this bias. The cation ($\mathbf{2A}^+$) is highly stabilized; the anion would need to possess a half-filled degenerate HOMO—at least in the idealized D_{3h} geometry.[15,16]

The extent to which such control is realized, however, is subject to experimental detail in a way that is theoretically less obvious. For example, protonation of the bicyclo[3.2.2]nonatrienyl anion by HCl (rather than by ROH) generates barbaralane (2-9%)[11b] in addition to bicyclo[3.2.2]nonatriene (71-79%)[11b] under kinetically controlled conditions.[18] Whatever its ultimate mechanistic rationale,[20] this experiment recalls (and was suggested by) the corresponding collapse of isomeric purity from solvolytically generated nonbornenyl and nonbornadienyl cations.[21] There, increased yields of tricyclic product are achieved when alcohols and carboxylic acids are replaced by the more nucleophilic borohydride and methoxide anions.

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(6) *M/e* 196, 198; ^{1}H NMR τ (CDCl$_3$) 4.14 (t, J = 7.5 Hz) and 4.36 (t, J = 7.5 Hz) (2.14), 5.73 (t, J = 7.5 Hz) and 5.95 (t, J = 2.5 Hz) (4.81), 7.24 (dt, J = 2.5, 7.5 Hz) (2.04) ppm. Anal. Calcd: C, 54.85; H, 4.60; Br, 40.55. Found: C, 54.72: H, 4.79; Br, 40.78.

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(9) (a) Mp 18.5°; *m/e* 152, 154; ^{1}H NMR τ(CDCl$_3$) 4.15 (t, J = 7.5 Hz) and 4.42 (t, J = 7.5 Hz) (1.99), 5.88 (t, J = 7.5 Hz) and 6.05 (t, J = 3.0 Hz) (5.00), 7.35 (dt, J = 3.0, 7.5 Hz) (1.99); Anal. Calcd: C, 70.83; H, 5.94; Cl, 23.23. Found: C, 70.77; H, 6.13; Cl, 23.20. (b) This structure had hitherto incorrectly been assigned to a material of somewhat different melting point (106°) and spectroscopic properties.[7] Professor Doering's gracious concurrence in this reevaluation is gratefully acknowledged.

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(11) (a) By ^{1}H NMR integration at τ 5.7–6.7 ppm. (b) By GC, using cumene as a calibrated internal standard.

(12) In 60% yield; *m/e* 132; ^{1}H NMR τ(CCl$_4$) 3.35–4.4 (m) (5), 5.15–5.5 (m) (1), 7.10 (m) (2), 7.9 (m) (1), and 9.00 (d, J = 7 Hz) (3) ppm.

(13) Neither the bromide nor the chloride react with methyl- or *n*-butyllithium at a preparatively convenient rate at ambient temperatures.

(14) *M/e* 174; ^{1}H NMR τ (CCl$_4$) 3.3–4.4 (m) (5), 3.25 (dt) (1), 7.0 (m) (2), 8.07 (m) (3), 8.68 (d, J = 4 Hz) (6), and 9.08 (t, J = 7 Hz) (3).

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(16) A once plausible alternative hypothesis—that solvolytic cation capture to generate barbaralyl derivatives reflects the influence of thermodynamic stability on a kinetically controlled product[5b]—is difficult to reconcile with the results of anion capture, nor is the greater thermodynamic stability of bridged oligocyclic cyclopropanes as universal as it once appeared.[17]

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(18) Ether solution at −78°. Such results should carefully be distinguished from the anomalous anionic isomerization of 2-methylbicyclo[3.2.2]nonatriene to 3-methylbarbaralane under conditions of partial thermodynamic control (KNH$_2$–NH$_3$, 50°).[19]

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(22) Partial financial support by U.S. Public Health Research Grant No. 10495 from the National Cancer Institute is gratefully acknowledged.

(23) Schleuderberg Fellow, 1972–1973.

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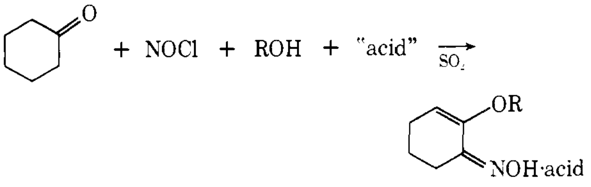
Received December 23, 1974

Nitrosation in Organic Chemistry. Nitrosolysis, a Novel Carbon-Carbon Bond Cleavage Effected through Nitrosation. Nitrosolysis of Ketones

Sir:

While cyclopentanone, cyclohexanone, and cycloheptanone undergo nitrosation to give the corresponding α,α'-dioximino ketones,[1,2] larger ring cyclic ketones[3] and aliphatic open chain ketones[1] give mononitrosation products.

We would like to report a new nitrosation technique for mononitrosation of cyclohexanone which led to the development of the nitrosolysis reaction—a novel single-step carbon-carbon bond cleavage of various ketones effected through nitrosation. Reaction of cyclohexanone with nitrosyl chloride in liquid sulfur dioxide in the presence of an alcohol and 1 equiv of a suitable acid (eq 1) provides an entry



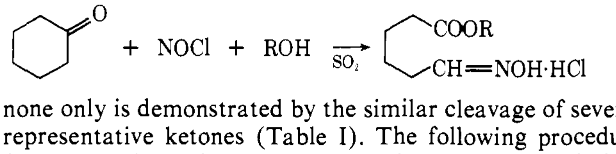
(1)

Table I. Nitrosolysis of Various Ketones[a]

Ketone	Alcohol	Products[b]	Yield,[c] %
Cyclohexanone	EtOH[d]	HON=CH$(CH_2)_4$COOEt	95
		2-Ethoxy-3-oximinocyclohexene	2
	n-BuOH–*i*-BuOH[e]	HON=CH$(CH_2)_4$COOBu-*n*	45
		HON=CH$(CH_2)_4$COOBu-*i*	45
4-*tert*-Butylcyclohexanone	EtOH	HON=CHCH_2CH(*t*-Bu)-CH_2CH_2COOEt	50
		2-Ethoxy-3-oximino-5-*tert*-butylcyclohexene	40
2-Methylcyclohexanone	EtOH	HON=C$(CH_3)(CH_2)_4$COOEt	45
		HON=CH$(CH_2)_3$CH(CH_3)COOEt	45
Cyclopentanone	EtOH	HON=CH$(CH_2)_3$COOEt	70
		2-Ethoxy-3-oximinocyclopentene	25
Cyclododecanone	EtOH	HON=CH$(CH_2)_{10}$COOEt	75
		2-Ethoxy-3-oximinocyclododecene	25
7-Tridecanone[f]	EtOH	$CH_3(CH_2)_5$COOEt	45
		$CH_3(CH_2)_4$CH=NOH	20

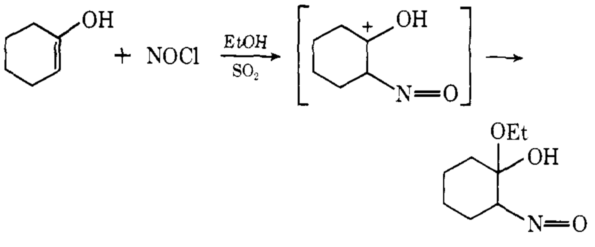
[a] For the experimental conditions and the ratios of the reagents see the representative procedure in the text. [b] The structure of the products was determined either by comparison with an authentic sample or by the usual spectroscopic and analytical means. [c] By GLPC. [d] Essentially the same results were obtained with methanol. [e] 1:1 mixture. [f] As much as 40% of the corresponding α-oximinoketone was also formed.

to a new class of cyclohexanone derivatives. On the other hand, when the above reaction with cyclohexanone is carried out without additional acid, cyclohexanone undergoes a cleavage reaction to provide ω-oximinocaproic acid ester (eq 2). That this novel cleavage is not limited to cyclohexanone only is demonstrated by the similar cleavage of several representative ketones (Table I). The following procedure for conversion of cyclohexanone into ethyl ω-oximinocaproate is illustrative. A three-neck 500-ml flask equipped with a mechanical stirrer, an inlet for the introduction of sulfur dioxide and nitrosyl chloride, and a Dry Ice condenser with a nitrogen bubbler was placed in a Dry Ice–acetone bath. A sulfur dioxide cylinder was connected to the inlet and about 200 ml of sulfur dioxide was distilled into the flask. A solution of cyclohexanone (19.68 ml, 200 mmol) in ethanol (17.6 ml, 300 mmol) was added with the aid of a syringe and the Dry Ice bath removed. Nitrosyl chloride (14.4 g, 220 mmol) was placed in a precooled 50-ml round-bottom flask protected with a nitrogen bubbler and equipped with an outlet connected via a stopcock to the inlet of the reactor. When the sulfur dioxide started to boil (−10°), the nitrosyl chloride container was gently warmed and simultaneously the stopcock was opened to introduce the nitrosyl chloride vapors slowly just above the well-stirred solution. The end of the reaction (15-20 min) was indicated by the appearance of a slight yellow color (excess of nitrosyl chloride) which did not decolorize immediately. The reaction mixture was evaporated in vacuo to a small volume, about 150 ml chloroform was added, and the solution was again briefly concentrated to remove the residual sulfur dioxide. The remaining chloroform solution was transferred to a separatory funnel, diluted with more chloroform to about 200 ml, and washed several times with water to remove hydrochloric acid. Gas chromatographic analysis of the solution indicated a 90-95% yield of ethyl ω-oximinocaproate. Evaporation of the chloroform afforded 33.0 g of slightly yellow oximino ester which, according to a 60-MHz NMR spectrum, was a mixture of approximately equal amounts of the syn and anti isomers. Mononitrosation of cyclohexanone to 2-methoxy-3-oximinocyclohexene was achieved by a slow evaporation of nitrosyl chloride (7.19 g, 110 mmol) just above a well-stirred solution of cyclohexanone (10.4 ml, 100 mmol) in sulfur dioxide (100 ml), containing methanol (4.05 ml, 100 mmol) and hydrogen chloride (100 mmol). After complete addition, the Dry Ice–acetone bath was removed and the reaction mixture stirred at reflux (ca. −10°) for 1 hr, transferred into a precooled flask and evaporated at 0°. About 20-25 g of a white soft solid was obtained which upon careful treatment with sodium bicarbonate in a minimal quantity of water afforded 2-methoxy-3-oximinocyclohexene,[4] mp 150-151° (hydrochloride, mp 113-115° dec. Anal. Calcd for $C_7H_{11}NO_2$: C, 59.56; H, 7.85; N, 9.92. Found: C, 59.60; H, 7.9; N, 10.03. NMR spectrum: δ 9.5 (s, 1, O*H*), 5.23 (t, 1, C*H*=C); 3.69 (s, 3, OC*H*$_3$), and a set of triplet, quartet, and quintet centered at δ 2.75, 2.25, and 1.69 ppm, respectively, each integrating for 2 H.



(2)

In spite of somewhat conflicting opinions about the mechanism of nitrosation of ketones,[5,6] there can be little doubt that the reaction involves an electrophilic attack of the nitrosation species on a double bond of the corresponding enols. Presumably, the observed ketone cleavage, e.g., of the cyclohexanone, may be explained by an effective trapping of the resulting 1-hydroxy-2-nitrosocarbonium ion with an alcohol as a nucleophile (eq 3) and subsequent acid catalyzed transformation of the thus obtained 1-hydroxy-1-alkoxy-2-nitroso intermediate to the ω-oximinocaproic acid ester (eq 4). The fact that the nitrosolysis reaction fails in solvents like chloroform, ether, hexane, or alcohols clearly points out the important function of sulfur dioxide. Because of its low nucleophilicity on the one hand and very



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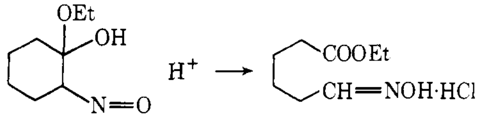
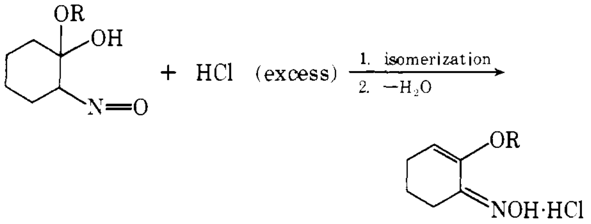


(4)

good solvating properties on the other, sulfur dioxide plays a dual role. It allows a sufficiently high concentration of nitrosonium ion and at the same time "stabilizes" the intermediate 1-hydroxy-2-nitrosocarbonium ion *without reacting with the positive charge*, thus making the reaction with the alcohol possible. Other polar but nonbasic solvents like nitromethane and sulfolane behave similarly, and thus the nitrosolysis reaction can also be carried out in these solvents. The successful outcome of this reaction must be due to at least in part to the fact that during the reaction cycle only a small amount of free hydrochloric acid is present.[7] Presumably, the hydrochloric acid generated in the reaction between nitrosyl chloride and the alcohol serves as the catalyst for the enolization of the ketone and the cleavage of the α-nitrosohemiketal and then becomes "neutralized" by the oxime produced.

When, however, the nitrosation of cyclohexanone was carried out in the presence of an additional equivalent of hydrogen chloride, the competing reaction, the acid catalyzed isomerization of the secondary nitroso group,[8] followed by water elimination to afford the 2-alkoxy-3-oximinocyclohexene, becomes more important and the carbon-carbon bond cleavage is suppressed (eq 5).



(5)

Clearly, the nitrosolysis reaction is a remarkably simple procedure for the carbon-carbon bond cleavage of a variety of ketones[10] providing products with valuable functional groups. In effect, the nitrosolysis reaction represents an advantageous supplement to a Beckmann fragmentation of the α-oximino ketones. The reaction is carried out under much milder conditions and eliminates the need for the prior preparation of the α-oximino ketones. It should be particularly useful for the transformation of cyclopentanone, cyclohexanone, and cyclohexanone derivatives where α-oximino ketones are extremely difficult to prepare.[3,11] Furthermore, similar reaction of cyclohexanone, but in the presence of an excess of added acid, provides for the first time a direct and convenient access to 2-alkoxy-3-oximinocyclohexene, a novel derivative of mononitrosated cyclohexanone.

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(4) The oximino enol ether hydrochloride is a fairly unstable material that decomposes at room temperature overnight, but could be stored over an extended period of time in a refrigerator. The free oximino enol ether is stable at room temperature and does not undergo appreciable decomposition over a period of several months. The chemistry of this interesting intermediate will be described elsewhere.
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(7) In this regard the commonly used technique for in situ generation of nitrosyl chloride, by the reaction of an alkyl nitrite and hydrogen chloride (e.g., ref 2), suffers from the disadvantage that the rate of addition of hydrogen chloride usually appears to be too fast, resulting in concomitant formation of the oximino enol ethers.
(8) It is of interest that the isomerization (eq 5) occurred most readily in the presence of hydrogen chloride or boron trifluoride etherate, and in the presence of other acids like sulfuric and methanesulfonic acid the isomerization apparently was not extensive. This fact is probably responsible for the successful nitrosolysis of cyclohexanone to ω-oximinocaproic acid with nitrosylsulfuric acid in concentrated sulfuric acid.[9]
(9) P. Lafont and M. Thiers, U.S. Patent 3,356,698 (1967).
(10) No attempts were made to optimize the reaction conditions for each individual ketone.
(11) After the completion of this work, Ohno and Kataoka[3] reported unsuccessful attempts to fragment α-oximinocyclohexanone.

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Received December 12, 1974

Reactions of Dioxetanes with Sulfoxylates and Sulfides. Preparation of Novel Tetraalkoxysulfuranes

Sir:

Sulfuranes, i.e., tetrasubstituted sulfur compounds, are a little known class of substances.[1] Recently various energy rich substances such as organic hypochlorites[2] and perfluorohypofluorites[3] have been allowed to react with divalent sulfur compounds to prepare sulfuranes and persulfuranes. Attempts to prepare sulfuranes by reaction of diethyl peroxide with divalent sulfur compounds have been fruitless.[4] It did seem, however, that the more reactive four-membered ring peroxides, dioxetanes,[5] might react with divalent sulfur compounds to give sulfuranes. In particular it seemed that sulfur compounds with electronegative ligands might lead to relatively stable sulfuranes. After the completion of this work Wasserman and Saito[6] reported that diphenyl sulfide does indeed react with several dioxetanes to give diphenyl sulfoxide. No evidence for the intervention of sulfuranes was obtained.

The dioxetanes, **1** and **2**, have been used in this study.[7] When **1** was allowed to react with **3** at −78° in methylene chloride a reaction mixture was obtained whose 100-MHz ^{1}H NMR spectrum at −60° showed singlet absorptions at δ 1.32, 1.47, 3.26, 3.66, each three hydrogens, and absorptions at δ 3.73 and 3.78, two hydrogens. The 20-MHz ^{13}C NMR spectra, decoupled and off-resonance decoupled, showed four methyl group carbons at δ 24.55, 26.00, 48.50, and 54.55. A methylene carbon was found at δ 70.32 and a quaternary carbon appeared at δ 83.69. When these reaction mixtures were allowed to warm to room temperature dimethyl sulfite and a nonvolatile, presumably polymeric, material were formed. These results are in concordance with the production of a tetraalkoxysulfurane, **5**, where the upfield ^{1}H and ^{13}C NMR chemical shifts are due to the appropriate absorptions of the elements of the methyl groups on the ring. The downfield absorptions are those of methyl group hydrogens and carbons. These are nonequivalent and environmentally quite different methoxy groups. These data cannot be used to exclude various conformers for **5**. For example the structure illustrated, a trigonal bipyramid, is in agreement with the data; however, a square pyramid also fits the data. Pseudorotations between various conformers which do not render the groups equivalent cannot be eliminated. It should be noted though that the methoxy groups experience a considerably different environment. This observation suggests a structure(s) where this is achieved.

Reaction of **1** with **4** at −78° gave reaction mixtures whose ^{1}H and ^{13}C NMR spectra at low temperatures are in agreement with the production of a sulfurane, **6**; i.e., aside from the complications introduced by the *n*-propyl groups the spectra were very similar to that of **5**. On warming reaction mixtures of **6** a smooth decomposition occurred with the production of *n*-propyl sulfite and isobutyraldehyde. The latter can be formed from **6** by heterolysis of the O-$C(CH_3)_2$ bond with hydride migration and S-O bond cleav-