Nitrosation in Organic Chemistry. 1-Hydroxy-2-(ω-methoxycarbonylbutyl)-4,5,6,7-tetrahydrobenzimidazole 3-Oxide. An Unusual Product from the Nitrosation of Cyclohexanone

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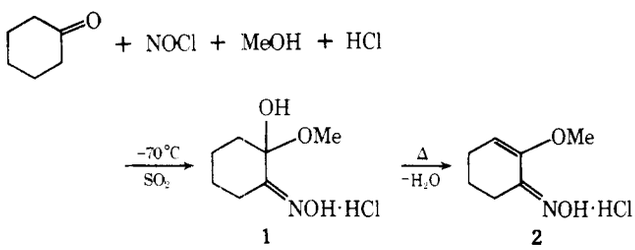
Received January 19, 1977

Nitrosation of cyclohexanone with nitrosyl chloride in liquid sulfur dioxide containing 1 equiv of methanol and at least 1 equiv of hydrogen chloride affords 2-methoxy-3-oximinocyclohexene hydrochloride. The reaction involves 1-hydroxy-1-methoxy-2-oximinocyclohexane hydrochloride as an intermediate. A reaction of this intermediate in a methanol solution with a solution of sodium hydroxide in the same solvent led to the formation of 1-hydroxy-2-(ω-methoxycarbonylbutyl)-4,5,6,7-tetrahydrobenzimidazole 3-oxide. The same product was also obtained by a reaction of methyl 6-oximinohexanoate with 1-methoxy-2-oximinocyclohexyl carbonium ion generated from either 2-methoxy-3-oximinocyclohexene, 2-oximinocyclohexanone dimethyl acetal, or 2-oximinocyclohexanone. A reduction of the above *N*-oxide with lithium aluminum hydride gave 2-(ω-hydroxypentyl)-4,5,6,7-tetrahydrobenzimidazole, while a treatment with sodium hydrosulfite in water afforded 2-(ω-methoxycarbonylbutyl)-4,5,6,7-tetrahydrobenzimidazole. The mechanism of the formation of the 1-hydroxy-2-(ω-methoxycarbonylbutyl)-4,5,6,7-tetrahydrobenzimidazole 3-oxide is discussed.

Recently we reported that nitrosation of cyclohexanone with nitrosyl chloride in liquid sulfur dioxide in the presence of an alcohol and at least 1 equiv of hydrogen chloride provides the corresponding 2-alkoxy-3-oximinocyclohexenes.[1,2a] When the reaction was carried out without the added hydrogen chloride, the alkyl 6-oximinohexanoates resulted.[1,2a] This novel carbon–carbon bond cleavage, the nitrosolysis reaction, was extended to other ketones.[1,2a] Furthermore, a reaction of cyclohexanone diethyl acetal with ethyl nitrite in liquid sulfur dioxide in the presence of ethanol and a catalytic amount of an acid afforded ethyl 5-cyanopentanoate, and other cyclic and open-chain ketone acetals behaved similarly providing the corresponding cleaved products.[2] The success of the nitrosolysis reaction was attributed to an efficient trapping of the α-nitrosohydroxy- or α-nitrosoalkoxycarbonium ion intermediates with an alcohol as a nucleophile, and facile in situ cleavage of the resulting α-nitrosohemiacetals or α-nitrosoacetals.[1,2a] We have also discussed how the nature of the nucleophile associated with the nitrosating reagent can dramatically change the course of the nitrosation of ketones,[2a] and in this paper we shall discuss the formation of another unusual product of nitrosation of cylcohexanone.

Results and Discussion

During the investigation of the mechanism of these reactions with cyclohexanone,[2a] a 100-MHz NMR spectrum of the reaction mixture after complete addition of the nitrosyl chloride to a solution of 1 equiv each of cyclohexanone, methanol, and hydrogen chloride in liquid sulfur dioxide at −70 °C suggested that the initial main reaction product was 1-hydroxy-1-methoxy-2-oximinocyclohexane hydrochloride (1). Indeed, evaporation of the reaction mixture at a low



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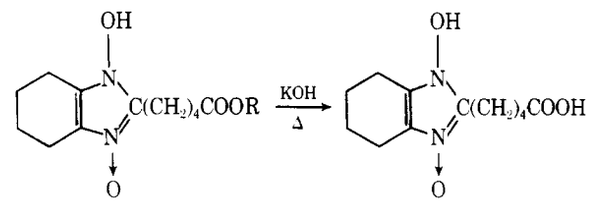
temperature afforded a white, soft solid, characterized as 1-hydroxy-1-methoxy-2-oximinocyclohexane hydrochloride[2a] (1), which at higher temperatures in solution or on isolation undergoes water elimination to give 2-methoxy-3-oximinocyclohexene hydrochloride (2).

In one experiment, the freshly isolated 1 was dissolved in methanol and to the solution was added 3 N NaOH at 0 °C. When an equivalent amount of the base has been added (pH 3–4), an instantaneous precipitation occurred. Filtration afforded a white, flaky solid, mp 178–179.5 °C, which according to elemental analysis, mass spectrum, IR, UV, and NMR spectra was 1-hydroxy-2-(ω-methoxycarbonylbutyl)-4,5,6,7-tetrahydrobenzimidazole 3-oxide (**3a**). When the above sequence of reactions was carried out in the presence of ethanol instead of methanol, and then 3 N NaOH was added to the corresponding ethanol solution at 0 °C, the ethyl ester, 1-hydroxy-2-(ω-ethoxycarbonylbutyl)-4,5,6,7-tetrahydrobenzimidazole 3-oxide (**3b**), mp 153.5–155 °C, was obtained.

Treatment of either **3a** or **3b** with a boiling 40% potassium hydroxide solution afforded the free acid, 1-hydroxy-2-(ω-carboxybutyl)-4,5,6,7-tetrahydrobenzimidazole 3-oxide (**4**), mp 191–193 °C.



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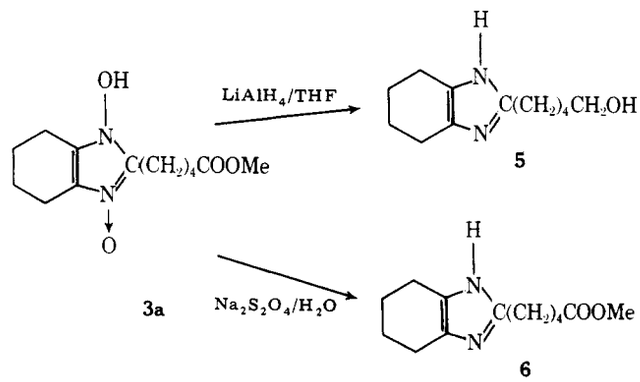
a, R = CH_3
b, R = CH_3CH_2

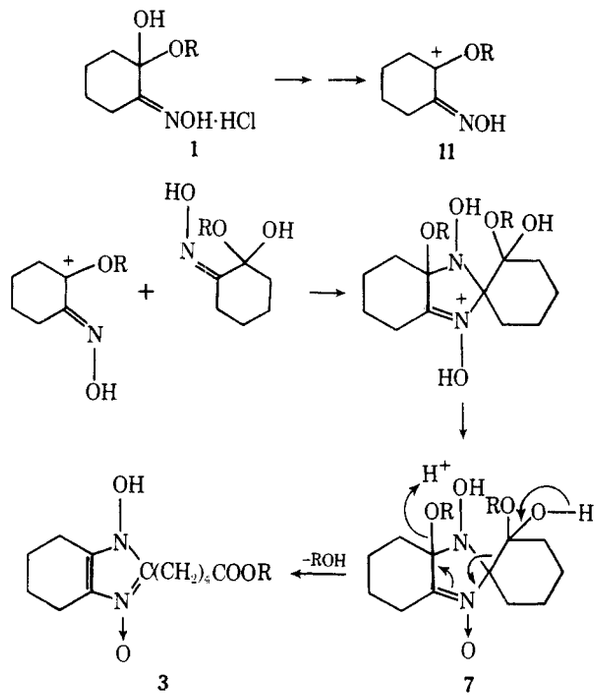
The reduction of **3a** in boiling tetrahydrofuran with lithium aluminum hydride gave 2-(ω-hydroxypentyl)-4,5,6,7-tetrahydrobenzimidazole (**5**) as a viscous oil. On the other hand,



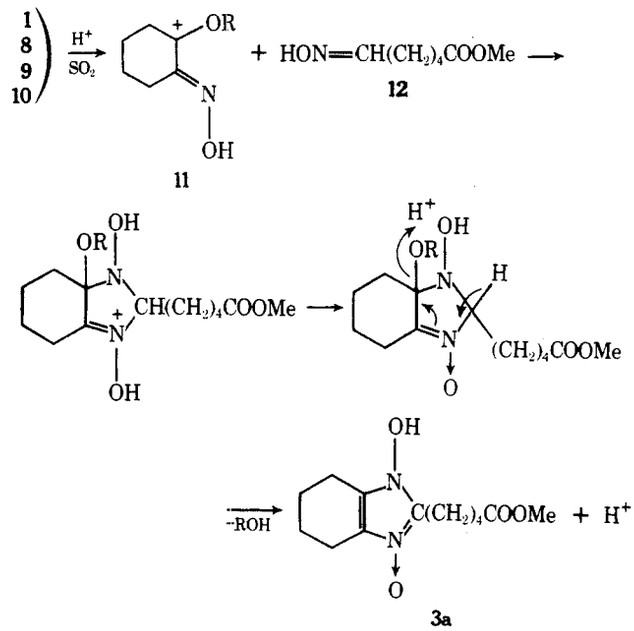
treatment of **3a** with an excess of sodium hydrosulfite in water[4] led to the reduction of only the 1-hydroxy and 3-oxide functions and afforded 2-(ω-methoxycarbonylbutyl)-4,5,6,7-tetrahydrobenzimidazole (**6**), mp 114–116 °C.

It is conceivable that formation of **3** may take place through an acid-catalyzed reaction of 1-hydroxy-1-methoxy-2-oximinocyclohexane (**1**) with itself, followed by an acid-catalyzed fragmentation of the resulting intermediate (**7**) (Scheme I).

Scheme I



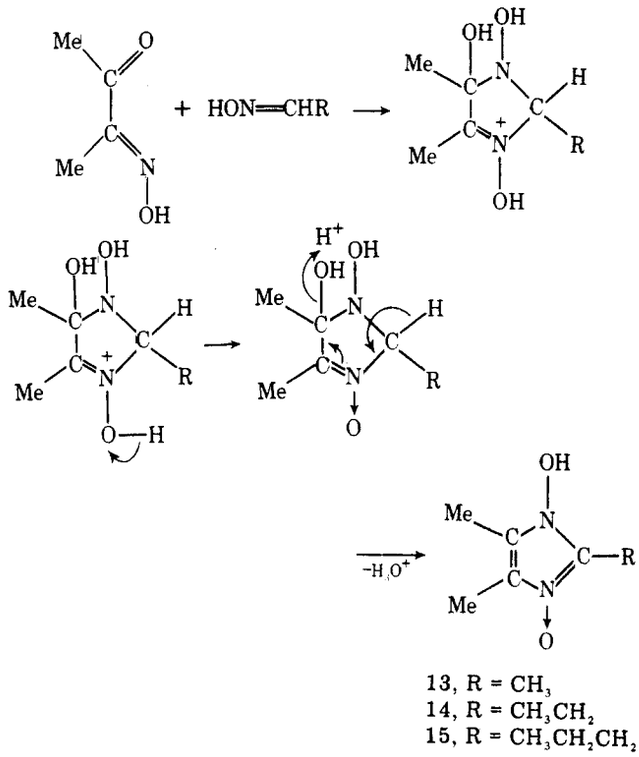
Alternatively, an acid-catalyzed reaction of either 1-hydroxy-1-methoxy-2-oximinocyclohexane (**1**), 2-methoxy-3-oximinocyclohexene (**8**),[1] 2-oximinocyclohexanone dimethyl ketal (**9**),[5] or 2-oximinocyclohexanone (**10**)[6] with methyl



ω-oximinocaproate (**12**)[2] gave the same product (**3a**). Presumably, the reaction involves the carbonium ion intermediate **11** (R = Me or H).

Diels and van der Leeden reported that treatment of biacetyl monoxime with hydrogen chloride afforded 4-hydroxy-3,4,6-trimethyl-1,2,5-oxadiazine hydrochloride.[7] They proposed that hydrogen chloride cleaved biacetyl monoxime to acetyl chloride and acetaldoxime. The latter then condensed with unchanged biacetyl monoxime to give the product. To support the above view, they carried out the condensation of biacetyl monoxime and acetaldoxime and obtained the free base which they believed to be 4-hydroxy-3,4,6-trimethyl-1,2,5-oxadiazine. Subsequently Wright showed that the correct structures for both Diels and van der Leeden products were, in fact, 1-hydroxy-2,4,5-trimethylimidazole 3-oxide (**13**) and the corresponding hydrochloride (**13a**),[4] and that biacetyl monoxime and propionaldoxime gave the corresponding 1-hydroxy-2-ethyl-3,4-dimethylimidazole 3-oxide (**14**).[4]

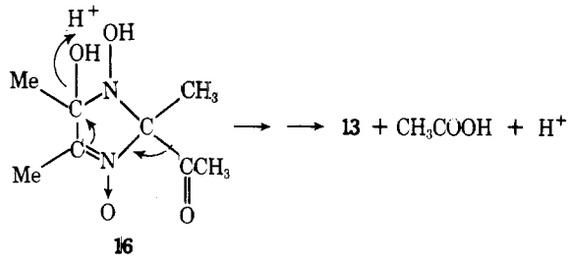
The originally proposed[7] cleavage of biacetyl monoxime with hydrogen chloride to acetyl chloride and acetaldoxime to our knowledge does not have a precedent in the literature. It seems highly unlikely that such a cleavage would indeed take place under the reaction conditions used. Although various α-oximino ketones undergo Beckmann fragmentation under the proper reaction conditions to provide the corresponding nitrile and either an acid or the corresponding ester,[8] we are aware of only one such fragmentation that was effected by hydrogen chloride.[9] Since the reaction between biacetyl monoxime and acetonitrile in the presence of hydrogen chloride did not produce any **13**, we concluded that acetonitrile was not an intermediate in the formation of **13**. Similarly, attempts to form **3a** by a reaction of either **8**, **9**, or **10** with methyl ω-cyanovalerate were not successful.



13, R = CH_3
14, R = CH_3CH_2
15, R = $CH_3CH_2CH_2$

When the reaction of biacetyl monoxime with hydrogen chloride was carried out according to the procedure of both Diels[7] and Wright,[4] acetic acid was found among the reaction products. While this fact alone does not provide any clues as to the possible mechanism of the reaction, it nevertheless suggests that the formation of **13** from biacetyl monoxime and hydrogen chloride may involve a self-condensation of the biacetyl monoxime, followed by a fragmentation of the resulting intermediate (**16**) to provide the observed **13** and acetic acid.

Reaction of either biacetyl monoxime with acetaldoxime and *n*-butyraldoxime to give **13** and **15**, respectively, or **8**, **9**, or **10** with methyl ω-oximinocaproate to give **3a** occurs readily



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under mild reaction conditions in sulfur dioxide at −10 °C in the presence of a catalytic amount of hydrochloric acid. Under similar reaction conditions, neither biacetyl monoxime nor **8**, **9**, and **10** gave the desired products, **13** or **3a**. On the other hand, when an equimolar mixture of biacetyl monoxime and *n*-butyraldoxime was treated with hydrogen chloride only **15** was obtained, but no evidence for the formation of either **13** or acetaldoxime could be ascertained. Evidently, formation of **13** from biacetyl monoxime and an aldoxime is a much more facile process than the reaction from biacetyl monoxime itself and hydrogen chloride.[4,7]

When either **8**, **9**, or **10** was treated with hydrogen chloride under the conditions of Diels[7] and Wright,[4] neither **3a** nor **4** was observed. Instead, **8** and **9** gave 2-methoxy-3-oximinocyclohexene hydrochloride, and **10** led to intractable tarry materials. Considering the formation of **3** from the reaction of cyclohexanone with nitrosyl chloride (vide supra), it is hard to see how the intermediate **1** may provide methyl ω-oximinocaproate, the second reaction component required for the formation of **3** from either **1**, **8**, **9**, or **10**. Consequently, one is almost forced to conclude that the formation of **3** indeed involves a self-condensation of **1** followed by a fragmentation as outlined in Scheme I. It should be remembered, however, that the reaction of cyclohexanone with nitrosyl chloride in sulfur dioxide in the presence of methanol, *but in the absence of externally introduced hydrogen chloride*, led to methyl ω-oximinocaproate.[2] In view of this fact, it is possible that some of **3** may also be formed by condensation of either **1**, **8**, **9**, or **10** with the methyl ω-oximinocaproate which may be produced in situ if some of the hydrogen chloride escaped accidentally from the sulfur dioxide solution.

Experimental Section

Instruments. Infrared spectra were recorded on a Beckman IR-9 spectrophotometer. Ultraviolet spectra were obtained on a Beckman DK-2A spectrophotometer. Proton magnetic resonance spectra were recorded on a Varian A-60, A-60A, or HA-100 NMR spectrometer, while carbon magnetic resonance spectra were recorded on a Varian XL-100 ^{13}C NMR spectrometer. All NMR spectra were measured using tetramethylsilane as an internal standard. Routine mass spectra were obtained on a Finnigan 3100 D mass spectrometer, while high-resolution mass spectra were obtained on an AEI M.S. 902. Gas–liquid phase chromatography was generally performed on a Hewlett-Packard 5700A instrument using a thermal conductivity detector and 6-ft columns packed with 10% SE-30 on Chromosorb W. Melting points and boiling points are uncorrected.

Materials. Most of the reagents and solvents used in this work were commercial products of high purity, checked by GLC, and used without further purification. The sulfur dioxide was MCB anhydrous grade and was passed through Linde AW-300 molecular sieves prior to use.

1-Hydroxy-2-(ω-methoxycarbonylbutyl)-4,5,6,7-tetrahydrobenzimidazole 3-Oxide (3a). A three-neck 500-mL flask equipped with a septum-capped inlet, a mechanical stirrer, inlets for the introduction of sulfur dioxide and hydrogen chloride, and a dry ice condenser protected with a nitrogen bubbler was placed in a dry ice–acetone bath at −70 °C. A sulfur dioxide cylinder was connected to one inlet and about 100 mL of sulfur dioxide was distilled into the flask. Methanol (200 mmol, 8.05 mL), dry hydrogen chloride (110 mmol), and cyclohexanone (100 mmol, 10.4 mL) were added in this order, and then nitrosyl chloride (6.87 g, 105 mmol) was introduced as a vapor above the surface of the stirred solution. The addition was continued until the solution became pale orange. Alternatively, after the addition of the hydrogen chloride, the nitrosyl chloride may be next added to the reaction flask (either as a vapor or a liquid) followed by the slow addition (2–3 min) of the cyclohexanone with a syringe. A slight exothermic reaction occurs in this case and the nitrosyl chloride is largely decolorized within 5 min. In either case, after the mixing of the reagents and the decolorization of the nitrosyl chloride,[10] stirring was continued for an additional 30 min, and the sulfur dioxide was then removed in vacuo at −40 to −50 °C to give **1** as a soft, white solid. After treatment with cold pentane and evaporation there was obtained about 20 g of **1** which was free from sulfur dioxide but still contained a small amount of methanol. The crude **1** was then dissolved in cold methanol and diluted to 250 mL in a volumetric flask. This solution was stable for long periods of time in a freezer but rapidly darkened if allowed to warm to room temperature.

A 50-mL aliquot of this solution was mixed with 50 mL of water and the resulting solution was titrated at 0 °C with an aqueous 1.00 N sodium hydroxide solution. At about pH 3.5 (the exact value varied from run to run), a white, flaky solid suddenly precipitated. The solid could either be isolated by filtration at this point (see below) or the titration could be continued. When the latter was done, an end point was reached that required slightly more than 1 equiv of base and corresponded to an equivalent weight of about 190–200. Further addition of base dissolved the solid (pH 8) and another end point which required an additional 0.5 equiv of base was reached ($pK_{a2} \simeq 7.5$). Titration with silver nitrate showed that there was only one chloride ion present. Thus, as expected, **1** contains two acidic protons but only one chloride ion.

A second 50-mL aliquot of the methanol solution of **1** was mixed with 50 mL of water and titrated with a 1.00 N sodium hydroxide solution until precipitation occurred. The solid was collected, washed with a little water and methanol, and dried under nitrogen to give 1.31 g (48.8%)[11] of fluffy, white **3a**: mp 178.0–179.5 °C; IR (KBr) 3430 (br, w, OH), 1732 (s, ester C=O), 1690 (w, C=N), and 1635 cm^{-1} (w, C=C); UV max ($CHCl_3$) 230 nm (log ε 4.000); NMR ($CDCl_3$) δ 16.3 (br s, 1, OH) 3.66 (s, 3, OCH_3), 2.77 (t, 2, J = 4.0 Hz, CH_2CO), 2.38 (m, b, CH_2C=C), and 1.73 ppm (m, 8, CH_2); ^{13}C NMR ($CDCl_3$) δ 173.5 (s, 1, C=O), 134.3 (s, 1, C=N), 121.8 (s, 2, C=C), 51.3 (q, 1, CH_3O), 33.5 (t, 1, CH_2C=O), 25.7 (t, 1, CH_2C=C), 24.5 (t, 1, CH_2C=C), 22.0 (t, 2, CH_2), 20.9 (t, 1, CH_2C=N), and 18.6 ppm (t, 2, CH_2); mass spectrum (70 eV) *m/e* (rel intensity) 268 (0.5, M^+), 252 (14, M − O), 251 (3, M − OH), 250 (9, M − H_2O), 235 (11, M − O − OH), 233 (31, M − H_2O − OH), 221 (14, M − O − CH_3O), 219 (6, M − H_2O − CH_3O), 175 (54, M − O − H_2O − $COOCH_3$), 149 (40, M − O − OH − CH_2=$CHCOOCH_3$), and 135 (base, M − O − OH − CH_2=$CHCH_2COOCH_3$).

Anal. Calcd for $C_{13}H_{20}N_2O_4$: C, 58.19; H, 7.51; N, 10.36. Found: C, 58.19; H, 7.49; N, 9.85.

1-Hydroxy-2-(ω-ethoxycarbonylbutyl)-4,5,6,7-tetrahydrobenzimidazole 3-Oxide (3b). The ethyl ester **3b** was prepared by the same procedure as above (**3a**) except that ethanol was used in place of methanol, mp 153.5–155 °C, high-resolution mass spectrum, 282.1583 (calcd for $C_{14}H_{22}N_2O_4$, 282.1578).

1-Hydroxy-2-(ω-carboxybutyl)-4,5,6,7-tetrahydrobenzimidazole 3-Oxide (4). A solution of 5.63 g (20.0 mmol) of the methyl ester **3a** and 8.00 g (20.0 mmol) of sodium hydroxide in 30 mL of water was heated at reflux for 2.5 h. After cooling, the pale yellow solution was acidified with 6 N hydrochloric acid to a pH of 3–4. The white precipitate was filtered, washed with water, and dried to give 4.92 g (96.9%) of **4**, mp 190–193 °C. Two recrystallizations from methanol–ether improved the melting point to 191–193 °C: IR (Nujol) 3480 (br, s, OH) and 1708 cm^{-1} (acid C=O); NMR (Me_2SO-d_6) δ 7.75–7.45 (br s, 2, OH and COOH) and 2.83–2.05 and 1.90–1.29 ppm (m, 16, CH_2).

Anal. Calcd for $C_{12}H_{18}N_2O_4$: C, 56.68; H, 7.13; N, 11.02. Found: C, 56.42; H, 7.28; N, 10.87.

2-(ω-Hydroxypentyl)-4,5,6,7-tetrahydrobenzimidazole (5). A suspension of 5.36 g (20.0 mmol) of **3a** in 150 mL of tetrahydrofuran was added over a 15-min period to a rapidly stirred suspension of 4.56 g (120.0 mmol) of lithium aluminum hydride in 150 mL of tetrahydrofuran and the resulting mixture was heated at reflux for 6 h. After the excess lithium aluminum hydride was decomposed, the resulting slurry was filtered and the solution dried and concentrated to give 2.90 g of a cloudy oil. The oil was chromatographed on a silica gel column using chloroform as the eluent to give **5** as a clear, yellow, viscous oil: IR (KBr) 3400–3200 (OH), 1650 (C=N), 1620 (C=C), 1050–1016 (C–O), and 650 cm^{-1} (trisubstituted imidazole); NMR (Me_2SO-d_6) δ 5.96 (s, 2, OH and NH), 3.60–3.19 (t, 2, $-CH_2O$), 2.69–2.11 (m, b, CH_2); mass spectrum *m/e* 208 (M^+).

2-(ω-Methoxycarbonylbutyl)-4,5,6,7-tetrahydrobenzimidazole (6).[12] A mixture of 2.68 g (10.0 mmol) of **3a** and 8.71 g (50.0 mmol) of

sodium hydrosulfite in 30 mL of water was heated at reflux for 5 h. After cooling, the solution was saturated with potassium carbonate, extracted with 250 mL of chloroform, dried (sodium sulfate), and concentrated to give 1.05 g (44.4%) of **6** as an off-white solid, mp 110–115 °C. Two recrystallizations from chloroform/hexane afforded white crystals: mp 114–116 °C; IR (KBr) 1730 (ester C=O), 1625 (C=N), and 1540 cm^{-1} (C=C); UV max (CH_3OH) 225 nm (ϵ 12 300); NMR ($CDCl_3$) δ 10.62 (s, 1, NH), 3.61 (s, 3, $COOCH_3$), 2.85–2.18 and 1.97–1.49 ppm (m, 16, CH_2); mass spectrum *m/e* 236 (M^+).

Anal. Calcd for $C_{13}H_{20}N_2O_2$: C, 66.08; H, 8.53; N, 11.85. Found: C, 65.83; H, 8.53; N, 11.37.

Reaction of 2-Methoxy-3-oximinocyclohexene (8) with Methyl ω-Oximinocaproate (12). Hydrogen chloride was bubbled for 10–25 s through a solution of 0.710 g (5.00 mmol) of **8** and 0.800 g (5.00 mmol) of **12** in 50 mL of liquid sulfur dioxide at −10 °C. After stirring for 3 h, the sulfur dioxide was replaced by chloroform, and the solution was neutralized with ammonia, filtered, and evaporated to give 1.17 g (87.4%) of **3a**, mp 175–179 °C.

Reaction of 2,2-Dimethoxycyclohexanone Oxime (9)[5] with Methyl ω-Oximinocaproate (12).[2] The same procedure was used as above to give **3a** in a 48.4% yield. **Reaction of 2-oximinocyclohexanone (10)[6] with Methyl ω-Oximinocaproate (12).** The same procedure as above was used to give **3a** in a 52.4% yield.

Reaction of 2-Methoxy-3-oximinocyclohexene (8) with Hydrogen Chloride. Using the same procedure as above, except in the presence of an equimolar amount of methanol, **8** was quantitatively recovered unchanged from the reaction mixture. The same result was obtained when hydrogen chloride was passed over the surface of a paste of **8** and methanol.

Reaction of 2,2-Dimethoxycyclohexanone Oxime (9) with Hydrogen Chloride. When the same procedure as above was used but in the absence of methanol, **9** was quantitatively converted into **8**. When hydrogen chloride was passed over the surface of solid **9**, **8** was obtained in an 85% yield.

Reaction of 2-Oximinocyclohexanone (10)[6] with Hydrogen Chloride. The same procedure as above was used in the presence of an equimolar amount of methanol to give **8** as the main product. When hydrogen chloride was passed over the surface of a paste of **8** and water, only tars were formed.

1-Hydroxy-2,4,5-trimethylimidazole 3-Oxide (13). A. Via Biacetyl Monoxime.[7] Hydrogen chloride was passed over 10.0 g (99.0 mmol) of solid biacetyl monoxime for 45 min. Initially, an exothermic reaction occurred and within 10 min the solid mass was completely converted into a yellow-orange liquid. After cooling, the liquid was extracted with ether and analysis of the other solution by GLC and mass spectrometry showed only acetic acid. The oil was dissolved in chloroform and after neutralization with ammonia and filtration, evaporation of the filtrate afforded 4.00 g (56.3%) of crude **13**, mp 183–187 °C dec (lit. 203 °C dec,[7] 189 °C dec.[4] The structure was confirmed by IR and NMR.[4]

B. Via Biacetyl Monoxime and Acetaldoxime. Hydrogen chloride was bubbled for 10 s through a solution of 0.510 g (5.00 mmol) of biacetyl monoxime and 0.300 g (5.00 mmol) of acetaldoxime in 50 mL of sulfur dioxide at −10 °C. Workup as above gave 0.530 g (74.8%) of **13**, mp 195–196 °C dec.

Attempts to prepare **13** by bubbling hydrogen chloride through a solution of biacetyl monoxime in sulfur dioxide, or biacetyl monoxime and acetonitrile in sulfur dioxide, gave a nearly quantitative recovery of starting materials.

1-Hydroxy-2-*n*-propyl-3,4-dimethylimidazole 3-Oxide (15). Compound **15** was prepared from *n*-butyraldoxime and biacetyl monoxime as above (method B) in a 78.6% yield, mp 171–175 °C dec. Two recrystallizations from ethanol gave a white solid: mp 178.5–179.5 °C dec; IR (KBr) 3450 (OH), 1632 (C=C or C=N), and 1300–1200 cm^{-1} (nitrone); NMR (Me_2SO-d_6) δ 10.93 (s, 1, OH), 2.74–2.53 (t, 2, CH_2C=C), 2.00 (s, 6, CH_3), 1.73–1.43 (m, 2, CH_2), and 0.92–0.71 ppm (t, 3, CH_3CH_2); mass spectrum *m/e* 170 (M^+).

Anal. Calcd for $C_8H_{14}N_2O_2$: C, 56.45; H, 8.29; N, 16.46. Found: C, 56.48; H, 8.65; N, 16.08.

Registry No.—**1**, 62344-90-5; **3a**, 62549-82-0; **3b**, 62549-83-1; **4**, 62549-84-2; **5**, 62549-85-3; **6**, 62549-86-4; **8**, 52841-56-2; **9**, 52540-36-0; **10**, 24858-28-4; **12**, 62344-93-8; **13**, 2654-28-6; **15**, 41933-67-9; methanol, 67-56-1; cyclohexanone, 108-94-1; nitrosyl chloride, 2696-92-6; ethanol, 64-17-5; biacetyl monoxime, 57-71-6; acetaldoxime, 107-29-9; butyraldoxime, 110-69-0.

References and Notes

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(8) See, for example, (a) A. Hassner and W. A. Wentworth, *Chem. Commun.*, 44 (1965); (b) A. Hassner, W. A. Wentworth, and I. H. Pomerantz, *J. Org. Chem.*, **28**, 304 (1963); (c) A. Hassner and I. H. Pomerantz, *ibid.*, **27**, 1700 (1962); (d) A. F. Ferris, G. S. Johnson, and F. E. Gould, *ibid.*, **25**, 496 (1960).
(9) C. W. Shoppee and S. K. Roy, *J. Chem. Soc.*, 3774 (1963).
(10) For NMR purposes, an aliquot was withdrawn at this point and sealed in a tube. The reaction was then followed by NMR by gradually raising the probe temperature.
(11) Higher yields of **3a** could be obtained by titrating the methanol solution directly with a methanolic 3 N sodium hydroxide solution.
(12) The procedure used was similar to that used by Wright (see ref 4).

Oxidation of Dibenzothiophene and Reaction of Dibenzothiophene 5,5-Dioxide with Aqueous Alkali

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Received November 1, 1976

Dibenzothiophene (1) has been oxidized with hydroperoxides, with hydroperoxides and catalysts, and with air in the presence of an organic solvent. The dibenzothiophene 5,5-dioxide (2) produced was converted to sodium 2-phenylphenolate (4) by reaction with aqueous alkali at 300 °C.

Thiophenes and condensed thiophenes are resistant to thermal extrusion of sulfur[1,2] and the reaction of these structures under acidic or basic conditions seems unattractive as a route to sulfur-free products.[3] However, unlike thiophenic systems, aliphatic sulfones form alkenes when treated with alkali at elevated temperatures.[4] Wallace[5] found the general order of reactivity for a series of aliphatic sulfur derivatives toward elimination with potassium *tert*-butoxide to be sulfone > sulfoxide ≫ sulfide.

The decomposition of dibenzothiophene 5,5-dioxide (2) with alkali was noted by Weissgerber and Kruber[6] and Courtot and Chaix.[7] Heimlich and Wallace[8] studied the