(40%) of a colorless liquid: bp 111-120° (0.05 mm); ir (CCl_4) 1774 and 1755 cm^{-1} (C=O); nmr (CCl_4) δ 1.90 (broad, 5 H), 2.10 (s, 3 H, $COCH_3$), 2.50 (broad, 2 H), 4.55 (broad, 1 H), 5.00 (m, 1 H).

Anal. Calcd for $C_9H_{12}O_4$: C, 58.69; H, 6.57. Found: C, 58.61; H, 6.41.

B. Oxidation of Ether 7 with Ruthenium Tetroxide.[13] To a solution of 200 mg (1.28 mmol) of ether **7** in 50 ml of carbon tetrachloride was added 2 ml of a carbon tetrachloride solution of ruthenium tetroxide [prepared by stirring 0.1 g (0.49 mmol) of ruthenium trichloride and 0.5 g (2.32 mmol) of sodium periodate in 25 ml of carbon tetrachloride and 10 ml of water for 20 hr] and a solution of 0.5 g (2.32 mmol) of sodium periodate in 25 ml of water. After the mixture was stirred vigorously for 2 days, isopropyl alcohol was added and the mixture was filtered. Concentration of the organic layer afforded 129 mg (55%) of lactone **6**, identical with material prepared in A.

6-*endo*-Acetoxy-2-oxabicyclo[2.2.2]octane (7). A. A solution of 5.59 g (30.0 mmol) of lactone **6**, 8.31 g (61 mmol) of trichlorosilane, and 0.22 g (1.5 mmol) of di-*tert*-butyl peroxide in a Pyrex tube (35 × 1.5 cm) was degassed by four freeze-pump-thaw cycles (0.01 mm). The tube was sealed and then irradiated as before for 4 hr. The contents of the tube were then poured into 200 ml of ether and 10% sodium hydroxide was added carefully until no further reaction occurred. After filtration, the filtrate was washed with saturated sodium bicarbonate (25 ml) and brine (25 ml), dried ($MgSO_4$), and concentrated. Distillation of the resulting oil in the Kugelrohr manner afforded 3.78 g (73%) of a light oil (70-80°, 0.01 mm): ir (CCl_4) 1740 cm^{-1} (C=O); nmr (CCl_4) δ 1.30-2.50 (broad, 7 H), 2.08 (s, 3 H, $COCH_3$), 3.70 (broad, 3 H, H_2COCH), 4.90 (m, 1 H, $HCOCOCH_3$).

Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.66; H, 8.06.

5-*endo*-Carbomethoxy-7-*endo*-acetoxy-2-oxabicyclo[2.2.2]octane (9). A solution of 5.0 g (21.0 mmol, freshly recrystallized) of lactone **8**,[14] 7.01 g (52.0 mmol) of trichlorosilane, 0.241 g (1.65 mmol) of di-*tert*-butyl peroxide, and 30 ml of tetrahydrofuran (doubly distilled from $LiAlH_4$) was placed in a Pyrex tube (35 × 1.5 cm) and degassed by eight freeze-pump-thaw (0.01 mm) cycles. The tube was sealed and irradiated as before for 12 hr at 50° (heat lamp) and at a distance of 11.5 cm from the lamp. Volatile material was removed by vacuum distillation (30°, 20 mm) and the residue was dissolved in a slurry of 100 ml of ethyl ether and 3 g of sodium bicarbonate. Water was added dropwise until gas evolution ceased. After stirring for 0.5 hr the mixture was dried ($CaCl_2$), filtered, and concentrated to give a light residue. Distillation afforded 2.40 g (50%) of product, bp 95-100° (0.04 mm), that was homogeneous by gas chromatography (160°, 5.0 min):[15] ir (CCl_4) 1745 cm^{-1} (C=O); nmr (CCl_4) δ 1.5-2.4 (broad, 6 H), 2.05 (s, 3 H, $COCH_3$), 3.65 (s, 3 H, $COOCH_3$), 3.75 (broad, 3 H, H_2COCH), 4.90 (m, 1 H, $HCOCOCH_3$).

Anal. Calcd for $C_{11}H_{16}O_5$: C, 57.89; H, 7.07. Found: C, 57.64; H, 6.86.

Registry No.—**2**, 4350-83-8; **3**, 279-87-8; **4**, 7702-72-9; **5**, 10479-79-5; **6**, 51608-92-5; **7**, 51608-93-6; **8**, 51608-94-7; **9**, 51608-95-8; **13**, 23477-88-5; *trans*-1,2-cyclohexanedimethanol, 25712-33-8.

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(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work.

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(5) The presence of ionic intermediates which might undergo ring opening is inferred from the highly acidic nature of the medium and the normal mode of hydride attack on carboxyl derivatives. Furthermore, the parallel increase in reduction efficiency with increasing substitution suggests ionic intermediates.

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(7) When the reduction of **6** was carried out with 4 equiv of trichlorosilane, the major product (60% yield) was the ethyl ether formed by further reduction of the acetate of **7**.

(8) Gas chromatographic analysis of the crude reaction mixture showed that ether **3** was the only volatile product present and that it had been formed in 67% yield (*p*-xylene internal standard). The low isolated yield is ascribed to its extreme volatility and resultant loss during work-up.

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(14) Details of the synthesis of triester **8** from *trans*-1,2,3,6-tetrahydrophthalic anhydride (75% yield) will be reported at a later date.

(15) The major contaminant in the reduction of **8** resulted from attack at the acetate carbonyl and ranged randomly from 15 to 35%.

Methoxymethyl Isocyanate from Thermal Rearrangement of 5-Methoxymethyldioxazolone

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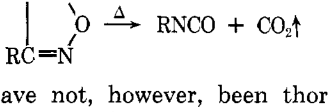
Received May 8, 1974

The acid-catalyzed reactions[1] of *N*-methylol and *N*-methoxymethyl derivatives have been utilized industrially. The formation of resins and modifications of cellulose employing urea-formaldehyde and melamine-formaldehyde chemistry are examples. Interst has developed in methoxymethyl isocyanate (MMI) as a modifying agent for incorporating *N*-methoxymethyl sites onto reactive polymers.[2-5] Such modifications have resulted in thermosetting lacquers, coatings, and resins suitable for industrial applications. Our efforts in this area were initially complicated by problems encountered in the synthesis of MMI.

The reported[3] synthesis of MMI involves the reaction of chloromethyl methyl ether with sodium cyanate in a mixed solvent system composed of DMF and a hydrocarbon, and isolation of the MMI by distillation (90°, 760 mm). We found the yields of MMI by this method to be low and variable. The highest yield of MMI we have realized by this procedure is 45%. The MMI was codistilled with toluene from the reaction mixture containing DMF-toluene as solvents. The utilization of this MMI-toluene solution was previously reported.[6] We would like to report a superior synthetic route for the generation of MMI in excellent yields in a hydrocarbon solvent.

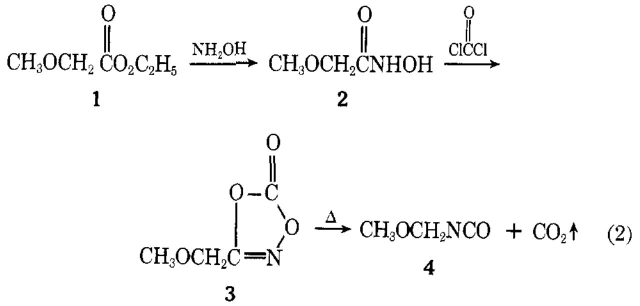
The thermal rearrangement of dioxazolones (nitrile carbonates) to aliphatic and aromatic isocyanates has been well documented.[7-12] The nature and scope of the rearrangement have not, however, been thoroughly investigated. We have applied the aforementioned thermal rearrangement of nitrile carbonates to the synthesis of MMI. The precursor dioxazolone (3) was prepared as shown in eq 2.



(1)

Ethyl methoxyacetate (**1**) was treated with hydroxylamine in methanol to produce methoxyacetohydroxamic acid (**2**). The hydroxamic acid **2** was then treated with excess phosgene, which resulted in the isolation of methoxymethyldioxazolone (**3**) in excellent yield.

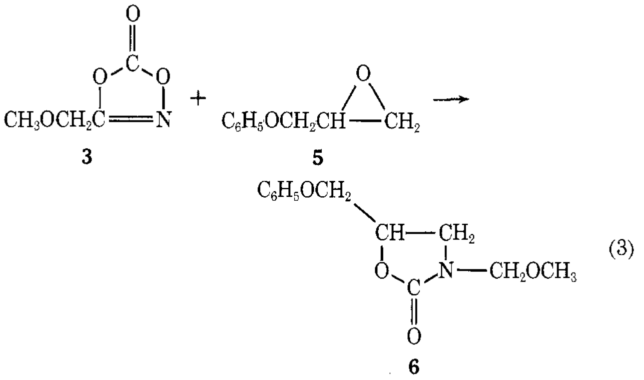
The dioxazolone **3** could be easily handled and was not a lachrymator. Analysis (neat) by differential scanning calo-



rimetry (DSC) indicated an initial decomposition point of 150° with rapid decomposition occurring at 170°. The decomposition of the dioxazolone **3** in solution could be easily followed by ir owing to its characteristic[6] carbonyl bands. The rearrangement of a 10% solution of dioxazolone **3** in DMF occurred at 130° with the appearance of the isocyanate band at 2250 cm^{-1}. Most of the dioxazolone **3** had decomposed after 1 hr, but the isocyanate band dropped in intensity and new bands appeared corresponding to the trimer (1,2,5-trimethoxymethyleneisocyanurate). This is consistent with the exclusive formation of trimer from the chloromethyl methyl ether and sodium cyanate reaction in DMF.[3] The decomposition of dioxazolone **3** in refluxing xylene (140°) was also investigated. After 16 hr, most of the dioxazolone **3** remained unreacted; however, a weak isocyanate band had developed at 2250 cm^{-1}.

The dioxazolone **3** was observed to decompose rapidly in refluxing xylene solution containing 2.5 mol % of a hydrocarbon-solubilized adduct of tributylphosphine oxide and lithium bromide. After 15 min, the infrared spectrum indicated the disappearance of dioxazolone **3** and the appearance of an intense isocyanate band at 2250 cm^{-1}. A conventional isocyanate (NCO) analysis[14] indicated 95% conversion to MMI.

As previously reported,[6,15] the MMI can be trapped with phenyl glycidyl ether under these conditions. Equimolar quantities of methoxymethyldioxazolone (**3**) and phenyl glycidyl ether (**5**) in xylene were added dropwise (15 min) to a refluxing solution of hydrocarbon-solubilized catalysts (2.5 mol %) in xylene. After the addition was completed, ir analysis indicated a trace of isocyanate, no dioxazolone, and an intense band at 1760 cm^{-1} (2-oxazolidone). Workup of the reaction mixture resulted in the isolation of 90% *N*-methoxymethyl-5-phenoxym ethylene-2-oxazolidone (**6**) that was identical with the known sample.[15] The thermal rearrangement of the dioxazolone (3) under these conditions produces excellent yields of MMI in xylene solution.



Experimental Section

General. Phosgene was obtained from Air Products and Chemicals, Inc., and was utilized without further purification. All other chemicals were obtained from Aldrich Chemical Co. Melting points are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Infrared absorption spectra were obtained on a Perkin-Elmer Model 337 spectrophotometer. The nmr spectra were determined on a Japan Electron Optics Lab 4H-100 spectrometer using TMS as internal standard and solvents were as indicated. The DSC data were obtained on a Du Pont 900 Thermal Analyzer in the DSC mode.

Methoxyacetohydroxamic Acid (2). The procedure of Jones and Powers[13] was employed. A solution of hydroxylamine hydrochloride (140 g, 2.0 mol) in methanol (750 ml) was prepared by heating to reflux. The solution was allowed to cool to 30° and a solution of potassium hydroxide (112 g, 2.0 mol) in methanol (300 ml) was added. The temperature of the resulting mixture was kept below 40° by the use of an ice bath. After 5 min the ethyl methoxyacetate was added and the flask was stoppered and allowed to stand overnight. The mixture was filtered and the filtrate was concentrated on a rotary evaporator. The resulting solid was recrystallized from ethyl acetate–ligroin, yielding 71 g of methoxyacetohydroxamic acid: mp 83–84° (lit.[13] mp 85.5°); nmr (DMSO-d_6) δ 10.58 (s, 1 H), 8.80 (s, 1 H), 3.76 (s, 2 H), 3.25 (s, 3 H).

5-Methoxymethyldioxazolone (3). The recrystallized methoxyacetohydroxamic acid (**2**, 30 g, 0.28 mol) was slurried with 400 ml of anhydrous ether and cooled to 0°. Excess phosgene (180 g, 1.8 mol) was bubbled into the stirred ether slurry. After the phosgene had been added, the clear solution was warmed to room temperature and flushed with dry nitrogen (8 hr) to remove the excess phosgene. The ether was removed on a rotary evaporator and the residue was distilled, yielding 34.0 g (92%) of methoxymethyldioxazolone (**3**): bp 52–54° (0.85 mm); ir (neat) 1825 and 1875 cm^{-1} (dioxazolone ring); nmr ($CDCl_3$) δ 4.39 (s, 2 H), 3.45 (s, 3 H).

Anal. Calcd for $C_4H_5NO_4$: C, 36.65; H, 3.84; N, 10.69. Found: C, 36.72; H, 3.79; N, 10.67.

Trapping of Methoxymethyl Isocyanate with Phenyl Glycidyl Ether. A xylene solution (100 ml) containing the hydrocarbon-solubilized adduct of tributylphosphine oxide (0.8 mmol, 3.5 mol %) and lithium bromide (0.57 mmol, 2.5 mol %) was prepared and dried as previously reported.[6] A xylene solution (10 ml) containing methoxymethyldioxazolone (3.0 g, 22.9 mmol) and phenyl glycidyl ether (3.4 g, 22.9 mmol) was added dropwise (15 min) to the refluxing solution of the hydrocarbon-solubilized catalyst. The reaction was judged complete by ir analysis and the solution was allowed to cool to room temperature. The xylene was removed on a rotary evaporator under vacuum and the solid product was recrystallized from carbon tetrachloride–hexane, yielding 90% of *N*-methoxymethylene-5- phenoxymethylene-2-oxazolidone (5.6 g, 20.6 mmol). This material was identical with a known sample previously prepared.[6]

Registry No.—**1**, 3938-96-3; **2**, 51821-07-9; **3**, 51821-08-0; **4**, 6427-21-0; **5**, 122-60-1; **6**, 34277-53-7.

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