1-propanol, 71-23-8; methyl *tert*-butyl ketone, 75-97-8; 4,5-dimethyl-5-*tert*-butyl-2-oxazolidone, 39922-63-9; sodium 2-methoxyethoxide, 3139-99-9; 2,3,3-trimethyl-1-butene, 594-56-9; bromoform, 75-25-2; 1,1-dibromo-2-methyl-2-*tert*-butylcyclopropane, 39922-65-1; $\alpha,\beta,\beta,\gamma$-tetramethyl-$\gamma$-valerolactone, 39922-59-3.

Reactions of 5,5-Disubstituted 3-Nitrosooxazolidones. New Syntheses of Vinyl Azides, Vinyl Isothiocyanates, Vinyl Diethyl Phosphonates, and Divinyl Ethers[1]

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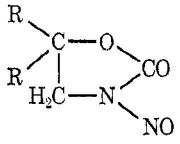
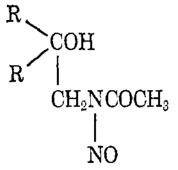
New syntheses of the α,β-unsaturated ketones, cyclohexylidenemethyl isopropyl ketone (**3**) and cyclohexylidenemethyl *tert*-butyl ketone (**4**), the divinyl ethers, 3-pentenyl ether (**6**) and cyclohexylidenemethyl 2,4-dimethyl-3-pentenyl ether (**7**), the vinyl azide, cyclohexylidenemethyl azide (**9**), the vinyl isothiocyanate, cyclohexylidenemethyl isothiocyanate (**10**), and the vinyl phosphonate, diethyl cyclohexylidenemethylphosphonate (**11**), result from the treatment of 1-(*N*-nitrosoacetylaminomethyl)cyclohexanol (**2a**) with bases in the presence of isobutyraldehyde, trimethylacetaldehyde, cyclohexanone, diethyl ketone, diisopropyl ketone, sodium azide, potassium isothiocyanate, and triethyl phosphite, respectively. The stereospecific cleavage of glyme to form 2-methoxyethyl *trans*-2,2,3-trimethyl-1-butenyl ether (**14b**) in 46% yield on treatment of 3-nitroso-5-methyl-5-*tert*-butyl-2-oxazolidone (**12**) with sodium phenoxide is explained by assuming the involvement of an unsaturated cationic intermediate. The reaction of 3-nitroso-4,5,5-trimethyl-2-oxazolidone (**15**) in 2-methoxyethanol containing sodium 2-methoxyethoxide yields 2-methoxyethyl 3-methyl-1-buten-3-yl carbonate (**16**, 22%) and other products in smaller yields.

In earlier work the products obtained on treating 5,5-disubstituted 3-nitrosoxazolidones (1) and nitrosoacetylaminomethylcarbinols (2) with alkaline reagents in the presence of other reactants were determined and their formation was explained by assuming the involvement of unsaturated cations (A)[3] or unsaturated carbenes (B).[4] In this paper further work designed to elucidate the reaction mechanisms involved and to expand the utility of the reactions for new syntheses is described.



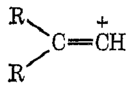
1

1a, RR = $-(CH_2)_5-$

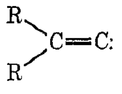


2

2a



A



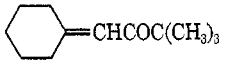
B

C, R,R = $-(CH_2)_5-$

The reactions of **1a** and **2a** with alkali in the presence of cyclohexene to yield bicyclo[4.1.0]hept-7-ylidenecyclohexane have been reported and explained by assuming the intervention of cyclohexylidenecarbene (C).[5] We wished to see if reaction of 1-(*N*-nitrosoacetylaminomethyl)cyclohexanol **2a** with the carbonyl group of aldehydes and ketones would yield allene epoxides.

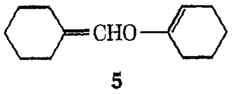
When a solution of **2a** and isobutyraldehyde in pentane containing Aliquat 336[6] was treated with aqueous sodium hydroxide at −10° the evolution of nitrogen was vigorous. From the reaction mixture a 36% yield of cyclohexylidenemethyl isopropyl ketone (**3**) was isolated. In a similar reaction involving trimethylacetaldehyde, only a 4.4% yield of cyclohexylidenemethyl *tert*-butyl ketone (**4**) was obtained. These reactions represent a new route to α,β-unsaturated ketones. Until further work is done on this reaction, speculation as to the mechanism will not be made.

3



4

When **2a** was treated under similar conditions with cyclohexanone, diethyl ketone, and diiosopropyl ketone there were obtained cyclohexylidenemethyl cyclohexenyl ether (**5**), cyclohexylidenemethyl 3-pentenyl ether (**6**), and cyclohexylidenemethyl 2,4-dimethyl-3-pentenyl ether (**7**) in 32, 22, and 4.4% yields, respectively. Although the yields are low (no attempts at maximization were made), these reactions are of interest because they illustrate a new synthesis of acylic divinyl ethers, a type of ether apparently unknown except for the parent divinyl ether.[7] The formation



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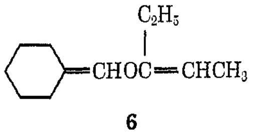

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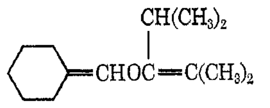

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[1] This research was supported by Grant G12445X from the National Science Foundation.

[2] Further details can be found in the Ph.D. thesis of W. C. Liang, The Ohio State University, 1972.

[3] M. S. Newman and C. D. Beard, *J. Amer. Chem. Soc.*, **92**, 7564 (1970), and references cited therein.

[4] M. S. Newman and Z. ud Din, *Syn. Commun.*, **1**, 247 (1971).

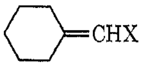
[5] M. S. Newman and C. D. Beard, *J. Amer. Chem. Soc.*, **92**, 4309 (1970).

[6] Methyl tricaprylylammonium chloride, General Mills Chemicals, Kankakee, Ill.

[7] J. U. Nef, *Justus Liebigs Ann. Chem.*, **298**, 327 (1897).

of vinyl ethers by the metal-catalyzed reaction[8] of ethyl diazoacetate with acetone and cyclohexanone and by pyrolysis[9] have been reported.

Since the reaction of nitrosooxazolidones (**1**, **1a**) with base in the presence of chloride, bromide, and iodide ions afforded high yields of terminal vinyl chlorides, bromides, and iodides,[5] classes of compounds not readily obtained by other methods, similar reactions were carried out with **2a** in the presence of iodide ion. Since a 72% yield of cyclohexylidenemethyl iodide (**8**) was obtained, we were encouraged to try similar reactions of **2a** in the presence of other nucleophilic reagents. When the reaction was carried out in the presence of azide ions a 56% yield of cyclohexylidenemethyl azide (**9**) was obtained. Thus a valuable synthesis of terminal azides is at hand. This new route to vinyl azides complements known methods.[10]



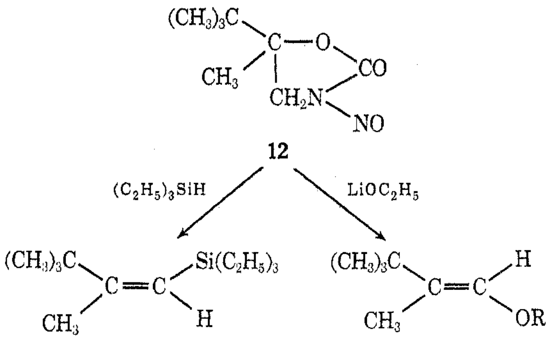
9, $X = N_3$
10, $X = SCN$
11, $X = PO(OC_2H_5)_2$

Similar reaction of **2a** with potassium thiocyanate afforded cyclohexylidenemethyl isothiocyanate (**10**) in 39% yield. This constitutes a new synthesis of terminal vinyl isothiocyanates, a class of compounds generally unknown except for the parent, vinyl isothiocyanate.[11]

When triethyl phosphite was used, **2a** reacted to form cyclohexylidenemethyldiethyl phosphonate (**11**) in 42% yield. Thus a new synthesis of phosphonates, quite different from all other methods,[12] is at hand. This and the above new reactions demonstrate anew the versatility of nitrosoacetylaminomethylcarbinols for the synthesis of substituted vinyl compounds. Although the syntheses of vinyl azides, isothiocyanates, and vinyl phosphonates have been demonstrated only with **2a**, undoubtedly similar reactions would occur with the nitrosooxazolidones (**1**). In our limited experience it is difficult to predict whether a better yield of product will be obtained by starting with a nitrosooxazolidone or a nitrosoacetylaminomethyl alcohol.[13]

In earlier work, the steric course of reactions in the carbenic and cationic modes of reaction of 5-methyl-5-*tert*-butyl-2-nitrosooxazolidone (**12**) were studied. In both cases, the intermediate was attacked at the position trans to the *tert*-butyl group.[14]

Evidence that the intermediate leading to **13** was an unsaturated carbene (B) was presented.[14] However, **14** could have been formed from A or B. Furthermore, under the reaction conditions (lithium ethoxide) designed to allow capture of a carbene by an allene, a 7% yield of **14** was obtained as a byproduct.[14] We now show that treatment of **12** with sodium methoxide in methanol affords an 86% yield of a mixture of *trans*-**14a** (97%) and *cis*-**14a** (3%). As mentioned,[15] we cannot be sure whether an unsaturated carbene or cation is involved in the formation of vinyl ethers. In order to determine unequivocally the steric course of reaction in which an unsaturated cation was the intermediate, we treated **12** with sodium phenoxide in glyme as described for an analogous case.[3] A 46% yield of 2-methoxyethyl *trans*-2,2,3-trimethyl-1-butenyl ether (**14b**) and a 53% yield of anisole were produced. Thus, the unsaturated cation formed from **12** reacted stereospecifically trans to the *tert*-butyl group. Interestingly, a small yield (7–8%) of methyl *tert*-butyl acetylene was produced (compare ref 3 and 13) in this reaction.

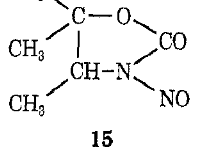


12

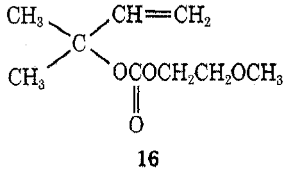
13

14, $R = C_2H_5$
14a, $R = CH_3$
14b, $R = CH_2CH_2OCH_3$

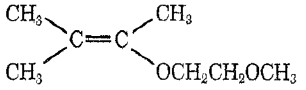
Since previous work on the alkaline treatment of nitrosooxazolidones had been confined almost exclusively to 5,5-dialkyl derivatives, we thought it of interest to study a case in which a 4-alkyl substituent was present because such a compound could not give rise to an unsaturated carbene.[16] Furthermore, the behavior of a trialkyl-substituted unsaturated cation compared to that of the unsymmetrical disubstituted variety (A) would be of interest. Accordingly, 3-nitroso-4,5,5-trimethyl-2-oxazolidone (**15**) was prepared. When a solution of **15** in 2-methoxyethanol saturated with sodium iodide was treated with sodium 2-methoxyethoxide,[5] no vinyl iodide was obtained. The main product obtained was 2-methoxyethyl 3-methyl-1-buten-3-yl carbonate (**16**) together with



15



16



18

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(10) "The Chemistry of the Azido Group," S. Patai, Ed., Wiley-Interscience, New York, N. Y., 1971, p 80 ff.

(11) (a) J. C. H. Hwa, *J. Amer. Chem. Soc.*, **81**, 3604 (1959); (b) E. Tobler and D. Foster, *Z. Naturforsch.*, **17**, 136 (1962).

(12) (a) Y. L. Gefter, "Organophosphorous Monomers and Polymers," Pergamon Press, Elmsford, N. Y., 1962, pp 26–27, and references cited therein; (b) W. H. Woodstock, U. S. Patent 2,471,472 (1949); *Chem. Abstr.*, **43**, 7499 (1949); (c) G. M. Kosolapoff, U. S. Patent 2,389,576 (1946); *Chem. Abstr.*, **40**, 1536 (1946); (d) D. Y. Wysocki, *Diss. Abstr.*, **B28** (4), 1437 (1967); (e) P. Tavs and H. Weitkamp, *Tetrahedron*, **26**, 5529 (1970).

(13) Compare M. S. Newman and S. J. Gromelski, *J. Org. Chem.*, **37**, 3220 (1972).

(14) M. S. Newman and T. B. Patrick, *J. Amer. Chem. Soc.*, **92**, 4312 (1970).

(15) M. S. Newman and A. O. M. Okorodudu, *J. Org. Chem.*, **34**, 1220 (1969).

(16) For one example of such a reaction see ref 15.

small amounts of 3-methyl-2-butanone (**17**) and 2-methoxyethyl 3-methyl-2-butenyl ether (**18**). When **15** in glyme was treated with sodium phenoxide, only a 2.6% yield of **18** and a corresponding 3.9% yield of anisole resulted. Hence the cleavage of glyme by the trimethylvinyl cation occurred to a very slight extent.[3] The above experiments indicate either that the trimethylvinyl cation is much less reactive than the disubstituted type (A) or that very little is formed because of competing reactions.

Experimental Section[17]

Cyclohexylidenemethyl Isopropyl Ketone (**3**).—To a stirred solution of 2.5 g (0.0125 mol) of **2a**[4] and 9 g (0.125 mol) of isobutyraldehyde in 15 ml of pentane containing 1 g of Aliquat 336[6] was added dropwise at −10° a 50% solution of sodium hydroxide in water. The theoretical amount of nitrogen was collected in 15 min. The mixture was then poured into 75 ml of a saturated sodium chloride solution and worked up as usual. Distillation at 60–137° (0.2 mm) yielded 2.18 g of colorless product. From the preparative vpc (column B, 125°, helium flow 120 cc/min, retention time 5.5 min) there was isolated 0.74 g (35.7%) of cyclohexylidenemethyl isopropyl ketone (**3**): ir (neat) 5.94 ($C{=}O$), 6.15 ($C{=}C$), and 6.90 μ [doublet, $(CH_3)_2CH-$]; nmr (CCl_4) τ 8.97 [d, $J = 7$ Hz, 6, $-CH(CH_3)_2$], 8.38 (m, 6, $-CH_2-$), 7.84 (m, 2, $CH_2C{=}$), 7.36 [m, $J = 7$ Hz, 1, $-CH(CH_3)_2$], 7.26 (m, 2, $CH_2C{=}$), 4.10 (m, 1, $={CH}$); uv (absolute EtOH) 241 mμ (ϵ 11,200); mass spectrum *m/e* 166.

Anal. Calcd for $C_{11}H_{18}O$: C, 79.5; H, 10.9. Found: C, 79.2; H, 11.1.

The 2,4-dinitrophenylhydrazone, mp 127.5–128.0°, mass spectrum *m/e* 346, was prepared.

Cyclohexylidenemethyl *tert*-Butyl Ketone (**4**).—In an analogous experiment involving 2.5 g of **2a** and 4.4 g of 2,2-dimethylpropanol was isolated by preparative vpc (column B, 135°, helium flow 130 cc/min) 0.10 (4.4%) of **4**: ir 5.87, 5.98, 6.20 μ ($C{=}C$); nmr (CCl_4) τ 8.87 [s, 9, $(CH_2)_3C-$], 8.36 (m, 6, $-CH_2-$), 7.80 (m, 2, $CH_2C{=}$), 7.25 (m, 2, $-CH_2C{=}$), 3.79 (m, 1, $={CH}$); mass spectrum *m/e* 180, exact mass measurement 180.1517 (calcd, 180.1519); uv (absolute EtOH) 241 mμ (ϵ 12,700). The 2,4-dinitrophenylhydrazone, mp 125.5–127.0°, mass spectrum *m/e* 360, was prepared.

Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.12. Found: C, 80.25; H, 11.19.

Cyclohexylidenemethyl Cyclohexenyl Ether (**5**).—To a stirred solution at 0–10° of 5.0 g of **2a** and 19.6 g of cyclohexanone in 30 ml of pentane containing Aliquat 336 was added 50% aqueous sodium hydroxide in tiny drops until about 95% of the theoretical nitrogen evolution had occurred (less than 30 min). The mixture was then treated with 100 ml of saturated sodium chloride solution and was worked up as usual to yield 2.1 g of colorless oil on distillation at 60–94° (0.05 mm). By glpc analysis the mixture was shown to contain approximately 1.6 g (32%) of **5**:[18] ir (neat) 6.00 and 8.50 μ; nmr (CCl_4) τ 8.44 (m, 10, ring $-CH_2-$), 7.92 (m, 8, $-CH_2C{=}C$), 5.28 (m, 1, $={CH_2C}-$), 4.10 (m, 1, $={CHO}-$); mass spectrum exact mass 192.1514 (calcd, 192.1516).

Anal. Calcd for $C_{13}H_{20}O$: C, 81.3; H, 10.5. Found: C, 81.3; H, 10.3.

Cyclohexylidenemethyl 3-Pentenyl Ether (**6**).—In an experiment similar to the above with 4.9 g of **2a** and 21 ml of diethyl ketone in 25 ml of pentane was obtained 22% of **6**. By preparative glpc on a 10 ft × 0.125 in. 5% SE-30 on Chromosorb W at 138° on a F & M Model 609 chromatograph was isolated a sample of **6** which showed two components, undoubtedly the cis and trans isomers (no attempt at separation was made), and had the following properties: ir (heat) 5.45 and 8.40 μ; nmr (CCl_4) τ 8.97, 8.92 (two triplets, $J = 7$ Hz, 3 CH_2CH_3), 8.42 [m, 9, $-(CH_2)_3-$ and $CH_3C{=}C$], 7.90 (m, 6, $-CH_2C{=}C$), 5.50 5.35 (2 q, $J = 7$ Hz, 1, $CH_3CH{=}$), 4.14 (m, 1, $={CH}$); mass spectrum exact mass 180.1515 (calcd, 180.1514). After treatment with dilute hydrochloric acid a mixture of 2,4-dinitrophenylhydrazone, of diethyl ketone, *m/e* 266, and cyclohexanecarboxaldehyde, *m/e* 292, was obtained.

Cyclohexylidenemethyl 2,4-Dimethyl-3-pentenyl Ether (**7**).—In a similar experiment (2.5 g of **2a**, 14 g of diisopropyl ketone) there was obtained 0.12 g (4.4%) of **7**: ir (neat) 6.00 and 8.45 μ; nmr (CCl_4) τ 9.00 [d, $J = 7$ Hz, 6, $-CH(CH_3)_2$], 8.38 [m, 12, $-(CH_2)_3-$ and $={C(CH_3)_2}$], 8.02 (m, 2, trans $CH_2C{=}CO-$), 7.78 (m, 2, cis $CH_2C{=}CO-$), 7.18 [m, 1, $-CH(CH_3)_2$], 4.34 (m, 1, $={CH}$); *m/e* 208 (calcd, 208).

Anal. Calcd for $C_{14}H_{24}O$: C, 80.7; H, 11.6. Found: C, 80.4; H, 11.6.

Reactions with 2a with Nucleophiles.—A solution of 2.50 g of **2a** in 15 ml of pentane was dropped into a stirred mixture of 20 g of sodium iodide, 1 g of sodium hydroxide, 0.75 g of Aliquat 336,[6] and 10 g of water held at 3–5°. After the usual work-up, distillation afforded 2.00 g (72%) of iodomethylenecyclohexane, identified by nmr and ir which were identical with those of the known compounds.[5] In a similar experiment, except that 10 g of sodium azide was used instead of sodium iodide, there was isolated 2.2 g of crude reaction product. Chromatography over 30 g of Woelm alumina, grade I, with hexane yielded 0.95 g (56%) of azidomethylenecyclohexane (**9**) as a pale yellow liquid: ir (neat) 4.75 ($={CN_3}$), 6.00 μ ($C{=}C$), nmr (CCl_4) τ 8.48 [m, 6, $-(CH_2)_3-$], 7.92 (m, 4, $-CH_2C{=}$), 4.16 (m, 1, $={CH}$). An analytical sample was obtained by bulb-to-bulb distillation at 0.1 mm.

Anal. Calcd for $C_7H_{11}N_3$: C, 61.3; H, 8.1; N, 30.6. Found: C, 61.4; H, 8.2; N, 30.8.

In a similar experiment except that 12.1 g of potassium thiocyanate was used, *distillation of the crude product* yielded 0.78 g (41%) of colorless cyclohexylidenemethyl thiocyanate (**10**) (>95% pure by glpc). A purer sample was obtained by preparative glpc (column A, 140°, helium flow 100 cc/min, retention time 5 min). Pure **10** had ir bands at 4.65 ($={CSCN}$), 6.20 μ ($C{=}C$, weak); nmr (CCl_4) τ 8.39 [m, 6, $-(CH_2)_3-$], 7.70 (m, 4, $-CH_2C{=}$), 4.28 (m, 1, $={CH}$); *m/e* 153 (calcd, 153).

Anal. Calcd for $C_8H_{11}NS$: C, 62.7; H, 7.2; N, 9.1; S, 20.9. Found: C, 62.6; H, 7.1; N, 9.3; S, 20.9.

A solution of 2.5 g of nitrosoamide **2a** in 25 ml of pentane was added dropwise to a stirred, ice-cold mixture of 10.4 g of triethyl phosphite, 1 g of sodium hydroxide, 1.5 g of water, and 1 g of Aliquat 336 during 25 min. After the evolution of nitrogen (72% of the theoretical amount in 15 min) the mixture was worked up as usual. Distillation of the residue at 55–120° (0.1 mm) yielded 1.75 g of products which by glpc (column B) showed three components at a column temperature of 115° (helium flow 87 cc/min) and one main component at a column temperature of 190° (helium flow 75 cc/min), 6 min, 1.22 g (42%) of cyclohexylidenemethyl diethyl phosphonate (**11**). Pure **11** had ir (neat) 6.14 ($C{=}C$), 8.07 ($P{=}O$), 9.50, 9.75, 10.45 μ (POC); nmr (CCl_4) τ 8.68 (t, $J = 7$ Hz, 6, $-CH_3$), 8.34 [m, 6, $-(CH_2)_3-$], 7.76 (m, 2, trans $CH_2C{=}CP$), 7.30 (m, 2, cis $CH_2C{=}CP$), 5.97 (m, $J = 7$ Hz, 4, $-CH_2CH_3$), 4.78 (d, $J = 17$ Hz, 1, $={CHP}$); mass spectrum exact mass, 232.1226 (calcd, 232.1228).

Anal. Calcd for $C_{11}H_{21}O_3P$: C, 56.9; H, 9.1; P, 13.3. Found: C, 56.8; H, 9.5; P, 13.5.

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[17] *All melting and boiling points are uncorrected.* Melting points were taken with a Thomas-Hoover capillary melting point apparatus. The thermometers for boiling point determination were not standardized. Microanalyses were performed by the M-H-W Laboratories, Garden City, Mich., and Chemalytics, Tempe, Ariz. Infrared absorption spectra were recorded on a Perkin-Elmer Infracord spectrophotometer. Nuclear magnetic resonance spectra relative to τ 10 for TMS were recorded on A-60 and A-60A nmr spectrophotometers, Varian Associates, Palo Alto, Calif. Vapor phase chromatographic analyses were recorded on a Varian Aerograph Model 1200 flame ionization gas chromatograph and a Varian Aerograph Model A-90P-3 gas chromatograph. A Varian Aerograph Autoprep, Model A-700, was used *for preparative vapor phase chromatography.* Column A represents a 10 ft × 0.375 in. column of 10% Carbowax 20M on Chromosorb W; column B represents a 5 ft × 0.25 in. column of 10% SE-30 on Chromosorb W. All vpc yields were based on the moles of the nitroso compounds used before decomposition. Ultraviolet spectra were recorded on a Perkin-Elmer Model 202 uv spectrophotometer. Mass spectra were recorded on an AEI Model MS-9 instrument by Mr. Richard Weisenberger. The phrase "worked up as usual" means that the reaction mixture was diluted with ice water and the products were extracted into ether. The ethereal extracts were washed with a saturated salt solution, and dried by filtration through a cone of anhydrous magnesium sulfate or by the addition of anhydrous magnesium sulfate followed by filtration through a pad of Celite. The solvents were removed by distillation or on a rotary evaporator. Unless otherwise specified, the nitrogen evolution usually finished as soon as all of the base had been added.

[18] In all of the experiments with **2a** minor amounts of cyclohexanone, cycloheptanone, and cyclohexanecarboxaldehyde were obtained and identified by retention times, formation of the known 2,4-dinitrophenylhydrazones, or mass spectral results.

3-Nitroso-5-methyl-5-*tert*-butyl-2-oxazolidone (12) was prepared as described.[14]

Ethyl 2,3-Dimethyl-3-hydroxybutanoate.—To a refluxing stirred mixture of 130 g of activated zinc,[19] 250 ml of benzene, 105 g of acetone, and 250 ml of ether was added 362 g of ethyl α-bromopropionate during 3 hr. After a further 1 hr at reflux a conventional work-up afforded 214 g (74%) of desired ester, bp 77–78° (10 mm).

Anal. Calcd for $C_8H_{16}O_3$: C, 60.0; H, 10.0. Found: C, 59.9; H, 10.1.

2,3-Dimethyl-3-hydroxybutanoic Acid Hydrazide.—To 194 g of the above ester was added 58 g of anhydrous hydrazine at 0–20°. After 1 day the excess hydrazine was removed in a vacuum desiccator over concentrated H_2SO_4. Recrystallization from 95% ethanol–chloroform yielded 112 g (63%) of colorless hydrazide, mp 124–125°.

Anal. Calcd for $C_6H_{14}N_2O_2$: C, 49.3; H, 9.6. Found: C, 49.5; H, 9.6.

4,5,5-Trimethyl-2-oxazolidone.—To a stirred solution of 73.1 g of hydrazide in 250 ml of 2 *N* hydrochloric acid was added a solution of 41.4 g of sodium nitrite in 120 ml of water during 3 hr while maintaining a temperature near 5°. The mixture was extracted with benzene–chloroform (3:1) and the cold extract was washed with cold saturated sodium chloride solution. This extract was then added during 1 hr to 100 ml of refluxing benzene. After removal of solvent on a rotary evaporator, distillation at about 105° (0.15 mm) yielded a solid which, on crystallization from benzene–petroleum ether (bp 65–70°), yielded 54 g (83%) of oxazolidone: mp 61.0–61.5°; ir (KBr) 3.03 (NH), 5.77 μ (C=O); nmr ($CDCl_3$) τ 8.80 (d, J = 7 Hz, 3, $-CHCH_3$), 8.64 (s, 3, CH_3), 8.52 (s, 3, CH_3), 6.30 (q, J = 7 Hz, 1, $CHCH_3$), 3.52 (m, 1, NH).

Anal. Calcd for $C_6H_{11}NO_2$: C, 55.8; H, 8.5. Found: C, 56.0; H, 8.7.

***N*-Nitroso-4,5,5-trimethyl-2-oxazolidone (15).**—To a stirred solution at 5° of 42 g of the above oxazolidone in 150 ml of 6 *N* hydrochloric acid was dropped a solution of 26.8 g of sodium nitrite in 100 ml of water. The yellow precipitate was collected, washed thoroughly with ice water, and dried *in vacuo* over P_2O_5. Recrystallization from ether–pentane afforded 47.7 g (93%) of **15**, mp 88–89° dec, ir (KBr) 5.57 μ (C=O). On standing at room temperature this compound decomposes so that a suitable C and H analysis could not be obtained.

Reactions of 12 with Nucleophiles. A. Decomposition with Sodium Methoxide in Methanol.—A slurry of 5.59 g (0.03 mol) of **12** in 30 ml of absolute methanol (freshly distilled over magnesium) was treated dropwise at 4° during 0.5 hr with a solution of 1.78 g (0.033 mol) of sodium methoxide in 10 ml of absolute methanol. After the theoretical amount of nitrogen had been evolved the mixture was worked up as usual. The residue was distilled to give 3.15 g (82%) of colorless materials at 63–65° (50 mm), which by vpc (column A, 40°, helium flow 100 cc/min) consisted of 97% of methyl *trans*-2,3,3-trimethyl-1-butenyl ether (**14a**) {ir (neat), bands at 5.95 (C=C), 8.90 μ ($C{=}COCH_3$); nmr (CCl_4) τ 8.98 [s, 9, $C(CH_3)_3$], 8.45 (d, J = 1 Hz, 3, $3H_3$), 6.49 (s, 3, $-OCH_3$), 4.27 (m, J = 1 Hz, 1, $=CH$); mass spectrum, mol wt 128, exact mass measurement 128.1202 (calcd, 128.1201)} and 3% of a compound which was undoubtedly the cis isomer.

Anal. Calcd for $C_8H_{16}O$: C, 74.9; H, 12.6. Found: C, 74.9; H, 12.6.

B. Decomposition with Sodium Phenoxide in Phenol–Glyme.—To a stirred solution of 5.1 g (0.044 mol) of sodium phenoxide and 33.6 g (0.4 mol) of phenol in 20 g of glyme was added dropwise at room temperature during 5 min a solution of 7.45 g (0.04 mol) of **12** in 16 g of glyme. The evolution of nitrogen was very slow. The theoretical amount was obtained only after 18 hr. After the usual work-up, which included four washes with 10% KOH, distillation gave three fractions. Preparative vpc (column A, helium flow 150 cc/min) gave pure materials from each of the fractions described below.

Fraction 1, bp 78–103°, column temperature 50°, 1.4 min, yielded 0.297 g (7.7%) of 2,2-dimethyl-3-pentyne identical with an authentic sample obtained from the Chemical Samples Co.

Fraction 2, bp 48–108° (20 mm), column temperature 110° (A) 3.5 min, yielded 2.28 g (52.7%) of anisole, identified by comparison with an authentic sample and (B) 4.7 min, yielded 3.15 g (45.7%) of 2-methoxyethyl *trans*-2,3,3-trimethyl-1-butenyl ether (**14b**): ir (neat) bands at 6.00 (C=C), 8.58, 8.92 μ; nmr (CCl_4) τ 8.97 [s, 9, $C(CH_3)_3$], 8.45 (d, J = 1.5 Hz, 3, $CH_3C=$), 6.67 (s, 3, $-OCH_3$), 6.10–6.63 (two groups of broad peaks, $-OCH_2CH_2OCH_3$), 4.13 (m, 1, $=CH$); mass spectrum m/e 172 (calcd, 172).

Anal. Calcd for $C_{10}H_{20}O_2$: C, 69.8; H, 11.6. Found: C, 70.1; H, 11.8.

Reactions of 3-Nitroso-4,5,5-trimethyl-2-oxazolidone (15) with Nucleophiles. A. In 2-Methoxyethanol Containing Sodium Iodide.—A 20% solution of sodium 2-methoxyethanolate in 2-methoxyethanol (20 g) was added dropwise during 10 min to a well-stirred solution of 2.37 g of **15** in 50 ml of 2-methoxyethanol saturated with sodium iodide (18 g/50 ml). The theoretical amount of nitrogen was evolved in 10 min. The temperature was maintained below 30° by cooling. The mixture was worked up as usual. Two fractions were collected by distillation. Pure samples were obtained by preparative vpc (column A).

Fraction 1, bp 35–70° (35 mm), column temperature 100°, helium flow 100 cc/min, <1 min, yielded 0.091 g (8.2%) of 3-methyl-2-butanone (**17**), identical with an authentic sample.

Fraction 2, bp 85–122° (35 mm), column temperature 132°, helium flow 100 cc/min, yielded (A) 1 min, 0.153 g (7.1%) of 2-methoxyethyl 3-methyl-2-butenyl ether (**18**) {ir (neat), 5.93 (C=C), 8.52 ($C{=}CO-$), 8.85 μ; nmr (CCl_4) τ 8.43 [broad s, 6, $(CH_3)_2C=$], 8.26 (broad s, 3, $CH_3C=$), 6.69 (s, 3, $-OCH_3$), 6.30–6.57 (complex m, 4, $-OCH_2CH_2OCH_3$); exact mass measurement, 144.1152 (calcd, 144.1150)} and (B) 3.5 min, 0.631 g (22.4%) of 2-methoxyethyl 3-methyl-1-buten-3-yl carbonate (**16**) {ir (neat), 5.73 (C=O), 6.10 (C=C, weak band), 7.90, 8.80 μ; nmr (CCl_4) τ 8.48 [s, 6, $(CH_3)_2C$], 6.68 (s, 3, $-OCH_3$), 5.74–6.60 (complex m, 4, $-OCH_2CH_2OCH_3$), 3.65–5.10 (multiple peaks, $-CH{=}CH_2$); mass spectrum mol wt 188}.

Anal. Calcd for $C_9H_{16}O_4$: C, 57.4; H, 8.6. Found: C, 57.4; H, 8.6.

For further identification a 2,4-dinitrophenylhydrazone, mp and mmp 119–120° with the 2,4-dinitrophenylhydrazone prepared from 3-methyl-2-butanone (**17**), was prepared from **18**.

Registry No.—**2a**, 37150-64-4; **3**, 39922-26-4; **3** DNPH, 39922-27-5; **4**, 775-10-0; **4** DNPH, 39922-29-7; **5**, 39922-30-0; *cis*-**6**, 39922-31-1; *trans*-**6**, 39922-32-2; **7**, 39922-33-3; **9**, 39922-34-4; **10**, 39922-35-5; **11**, 39922-36-6; **12**, 29558-58-5; *cis*-**14a**, 39922-38-8; *trans*-**14a**, 39922-39-9; *trans*-**14b**, 39922-40-2; **15**, 39922-41-3; **16**, 39922-42-4; **16** DNPH, 39922-45-7; **17**, 563-80-4; **17** DNPH, 3077-97-2; **18**, 39922-44-6; isobutyraldehyde, 78-84-2; Aliquat 336, 13275-89-3; 2,2-dimethylpropanal, 630-19-3; cyclohexanone, 108-94-1; diethyl ketone, 96-22-0; diisopropyl ketone, 565-80-0; sodium azide, 12136-89-9; potassium thiocyanate, 333-20-0; triethyl phosphite, 78-38-6; ethyl 2,3-dimethyl-3-hydroxybutanoate, 34849-39-3; ethyl α-bromopropionate, 535-11-5; 2,3-dimethyl-3-hydroxybutanoic acid hydrazide, 5454-77-3; hydrazine, 302-01-2; 4,5,5-trimethyl-2-oxazolidone, 39922-48-0; sodium methoxide, 124-41-4; sodium phenoxide, 139-02-6; 2,2-dimethyl-3-pentyne, 999-78-0.

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(19) L. F. Fieser and W. S. Johnson, *J. Amer. Chem. Soc.*, **62**, 576 (1940).