Registry No.—**1**, 1826-11-5; **2**, 10045-48-4; **3**, 40187-13-1; **4**, 40187-14-2; oxalic acid, 144-62-7; chloroacetaldehyde dimethyl acetal, 97-97-2; thiobenzamide, 2227-79-4; acetaldehyde, 75-07-0; phosphorus pentachloride, 10026-13-8; *p*-nitrobenzoyl chloride, 122-04-3.

The Formation of Allenes on Alkaline Treatment of 3-Nitroso-4,5,5-trialkyl-2-oxazolidones[1]

MELVIN S. NEWMAN* AND VING LEE[2]

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210

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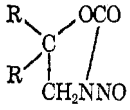
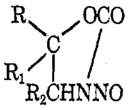
On treatment of 3-nitroso-4-methyl-5,5-pentamethylene-2-oxazolidone (**3**) with sodium 2-methoxyethoxide in 2-methoxyethanol, or with sodium methoxide in methanol, $\sim$15–20% yields of 1,1-pentamethyleneallene (**4**) are obtained, together with several other compounds. Similarly, 3-nitroso-4,5,5-trimethyl-2-oxazolidone (**11**) yields 6–7% 1,1-dimethylallene (**13**), and 3-nitroso-4,5-dimethyl-5-*tert*-butyl-2-oxazolidone (**12**) yields 1-methyl-1-*tert*-butylallene (**14**) in 15% yield. The reaction of pinacolone with zinc and methyl α-bromopropionate yields the expected mixture of diastereoisomers of methyl 3-hydroxy-2,3,4,4-tetramethylpentanoate (**15**), if carried out under mild conditions. Long refluxing, however, results in the formation of $\alpha,\beta,\beta,\gamma$-tetramethylvalerolactone (**16**).

Studies of the reactions which occur when 3-nitroso-5,5-dialkyl-2-oxazolidones (**1**) are treated with bases



1

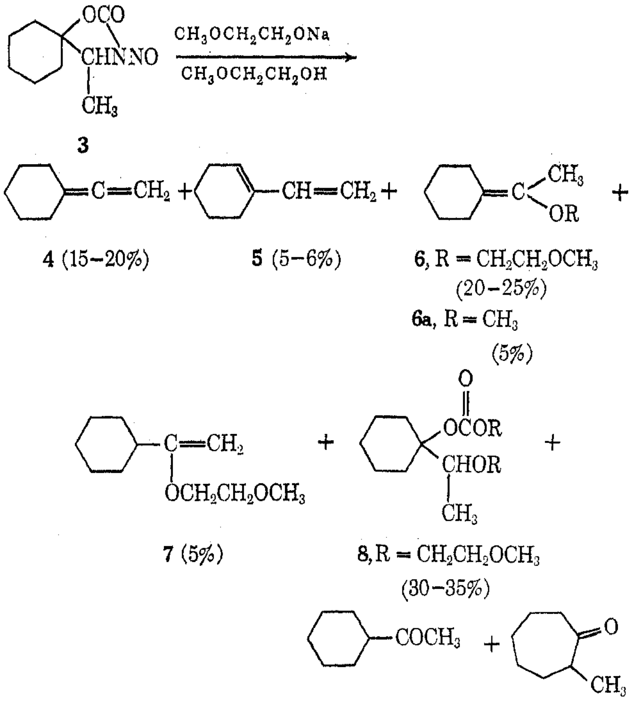


2

have proved of interest not only because of the wide variety of products produced but also because of the multiplicity of mechanistic interpretations used to account for the results.[3] The present study on the reactions of 3-nitroso-4,5,5-trialkyl-2-oxazolidones (**2**) was undertaken for three main reasons: (1) to find out the synthetic utility of such reactions, (2) to learn more about the behavior of unsaturated cations, and (3) to compare the products formed from diastereoisomers of type **2**.

The most detailed study of reaction products was carried out with 3-nitroso-4-methyl-5,5-pentamethylene-2-oxazolidone (**3**) when treated with sodium 2-methoxyethoxide in 2-methoxyethanol. The main products were 1,1-pentamethyleneallene[4] (**4**), 1-(2-methoxyethoxy)ethylidenecyclohexane (**6**), and 1-[1-(2-methoxyethoxy)ethyl]cyclohexyl 2-methoxyethyl carbonate (**8**). Smaller amounts of 1-vinylcyclohexene[5] (**5**), 1-methoxyethylidenecyclohexane (**6a**), 1-(2-methoxyethoxy)vinylcyclohexane (**7**), methyl cyclohexyl ketone (**9**), and 2-methylcycloheptanone (**10**) were present. Because of the large number of products formed and the fact that none is formed in a large yield, the utility of such reactions will probably be minimal. Probably the most interesting result is that a new allene synthesis has been discovered.

The formation of these compounds may be explained



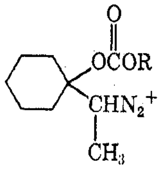
3

4 (15–20%) **5** (5–6%) **6**, R = $CH_2CH_2OCH_3$ (20–25%) **6a**, R = CH_3 (5%)

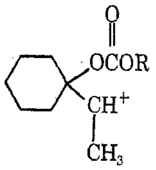
7 (5%) **8**, R = $CH_2CH_2OCH_3$ (30–35%)

9 (5%) **10** (5%)

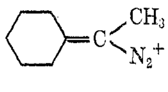
by assuming attack of the alkoxide ion at the carbonyl group of **3** followed by changes outlined previously[3c,d] to yield the intermediate (A). Loss of nitrogen from



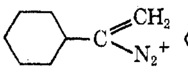
A



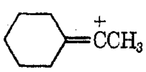
B



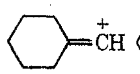
C



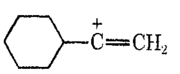
D



E



F



G

A yields cation B, which can react with solvent to produce **8**.[6] Base-catalyzedel imination of alkylcar-

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(1) This work was supported in part by Grant 12445X of the National Science Foundation.

(2) This work was done in an undergraduate research program by Mr. Ving Lee during 1970–1971.

(3) (a) M. S. Newman and A. Kutner, *J. Amer. Chem. Soc.*, **73**, 4199 (1951); (b) M. S. Newman and S. J. Gromelski, *J. Org. Chem.*, **37**, 3220 (1972); (c) M. S. Newman and C. D. Beard, *J. Amer. Chem. Soc.*, **92**, 4309 (1970); (d) *J. Org. Chem.*, **35**, 2412 (1970); (e) M. S. Newman and T. B. Patrick, *J. Amer. Chem. Soc.*, **91**, 6461 (1969); (f) *ibid.*, **92**, 4312 (1970), and references cited therein.

(4) W. J. Bailey and C. R. Pfeifer, *J. Org. Chem.*, **20**, 95 (1955).

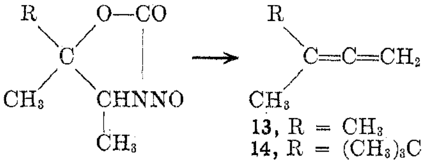
(5) J. W. Cook and C. A. Lawrence, *J. Chem. Soc.*, 58 (1938).

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

bonic acid yields C, which can undergo a hydride shift to yield D. Loss of a proton and nitrogen from C or D yields the allene **4**. The small amount of diene **5** may arise from a precursor to **4** during the reaction. Loss of nitrogen from C yields the unsaturated cation E, which can react with methoxyethanol to yield **6** as in analogous cases,[6] or can cleave the solvent to yield **6a** as described for the case of an unsymmetrically disubstituted unsaturated cation,[3c] F. Loss of nitrogen from D can lead *via* **6** to **7** in the same way that **6a** is formed from B. The ketone **9** can arise from reaction of E or G with water, and the formation of the ring-expanded ketone **10** can be explained by rearrrangement of E followed by hydration.

On treatment of **3** with sodium methoxide in methanol, the yield of allene **4** was about the same as when sodium 2-methoxyethoxide was used. In addition, about 25–30% of 1-vinylcyclohexanol and 20–25% of **6a** were formed in addition to smaller amounts of 2-methylcycloheptanone (**10**), cyclohexyl methyl ketone, and other products.

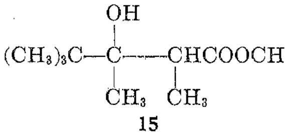
In order to test the generality of the new allene synthesis observed, 3-nitroso-4,5,5-trimethyl-2-oxazolidone (**11**) and 3-nitroso-4,5-dimethyl-5-*tert*-butyl-2-oxazolidone (**12**) were prepared and treated with base. From **11** a 6–7% yield of 1,1-dimethylallene (**13**) and from **12** a 15% yield of 1-methyl-1-*tert*-butylallene (**14**) were obtained in addition to a number of other products similar to those obtained from **3**.



11, R = CH_3
12, R = $(CH_3)_3C$

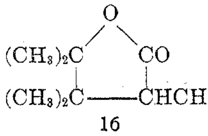
13, R = CH_3
14, R = $(CH_3)_3C$

The compound **12** was studied because we wished to see if the diastereoisomers would give different results. However, since it was not feasible to separate the diastereoisomeric methyl 3-hydroxy-2,3,4,4-tetramethylpentanoates (**15**) obtained on treatment of methyl *tert*-butyl ketone with methyl α-bromopropionate and zinc, this objective was not attained. Only one crystalline pure hydrazide was obtained from **15**. Interestingly, in the Reformatsky reaction appreciable amounts of α,β,β,γ-tetramethyl-γ-valerolactone (**16**) were obtained. The formation of this compound could be largely avoided if only slight (*ca.* 5%) excesses of zinc and bromo ester were used and if the ratio of ether to benzene was greater than one. Treatment of **15** with zinc and bromo ester, or with hot dilute sulfuric acid, resulted in rearrangement to **16**.[7] If the Reformatsky reaction was carried out with excesses of zinc and bromo ester and refluxing was continued for long periods, **16** was the major product.



$$(CH_3)_3C-\overset{OH}{\underset{CH_3}{C}}-\underset{CH_3}{CH}COOCH_3$$

15



16

Experimental Section[8]

Methyl 3-Hydroxy-2-methyl-3,3-pentamethylenepropanoate*.—To a solution of 98.8 g of freshly distilled cyclohexanone in 200 ml of dry ether and 150 ml of benzene containing 66 g of activated[9] zinc was added 186 g of methyl 2-bromopropanoate as rapidly as the rate of reflux of solvent would permit. By 30 min after addition the zinc had all disappeared. After a conventional work-up, 150 g (80%) of redistilled hydroxy ester was obtained, bp 116–117° (10 mm) (98% pure by glpc).

Anal. Calcd for $C_{10}H_{18}O$: C, 64.5; H, 9.8. Found: C, 64.4; H, 9.8.

The corresponding ethyl ester*, bp 132.5–133° (17 mm), was obtained in 80% yield.

Anal. Calcd for $C_{11}H_{20}O_3$: C, 66.0; H, 10.0. Found: C, 66.3; H, 10.1.

4-Methyl-5,5-pentamethylene-2-oxazolidone*.—A solution of 37.2 g of the above methyl ester in 100 ml of 1-propanol and 14 ml of anhydrous hydrazine was refluxed for 24 hr. After removal of solvent on a rotary evaporator the residue was taken into cold chloroform. The crude hydrazide was extracted with two 150-ml portions of cold 3 *M* hydrochloric acid. These extracts were treated in an ice bath with a solution of 14 g of sodium nitrite in 100 ml of water. After the excess nitrite was destroyed with bisulfite, the crude azide was extracted with chloroform. After washing with saturated salt solution, the chloroform extract was added dropwise to a heated flask to effect rearrangement of the azide. After removal of solvent the residue was recrystallized from 9:1 cyclohexane–benzene to yield 30.5 g (92%) of colorless oxazolidone, mp 109–110°.

Anal. Calcd for $C_9H_{15}NO_2$: C, 63.9; H, 8.9; N, 8.2. Found: C, 64.1; H, 8.9; N, 8.1.

3-Nitroso-4-methyl-5,5-pentamethylene-2-oxazolidone* (**3**).—This compound was prepared essentially as described for similar compounds[3b] in 90% yield as orange, elongated prisms, mp 43–44°, from 9:1 pentane–cyclohexane. This compound was used immediately after preparation because it was fairly unstable at room temperature. All samples sent for analysis decomposed in transit. However, the ir (5.55 μ) and nmr ($CDCl_3$) {τ 8.80 (d, *J* = 6.5 Hz, 3, $CHCH_3$), 8.34 [broad m, 10, $-(CH_2)_5-$}, 5.78 (q, *J* = 6.5 Hz, 1, $CHCH_3$)} were consistent with the proposed structure.

3-Nitroso-4,5,5-trimethyl-2-oxazolidone* (**11**).—This compound, mp 88–89°, was prepared in 93% yield as described.[3b,10]

Methyl 3-Hydroxy-2,3,4,4-tetramethylpentanoates (**15**).—About 100 ml of benzene was distilled from the reaction flask containing 70 g of activated zinc.[9] On cooling, 200 ml of dry ether and 0.5 g of iodine were added. To the reheated solution was added dropwise a solution of 101 g of methyl *tert*-butyl ketone and 175 g of methyl 2-bromopropanoate in 200 ml of ether. Once the exothermic reaction had commenced, heating was discontinued and the rate of addition was adjusted to control the reaction. After about half had been added 250 ml of ether was added. The mixture was stirred for 45 min at the end (until most of the zinc had reacted). After 400 ml of ammoniacal concentrated ammonium chloride solution was added, the solids were filtered and the filtrate was worked up in a conventional way to yield 122 g (65%) of **15**, bp 93–95° (15 mm). Nmr analysis indicated that a mixture of the diastereoisomers of **15** (about 9:2) was present. Pure samples of each were obtained by preparative glpc using 10% FFAP on Chromosorb W at 135°.

Isomer I had nmr [$(CH_3)_4Si$-10] τ 9.10 [s, 9, $C(CH_3)_3$], 8.92 (s, 3, CH_3COH), 8.83 (d, *J* = 7.0 Hz, 3, CH_3CH), 7.27 (q, *J* = 7 Hz, 1, $CHCH_3$), 6.7 (broad s, 1, OH), 6.34 (s, 3, OCH_3). Isomer II was similar except that the OH was at τ 8.14. The bands at τ 8.14 and 6.7 were used to estimate the proportions of I and II.

Anal. Calcd for $C_{10}H_{20}O_3$: C, 63.8; H, 10.6. Found (for I): C, 64.0; H, 10.5. Found (for II): C, 63.8, H, 10.8.

α,β,β,γ-Tetramethyl-γ-valerolactone (**16**).—When the Reformatsky reaction described above was carried out with excess zinc and bromo ester and the reaction mixture was refluxed for 8 hr the product boiled mostly at 105–110° (10 mm). On standing

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[7] See A. W. Burgstahler and D. E. Wetmore, *J. Org. Chem.*, **26**, 3516 (1961), for a similar rearrangement.

[8] All compounds marked with an asterisk had nmr spectra [CCl_4, $(CH_3)_4Si$] and apparent peak (mass spectrum) consistent with the assigned structures. We thank Mr. Richard Weisenberger for the mass spectra.

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

[10] See Ph.D. Thesis of W. Liang, The Ohio State University, 1972, for details.

16 crystallized in large crystals: mp 64–65°; nmr ($CDCl_3$) τ 9.10 (s, 3, CH_3CH_3CO–), 8.95 (s, 3, CH_3CH_3CO), 8.90 (d, J = 7 Hz, 3, CH_3CH), 8.65 [s, 6, $(CH_3)_2C$], 7.3 (q, J = 7 Hz, 1, CH_3CH); ir (KBr) 3450 (due to enolization of carbonyl), 1745 cm^{-1} ($C=O$); mass spectrum m/e 156.

Anal. Calcd for $C_9H_{16}O_2$: C, 69.2; H, 10.3. Found: C, 69.4; H, 10.3.

The same lactone was obtained in 90% yield when a mixture of 17.3 g of **15**, 4 ml of 98% H_2SO_4, and 80 ml of water was refluxed for 4 hr.

3-Nitroso-4,5-dimethyl-5-*tert*-butyl-2-oxazolidone (12).—In a typical experiment a solution of 93 g of the diastereoisomers **15**, 80 ml of hydrazine, and 200 ml of 1-propanol was slowly warmed to reflux and held there for 24 hr. After removal of solvent on a rotary evaporator the residue was triturated with pentane. The solid (60 g, 65%) was collected and kept over H_2SO_4 in a desiccator overnight. No attempts were made to process the hydrazide in the mother liquor. The crude hydrazide (40 g) was added to a cold solution of 40 ml of 35% HCl in 400 ml of water layered with 100 ml of chloroform. A solution of 14 g of sodium nitrite in 60 ml of water was dropped in (cold) and the mixture was well stirred for 40 min. The yellow $CHCl_3$ layer was separated, washed twice with saturated salt solution, and then added slowly to refluxing benzene (100 ml). The resulting product on distillation, 175–180° (1 mm), yielded a yellow solid which on crystallization from 10:1 Skellysolve B–benzene afforded 32.0 g (88% based on hydrazide) of 4,5-dimethyl-5-*tert*-butyl-2-oxazolidone, mp 108–109°, as colorless crystals: nmr ($CDCl_3$) τ 9.0 [s, 9, $(CH_3)_3C$], 8.76 (d, J = 7 Hz, 3, CH_3CH), 8.70 [s, 3, $CH_3CC(CH_3)_3$], 5.96 (q, J = 7 Hz, 1, CH_3CH), 2.92 (broad m, 1, NH); ir (KBr) 3250 (NH), 1725 cm^{-1} ($C=O$).

Anal. Calcd for $C_9H_{17}NO_2$: C, 63.2; H, 10.0. Found: C, 63.4; H, 10.0.

Nitrosation according to method B[3a] yielded **12** in 82% yield after recrystallization from pentane as yellow crystals: mp 48–49°; nmr ($CDCl_3$) τ 9.0 [s, 9, $(CH_3)_3C$], 8.71 (d, J = 7 Hz, 3, CH_3CH), 8.70 [s, 3, $CH_3CC(CH_3)_3$], 5.6 (q, J = 7 Hz, 1, CH_3CH); ir (KBr) 1800 cm^{-1} ($C=O$). Suitable microanalyses were not obtained because of deterioration of the samples en route.

Alkaline Treatment of 3.—In a typical experiment 35 ml of a 1.2 *M* solution of sodium 2-methoxyethoxide in 2-methoxyethanol was added dropwise during 15–20 min to a solution of 7.42 g of **3** in 30 ml of 2-methoxyethanol. About 85–90% of the theoretical nitrogen was collected. The reaction mixture was added to saturated salt solution and the organic products were extracted with ether. The ether was removed by distillation through a 6 ft × 0.5 in. glass helices packed column and the residue was distilled at 17 mm to yield the following five fractions: I, up to 41°, 4.0 g; II, 133–140°, 0.92 g; III, 158–167°, 0.72 g; IV, 167–177°, 0.96 g; and V, 188–198°, 3.65 g. Fractions I–IV were analyzed by glpc on a 10 ft × 0.25 in. column (column A) packed with 10% SF-96 (a silicone) on firebrick (Chromosorb P) with a helium flow of 50–60 ml/min at temperatures of 125–145°. In fraction I (mainly solvent) there was pentamethyleneallene (**4**) in 15–20% yield based on starting **3**, proved by comparison with an authentic[4] sample by ir, glpc retention time, and nmr. From II there were three peaks with retention times of 1.5, 2.0, and 2.5 min (column T, 135°). The first two peaks were shown to be vinylcyclohexene[5] (**5**) and methyl cyclohexyl ketone (**9**) (Chemical Samples Co.) by comparison with authentic samples. Each was present in about 5% yield based on starting **3**.[11] Preparative glpc of the 2.5-min fraction on a 9.5 ft × 0.25 in. column (column B) packed with Carbowax 4000 monostearate on Chromosorb W at 120° (helium flow 40 ml/min) gave a 1.4-min (retention time) fraction shown to be **6a** and a 2.3-min fraction shown to be **10**. Each was present in about 5% yield based on **3**. Authentic **6a** was prepared in 25% yield from **3** and sodium methoxide in methanol as a colorless liquid: bp 90–97° (100–110 mm); nmr ($CDCl_3$) τ 9–7.5 [m, 10, –$(CH_2)_5$–], 8.25 (s, 3, $CH_3C=$], 6.60 (s, 3, CH_3O).

Anal. Calcd for $C_9H_{16}O$: C, 77.1; H, 11.5. Found: C, 76.9; H, 11.5.

The identity of the 2.3-min fraction was established by comparison (ir, nmr, glpc) with authentic 2-methylcycloheptanone obtained from Professor R. Ouellette and M. S. Jerristaty.

Preparative glpc of fraction III and IV on a 10 ft × 0.25 in. column packed with SF 96 (a fluorinated silicone) on firebrick (Chromosorb P) at 145° with a helium flow of 50 ml/min yield a 7-min fraction and an 8-min fraction. The 7-min fraction was shown to be **7** by nmr, mass spectrum, and the formation of the 2,4-dinitrophenylhydrazone derivative identical with that formed from cyclohexyl methyl ketone*.[12] The 8-min fraction was shown to be **6** by nmr ($CDCl_3$) τ 9.0–7.5 [m, 10, –$(CH_2)_5$–], 8.20 (s, 3, $=CCH_3$), 6.6 (s, 3, OCH_3), 6.0–6.5 (m, 4, –CH_2CH_2–).

Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.7; H, 10.9. Found: C, 71.8; H, 11.0.

On treatment with 2,4-dinitrophenylhydrazone reagent, the 2,4-dinitrophenylhydrazone derivative, mp and mmp with an authentic sample[12] 138–139°, was obtained.

Fraction V was essentially pure **8** as shown by the following: ir (film) 1730 ($O_2C=O$), broad bands at 1175–1000 cm^{-1} (OC); nmr ($CDCl_3$) τ 9.0–7.5 [m, 10, –$(CH_2)_5$–], 8.85 (d, J = 7 Hz, 3, CH_3CH), 6.7–6.2 (m, 8, OCH_2CH_2O), 6.70 (s, 6, OCH_3), 6.1 (q, J = 7 Hz, 1, $CHCH_3$).

Anal. Calcd for $C_{15}H_{28}O_6$: C, 59.2; H, 9.2. Found: C, 59.6; H, 9.1.

When 3.71 g of **3** in 40 ml of methanol was treated with a solution of sodium methoxide in methanol about 90% of the theoretical nitrogen was rapidly evolved. After a work-up similar to that described above two fractions, I, 1.2 g, bp up to 60° (100 mm), and II, 2 1 g, bp 80–115° (105 mm), were isolated. Fraction I consisted of a mixture of **4** and methanol. By glpc on column A it was estimated that a 10–15% yield of **4** was at hand. Analysis of fraction II on column A at 125° with a helium flow of 50 ml/min showed the presence of **4** (5% so that the total yield of **4** was 15–20%), 9.2 min, cyclohexyl methyl ketone (5–10%), 12.8 min, and a mixture of **10** (5–10%) and **6a** (20–25%), 14.7 min. The vinylcyclohexanol proved identical with an authentic sample[5] prepared by reduction of ethynylcyclohexanol over a Lindlar catalyst.[13]

When 7.9 g of **11** in 40 ml of propanol was treated with a solution of sodium propoxide in propanol 85% of the thoretical nitrogen was rapidly evolved. The mixture was then heated to 60° and a distillate consisting mostly of 1,1-dimethylallene (**13**) and propanol was obtained. The yield of **13** was determined to be about 6–7% by infrared analysis (using the band at 1950 cm^{-1} of solutions of authentic **13**[12] in propanol.

A solution of 10.0 g of **12** in anhydrous methanol was treated with sodium methoxide (85% N_2 formed) as in the case of **3**. After a similar work-up, distillation yielded two fractions, I, up to 45° (15 mm), and II, 45–60° (15 mm). Analysis of I by glpc on column A at 126–130° with a helium flow of 15–20 ml/min showed **14** in about 15% yield, retention time 5.5 min. The structure of **14** was established by comparison with an authentic sample: ir 840 cm^{-1} ($C=CH_2$), 1950 ($C=C=C$); nmr ($CDCl_3$) τ 8.98 [s, 9, $C(CH_3)_3$], 8.33 (m, 3, $CH_3C=$), 4.50 (m, 2, $=CH_2$). The authentic sample was synthesized from 2,3,3-trimethyl-1-butene and bromoform to yield 1,1-dibromo-2-methyl-2-*tert*-butylcyclopropane (45%) which on treatment with methyllithium afforded pure **14** in 80% yield.[14]

Anal. Calcd for C_8H_{14}: C, 87.2; H, 12.8. Found: C, 86.9; H, 12.7.

Anal. Calcd for $C_8H_{14}Br_2$: C, 35.6; H, 5.2; Br, 59.2. Found: C, 35.3; H, 5.1; Br, 59.1.

In addition to **14**, six other compounds were isolated by preparative glpc on column A. As each was present in 5–10% yield, no further description of them will be made.

Registry No.—**3,** 39922-49-1; **4,** 5664-20-0; **6,** 39922-51-5; **6a,** 26473-57-4; **8,** 39922-53-7; **11,** 39922-41-3; **12,** 39922-55-9; **13,** 598-25-4; **14,** 7417-50-7; **15,** 39922-57-1; **15** stereoisomer, 39922-58-2; methyl 3-hydroxy-2-methyl-3,3-pentamethylenepropanoate, 31042-01-0; ethyl 3-hydroxy-2-methyl-3,3-pentamethylenepropanoate, 39922-60-6; methyl 2-bromopropanoate, 5445-17-0; cyclohexanone, 108-94-1; 4-methyl-5,5-pentamethylene-2-oxazolidone, 16112-64-4;

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(11) All percentages quoted on compounds analyzed for by glpc are calculated back to the starting nitrosooxazolidones.

(12) An authentic sample was obtained from Chemical Samples Co.

(13) H. Lindlar, *Helv. Chim. Acta*, **35**, 446 (1952).

(14) L. Skattebøl and S. Solomon, *Acta Chem. Scand.*, **17**, 1683 (1963).

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; α,β,-β,γ-tetramethyl-γ-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]

MELVIN S. NEWMAN* AND WEI C. LIANG[2]

Evans Chemistry Laboratory of The Ohio State University, Columbus, Ohio 43210

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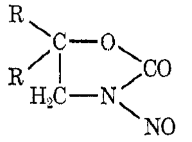
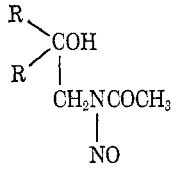
New syntheses of the α,β-unsaturated ketones, cyclohexylidenemethyl isopropyl ketone (**3**) and cyclohexylidenemethyl *tert*-butyl ketone (**4**), the divinyl ethers, 3-pentenyl ether (**6**) and cyclohexylidenemethyl 2,4-dimethyl-3-pentenyl ether (**7**), the vinyl azide, cyclohexylidenemethyl azide (**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$_2$)$_5$−



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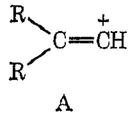
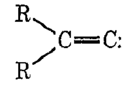
2a



A

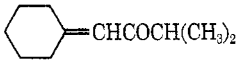


B

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.



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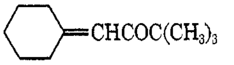

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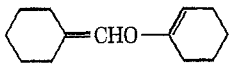
When **2a** was treated under similar conditions with cyclohexanone, diethyl ketone, and diisopropyl ketone there were obtained cyclohexylidenemethyl cyclohexenyl ether (**5**), cyclohexylidenemethyl 3-pentenyl ether (**6**), and cyclohexylidenemethyl 2,4-dimethyl-3-pentenyl ether (**7**) in 32, 22, 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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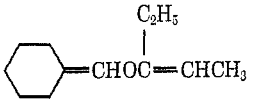

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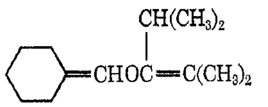

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[1] This research was supported by Grant G12445X from the National Science Foundation.

[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).