The Formation of Unsaturated Carbenes by Alkaline Treatment of N-Nitrosooxazolidones[1,2]

MELVIN S. NEWMAN AND ABRAHAM O. M. OKORODUDU

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

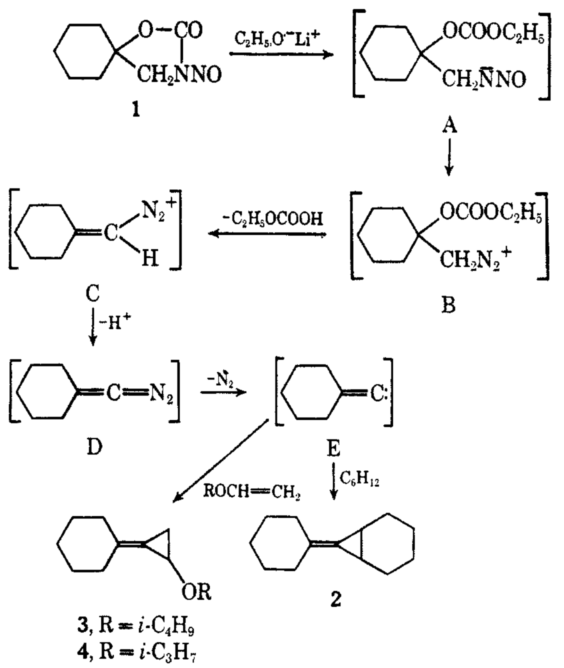
Received December 9, 1968

Treatment of 5,5-disubstituted N-nitrosooxazolidones with alkoxides initiates a series of reactions which are best explained by postulating the formation of unsaturated carbenes, $:C{=}CR_2$. The latter react with olefins, such as cyclohexene or alkyl vinyl ethers, to yield disubstituted methylenecyclopropanes, and with alcohols, ROH, by insertion into the O–H bond to yield vinyl ethers, $R_2C{=}CHOR'$ (see Table I). Treatment of 3-nitroso-1-oxa-3-azaspiro[4.5]decan-2-one (1) with sodium hydroxide in D_2O and with sodium methoxide in CH_3OD affords $(CH_2)_5CHCDO$ (after treatment with H_2O) and $(CH_2)_5C{=}CDOCH_3$, respectively. The mechanistic implications of these facts are discussed.

In previous work on the behavior of nitrosooxazolidones when treated with bases, all of the products isolated could be satisfactorily accounted for by posulating the intermediacy of unsaturated carbonium ions.[3-6] As a result of the development of carbene chemistry, Hine suggested that in certain cases an unsaturated carbene might be involved instead.[7] That this hypothesis is correct has recently been demonstrated.[8] In this paper a more detailed account of this work is given.

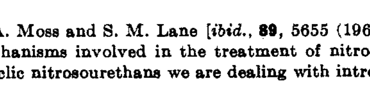
When 3-nitroso-1-oxa-3-azaspiro[4.5]decan-2-one (**1**) was suspended (partly dissolved) in cyclohexene and treated with lithium ethoxide[9] at room temperature an exothermic reaction took place rapidly to afford a good yield (isolated) of bicyclo[4.1.0]hept-7-ylidenecyclohexane (**2**).[10] In similar reactions of **1** with isobutyl vinyl ether and isopropyl vinyl ether, there were obtained 2-isobutoxycyclohexylidenecyclopropane (**3**) and 2-isopropoxycyclohexylidenecyclopropane (**4**) in good yields (isolated), respectively. Since the formation of cyclopropane rings by reaction of suitable precursors in the presence of olefins is generally accepted as evidence that a carbene is involved, the above reactions provide evidence that the unsaturated carbene (E) is an intermediate, as shown in Scheme I.

SCHEME I



The explanation (see Scheme I) for the paths by which the products are formed starts out as before[4] by assuming attack of ethoxide ion at the carbonyl function of **1** to yield intermediate A. As in previous cases[3,4] no attempt is made to time proton movements in the intermediate stages of conversion of the ring-opened intermediate, A, to the diazonium ion, B.[11] We believe that the diazonium character imparted to the nitrogens is responsible for increased acidity of the hydrogens on the adjacent carbon.[12] Thus the base-promoted elimination of ethyl bicarbonate to form C is facilitated. As Hine hypothesized[7] C can then lose a proton to yield D which loses nitrogen to form the unsaturated carbene (E), which reacts as expected with the olefins indicated to give **2**, **3**, and **4**.

Alternately, C could first lose nitrogen to yield the unsaturated carbonium ion (F), which might lose a proton to yield E or react directly to give other products.[13]



---

[1] This research was supported by Research Grant GP-5552X from the National Science Foundation.

[2] Taken from the Ph.D. thesis presented by A. O. M. O. to The Ohio State University, 1968.

[3] M. S. Newman, *J. Amer. Chem. Soc.*, **71**, 378 (1949).

[4] M. S. Newman and A. Kutner, *ibid.*, **73**, 4199 (1951).

[5] M. S. Newman and W. M. Edwards, *ibid.*, **76**, 1840 (1954).

[6] M. S. Newman and A. E. Weinberg, *ibid.*, **78**, 4654 (1956).

[7] J. Hine, "Divalent Carbon," The Ronald Press Co., New York, N. Y., 1964, pp 89–90. Other references in which unsaturated carbenes are suggested are as follows: (a) A. A. Bothner-By, *J. Amer. Chem. Soc.*, **77**, 3293 (1955); (b) D. Y. Curtin, E. W. Flynn, and R. F. Nystrom, *ibid.*, **80**, 4599 (1958); (c) W. M. Jones, M. H. Grasley, and W. S. Brey, Jr., *ibid.*, **85**, 2754 (1963); (d) D. Y. Curtin, J. A. Kampmeier, and B. R. O'Connor, *ibid.*, **87**, 863 (1965); and (e) K. L. Erickson and J. Wolinsky, *ibid.*, **87**, 1142 (1965).

[8] M. S. Newman and A. O. M. Okorodudu, *ibid.*, **90**, 4189 (1968).

[9] Prepared as described in W. M. Jones, M. H. Grasley, and W. S. Brey, Jr., *ibid.*, **85**, 2754 (1963).

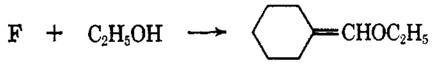
[10] M. Tanabe and R. A. Walsh, *ibid.*, **85**, 3522 (1963).

[11] See R. A. Moss and S. M. Lane [*ibid.*, **89**, 5655 (1967)] for a discussion of the mechanisms involved in the treatment of nitrosourethans with alkali. The cyclic nitrosourethans we are dealing with introduce additional complications concerning mechanism but much is common to the two systems. In the cyclic urethans, the elimination of a monoalkyl carbonate introduces unsaturation into the molecule, a feature absent in the other cases discussed by Moss and Lane.

[12] For discussions of similar problems in reactions of nitrosamides with bases, see E. H. White, *ibid.*, **77**, 6014 (1955), and J. H. Bayless, A. T. Jurewicz, and L. Friedman, *ibid.*, **90**, 4465 (1968).

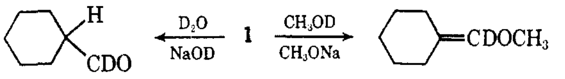
[13] In W. Kirmse ["Carbene Chemistry," Academic Press, New York, N. Y., 1964, p 90], the hypothesis is made that diphenylcarbene adds a proton to form diphenylcarbonium ion prior to formation of benzhydryl methyl ether.

In order to try to distinguish between paths C → D → E and C → F → E the reaction of **1** with lithium ethoxide in the presence of a solvent composed of equimolar amounts of ethanol and cyclohexene was studied. The hypothesis was that E would react preferentially with cyclohexene to give **2** while F would react preferentially with ethanol to give the vinyl ether, ethoxymethylenecyclohexane (**5**). The ratio of **2** to **5** found would show the fate of C. These studies showed that larger amounts of **5** were formed (ratios of about 5–7 to 1) in the temperature ranges of about 25–65°, the higher ratios occurring at the higher temperature (see the Experimental Section).



5

After these results were obtained we realized that the formation of vinyl ethers did not prove that an unsaturated carbonium ion[6] is involved. The vinyl ether, **5**, might be formed by insertion of the unsaturated carbene, E, into the O–H bond of ethanol[14] and hence both **2** and **5** might be formed from E. Accordingly, a solution of **1** in CH_3OD was treated with dry sodium methoxide. The methylenic hydrogen in the **5a** formed was mainly deuterium. Treatment of **5** with sodium methoxide in CH_3OD did not result in incorporation of deuterium at the methylenic position. Similarly, when **1** was treated with alkali in D_2O the deuterated cyclohexylmethanal (**6**) was formed as during the work-up equilibration of the α hydrogen with water occurred.

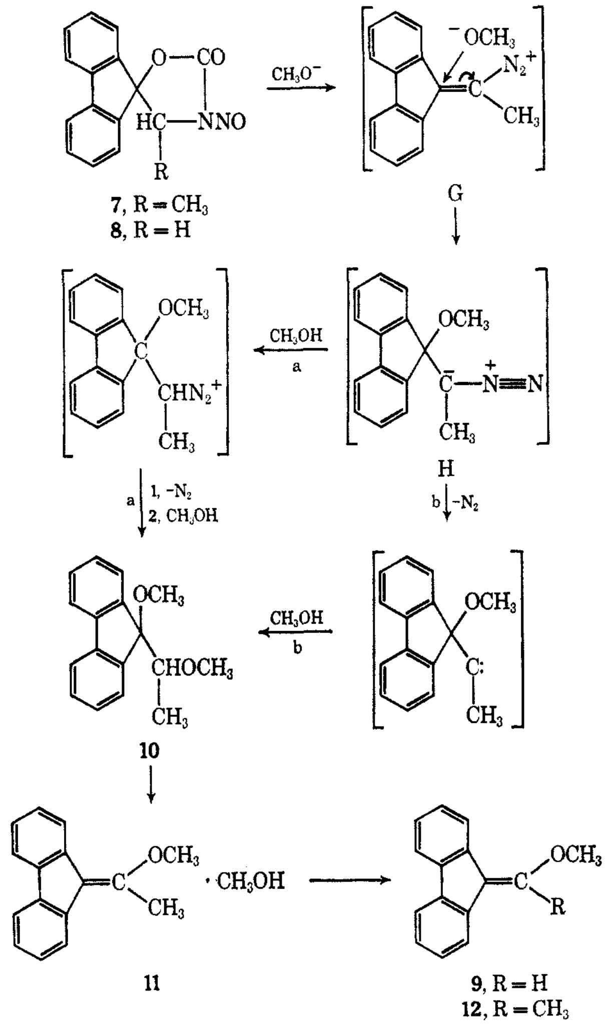


6 **5a**

These experiments indicate strongly that the unsaturated carbene (E) is the intermediate. If the unsaturated carbonium ion (F) were the precursor of **5a**, the methylenic hydrogen should be protium. A recent experiment performed by Dr. T. Patrick showed that when **1** was treated with insufficient sodium methoxide in CH_3OD, the **1** isolated after partial reaction contained no deuterium. This finding reinforces the argument that the path C → D → E is correct since deuterium exchange in **1** prior to reaction is ruled out. However, the possibility still remains that there may be deuterium exchange of some intermediate prior to the formation of E or F.

Since, in the work discussed above, the timing of the loss of a proton from the carbon to which the nitrogen was attached was involved, experiments were desired in which there was no hydrogen to be lost and hence the formation of an unsaturated carbene would be impossible. Accordingly, we prepared 3-nitroso-4-methylspiro[fluorene-9′,5-oxazolidin]-2-one (**7**) for study. This compound was chosen since a similar compound (**8**) without the 4-methyl group had already been shown[6] to yield 9-(methoxymethylene)fluorene (**9**) in 87% yield on treatment with methanolic potassium hydroxide. When a solution of **7** in methanol was treated with sodium methoxide at 5–10° there was formed in high yield a mixture composed of 9-methoxy-9-(1-methoxyethyl)-fluorene (**10**) and 9-(1-methoxyethylidene)fluorene methanolate (**11**) in a ratio of about 19:1 (see Experimental Section for details). On heating this mixture under vacuum the methanol was lost to yield 9-(1-methoxyethylidene)fluorene (**12**). The latter (**12**) could be partly reconverted into the alcoholate (**11**) on treatment with methanol but **11** could not be converted into **10** by treatment with neutral or alkaline methanol.[15] On gentle warming or on standing at room temperature **10** was easily converted into **11**. Thus **10** is shown to be the first product formed in the reaction of **7** with sodium methoxide in methanol and therefore an unsaturated carbonium is not the reactive intermediate, for, if it were, **11** and **12** would be expected to be formed but not **10**. Our explanation for the above results is shown in Scheme II.

Scheme II



The conversion of **7** into G takes place as described for the conversion of **1** into A. Attack of methoxide ion at the 9 position of G leads to the hypothetical dipolar ion (H)[16] which could then yield the final product **10** by

---

[14] Tanabe and Walsh[10] reported the formation of a vinyl ether in a reaction involving an unsaturated carbene but did not attribute this to insertion of the carbene into the O–H bond of the alcohol. The formation of ethers by reaction of carbenes with alcohols has been reported. See R. M. G. Nair, E. Meyer, and G. W. Griffin, *Angew. Chem. Intern. Ed. Engl.*, **7**, 463 (1968), and references therein. In a private communication, Dr. J. Wolinsky of Purdue University has informed me that bromomethylenecyclohexane reacts with potassium *t*-butoxide to yield *t*-butoxymethylenecyclohexane.

[15] G. Wittig and M. Schlosser [*Ber.*, **94**, 1373 (1961)] showed that 9-(methoxymethylene)fluorene is converted into the 9-ethoxy compound on treatment with sodium ethoxide.

[16] For a discussion of reactions of a similar species, see ref 9.

paths a or b. Further work is in progress in an attempt to distinguish between these paths. In the earlier work[6] in which **8** was reported to yield **9** directly, no precautions regarding heating of the reaction product were taken so that if a compound comparable to **10** had been formed it would have been converted into **9**. Regardless of the details of mechanism regarding vinyl ether formation, further study of this method was undertaken and is described below.

Previous methods of forming vinyl ethers have involved acid-catalyzed reactions[17] or Wittig reagents.[18] The method starting from oxazolidones is unique in that basic reagents are used under very mild conditions.

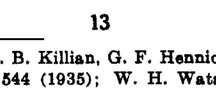
The nitrosooxazolidones studied were **1**, **7**, **8**, **13**, and **14**. In general a solution of the nitrosooxazolidone in an alcohol at 0–5° was treated with a solution of 1 equiv of the corresponding sodium alkoxide. Nitrogen evolution was vigorous and controlled by the rate of addition of the alkali. The yields of vinyl ethers were generally very good and are reported in Table I. It may be seen that a general method for preparing vinyl ethers under alkaline conditions is at hand, except for the β-styryl vinyl ethers which would result from **13**. In the case of this phenyl derivative the formation of phenylacetylene takes precedence over vinyl ether formation.

Table I

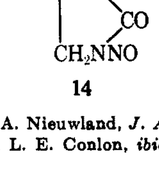
Vinyl Ether Formation from Nitrosooxazolidones

Nitroso-oxazolidone	Alcohol[a]	Product	Yield,[b] %
1	Methyl	Methyl ether[c]	85
1	Ethyl	Ethyl ether[c]	84
1	Propyl	1-Propyl ether[c]	80 (90)[d]
1	Isopropyl	2-Propyl ether[c]	71 (82)[d]
1	Butyl	1-Butyl ether[c]	85 (89)[d]
1	*t*-Butyl[e]	*t*-Butyl ether[c]	65 (72)[d]
1	Methallyl	Methallyl ether[c]	62[f]
14	Methyl	Methyl ether[c]	72
14	Butyl	1-Butyl ether[c]	64
13	Methyl	$C_6H_5C\equiv CH$[g]	65
13	Ethyl	$C_6H_5C\equiv CH$[g]	54
7	Methyl	Methyl ether[c]	85[h]
7	Ethyl	Ethyl ether[c]	81[h]
8	Methyl	Methyl ether[c]	90[h,i]
8	Ethyl	Ethyl ether	80[h,i]

[a] A solution of sodium alkoxide in the corresponding alcohol was used. [b] The yield represents distilled product homogenous by vpc. [c] All products were vinyl alkyl ethers, the vinyl group being that determined by the starting nitrosooxazolidone. [d] The yields in parentheses mean that additional vinyl ether was present in the forerun (see Experimental Section). [e] Potassium *t*-butoxide was used. [f] See Experimental Section for details. [g] The crude product contained some vinyl ether but no attempt was made to determine the yield accurately. [h] These products were isolated as solids by crystallization. [i] The initially found product was not the vinyl ether but the latter was formed on warming (see text).

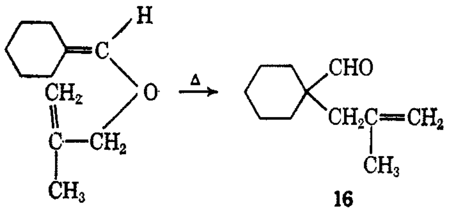


13



14

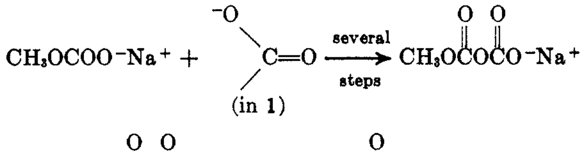
A synthetic use for the synthesis of tertiary aliphatic aldehydes is illustrated by the pyrolysis of methallyloxymethylenecyclohexane (**15**) to 1-methallylcyclohexanecarboxaldehyde (**16**). This Claisen-type rearrangement of allyl ethers has been reported.[19]



15 **16**

In general the reaction of **1** with alcohols took place rapidly as judged by the fact that the theoretical amount of nitrogen was evolved within minutes after the addition of 1 equiv of sodium alkoxide had been completed. However, if only catalytic amounts of sodium methoxide were used the rate of nitrogen evolution became quite slow (after the initial rapid evolution on addition of the methoxide) and about 1 day was required until gas evolution ceased. In these cases about 2 equiv of gas, one each of nitrogen and carbon dioxide, were evolved. We explain this fact by assuming that the base which attacks the carbonyl group in **1** (as in Scheme I) is sodium methylcarbonate (after the initially used sodium methoxide is converted into sodium methylcarbonate). By a series of steps similar to those in Scheme I there is generated a sodiomethyl derivative of carbonic acid anhydride, $NaOCOOCOOCH_3$, which decomposes into sodium methylcarbonate and CO_2 as shown in Scheme III.

Scheme III



$$CH_3OCOO^-Na^+ + \underset{\text{(in 1)}}{{}^-O\diagdown C{=}O} \xrightarrow[\text{steps}]{\text{several}} CH_3O\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}O^-Na^+$$

$$CH_3O\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}O^-Na^+ \longrightarrow CH_3O\overset{O}{\overset{\|}{C}}O^-Na^+ + CO_2$$

The fact that sodium methylcarbonate is a much weaker base than sodium methoxide accounts for the slower rate of reaction. The only alternate explanation for the facts involves a slow decomposition of $CH_3OCOO^-Na^+$ into CO_2 and $CH_3O^-Na^+$. We think the latter possibility is extremely unlikely.

Experimental Section[20]

Nitrosooxazolidones.—The known compounds, **1**,[3] **8**,[6] and **13**[4] were prepared essentially as described. The preparation of 3-nitroso-4-methylspiro[fluorene-9′,5-oxazolidin]-2-one (**7**) was started by a Reformatsky reaction of 36 g of fluorenone,[21] 51 g of ethyl α-brompropionate, and 22 g of activated zinc[22] in benzene to yield crude ethyl 2-(9-hydroxy-9-fluorenyl)propionate, which was not characterized but treated in 40 ml of methanol with 12.8

---

[17] D. B. Killian, G. F. Hennion, and J. A. Nieuwland, *J. Amer. Chem. Soc.*, **57**, 544 (1935); W. H. Watanabe and L. E. Conlon, *ibid.*, **79**, 2828 (1957).

[18] G. Wittig and M. Schlosser, *Ber.*, **94**, 1373 (1961); G. Wittig, W. Böll, and K. H. Krück, *ibid.*, **95**, 2514 (1962).

[19] C. D. Hurd and M. A. Pollack, *J. Amer. Chem. Soc.*, **60**, 1905 (1958).

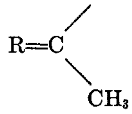
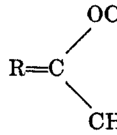
[20] All melting points and boiling points are uncorrected. All microanalyses by the Galbraith Laboratories, Inc., Knoxville, Tenn. The term "worked up in the usual way" means that a solution of the products in an organic solvent, after washing with dilute alkali and/or acid, water, and saturated salt solution, was filtered through a cone of anhydrous magnesium sulfate. The solvent was then removed on a rotary evaporator.

[21] Prepared in 81% yield as described by E. H. Huntress, E. B. Hershberg, and I. S. Cliff, *ibid.*, **53**, 2720 (1931).

[22] L. F. Fieser and W. S. Johnson, *ibid.*, **62**, 576 (1940).

TABLE II

VINYL ETHERS

Vinyl ether	Registry no.	Bp (mm),[a] °C	Calcd, %		Found, %	
			C	H	C	H
$(CH_2)_4C{=}CHOCH_3$	19684-48-1	58 (45)	74.9	10.8	75.1	10.9
$(CH_2)_4C{=}CHOC_4H_9$-*n*	19684-49-2	105-107 (48)	77.9	11.8	77.9	12.0
$(CH_2)_5C{=}CHOCH_3$[b]		85-89 (60)	76.1	11.2	76.3	11.4
$(CH_2)_5C{=}CHOC_2H_5$	19684-50-5	100 (100)	77.1	11.5	77.2	11.5
$(CH_2)_5C{=}CHOC_3H_7$-*n*	19684-51-6	112-114 (60)	77.9	11.8	77.8	11.8
$(CH_2)_5C{=}CHOC_3H_7$-*i*	19684-52-7	105-106 (65)	77.9	11.8	77.8	11.8
$(CH_2)_5C{=}CHOC_4H_9$-*n*[b]		105 (22)	78.5	12.0	78.4	12.1
$(CH_2)_5C{=}CHOC_4H_9$-*t*	19684-53-8	77-80 (10)	78.5	12.0	78.5	12.0
$(CH_2)_5C{=}CHOC_4H_7$[c]	19736-55-1	58-60 (1.5)	79.5	10.9	79.4	10.9
$R{=}CHOC_2H_5$[d,e]	19684-54-9	64-65[f]	86.3	6.3	86.6	6.6
 $R{=}C(OCH_3)(CH_3)$[e]		150 (0.4)	86.3	6.3	86.5	6.4
 $R{=}C(OC_2H_5)(CH_3)$[e,g]	19684-55-0	145-150 (0.4)	86.4	6.8	86.5	6.7

[a] Boiling point of the fraction on which analyses were obtained at the pressure listed. [b] Reported previously by G. Wittig, W. Böll, and K. H. Krück, *Ber.*, **95**, 2514 (1962). [c] The methallyl group. [d] The corresponding methoxy compound has been reported.[6] [e] R = fluorenylidene. [f] Melting point. [g] Mp 70-71°.

g of anhydrous hydrazine. After standing for 15 hr at room temperature the alcohol was removed on a rotary evaporator and the excess hydrazine by keeping *in vacuo* over concentrated H_2SO_4. The crude solid was recrystallized from alcohol to give 48.5 g (90% from fluorenone) of 2-(9-hydroxy-9-fluorenyl)propionic acid hydrazide, mp 164-165°.

Anal. Calcd for $C_{16}H_{16}N_2O_2$: C, 71.6; H, 6.0; N, 10.4. Found: C, 71.6; H, 6.0; N, 10.3.

A solution of 13 g of $NaNO_2$ in 100 ml of water was added to a well-stirred solution of 46 g of the above hydrazide in 150 ml of 2 *N* HCl at 5-10°. Urea was added to destroy the excess HNO_2, then 100 ml of benzene and 200 ml of Skellysolve B (petroleum ether, bp 65-70°) were added. On warming to 70° gas evolution became vigorous (efficient provision for reflux important) and a solid began to precipitate. After all gas had been evolved and the mixture was cooled the solid was collected, dried, and recrystallized from benzene-alcohol to yield 34 g (80%) of 4-methylspiro[fluorene-9',5-oxazolidin]-2-one, mp 234-235°. A sample was sublimed for analysis.

Anal. Calcd for $C_{16}H_{13}NO_2$: C, 76.5; H, 5.2; N, 5.6. Found: C, 76.7; H, 5.4; N, 5.6.

A solution of 9.1 g of nitrosyl chloride in 30 ml of acetic anhydride was added slowly to a stirred suspension of 30.0 g of the above oxazolidone in 150 ml of dry pyridine at 0-5°. After stirring for a further 40 min the mixture was poured into ice water. The precipitate was collected, washed well with ice water, and dried *in vacuo*. Recrystallization from ethanol-Skellysolve B afforded 30.1 g (90%) of **7**, mp 156-157°.

Anal. Calcd for $C_{16}H_{12}N_2O_3$: C, 68.6; H, 4.3; N, 10.0. Found: C, 68.9; H, 4.5; N, 9.8.

The preparation of **14** is described below. Methyl 1-hydroxycyclopentylacetate, bp 90-92° (2 mm), was prepared in 64% yield by a Reformatsky reaction from cyclopentanone and methyl bromoacetate. To a stirred solution of 101 g of the hydroxy ester in 10 ml of dry methanol was added 42 g of anhydrous hydrazine. The mixture warmed spontaneously to 50° and solidified in 15 min. The solid was collected on a filter, washed with Skellysolve B, and dried *in vacuo* for 1 hr over concentrated H_2SO_4 to remove excess hydrazine. Recrystallization from methanol afforded 80 g (80%) of 1-hydroxycyclopentylacetic acid hydrazide, mp 142-144°. The analytical sample, mp 144.6-145.4°, was prepared by recrystallization from alcohol.

Anal. Calcd for $C_7H_{14}N_2O_2$: C, 53.1; H, 8.9; N, 17.7. Found:[23] C, 53.3; H, 8.7; N, 17.9.

A solution of 18 g of sodium nitrite in 30 ml of water was added dropwise to a stirred solution of 40 g of hydrazide in 150 ml of 2 *N* hydrochloric acid held at 8-12°. Then 150 ml of Skellysolve B was added and the mixture heated under reflux slowly to 65° when the evolution of nitrogen became vigorous. After standing overnight the solid was collected and added to more of the same obtained by further benzene-ether extraction of the aqueous layer. The combined solids were dried and recrystallized from benzene-Skellysolve B to yield 29.2 g (82%) of 1-oxa-3-azaspiro[4,4]nonan-2-one, mp 100-102°. The analytical sample, mp 100.8-101.6° cor, was prepared by crystallization from benzene-Skellysolve B.

Anal. Calcd for $C_7H_{11}NO_2$: C, 59.6; H, 7.9; N, 9.9. Found:[23] C, 59.9; H, 7.7; N, 10.1.

To a stirred mixture of 28.2 g of this oxazolidone in 55 ml of water, 55 ml of acetic acid, and 55 ml of concentrated HCl at 0-5° was added dropwise a solution of 14.5 g of sodium nitrite in 100 ml of water during 1 hr. The solid was collected, was washed with cold water, and dried *in vacuo*. Recrystallization from benzene-Skellysolve B gave 33.0 g (98%) of pale yellow **14**, mp 96.0-97.5°. The analytical sample, mp 97.6-98.2° with sintering at 94°, was prepared by crystallization from benzene-Skellysolve B.

Anal. Calcd for $C_7H_{10}N_2O_3$: C, 49.4; H, 5.9. Found:[23] C, 49.2; H, 5.8.

Preparation of Vinyl Ethers (Table I).—The general procedure involved adding a solution of the sodium alkoxide in the alcohol in question to a cold (0-5°) suspension (part solution) of the nitrosooxazolidone in the same alcohol. Evolution of nitrogen was rapid and controlled by the rate of addition of alkoxide. After slightly more than 1 equiv of base had been added the theoretical amount of nitrogen was evolved. The mixture was then poured into water and the product extracted with ether-benzene as usual. Distillation was effected through a Nester-Faust spinning-band column. The yields of vinyl ethers having the boiling points listed in Table II are recorded in Table I. The infrared and nuclear magnetic resonance spectra are contained in the Ph.D. thesis[2] and were consistent with the structures assigned.

1-Methallylcyclohexanecarboxaldehyde (**16**).—A solution made by treating 10 g of sodium with 240 ml of methallyl alcohol was added slowly to a stirred ice-cold suspension of 18.4 g of **1** in 50 ml of methallyl alcohol until the theoretical amount of nitrogen had been collected. The mixture was worked up by diluting with water and worked up in the usual way. If distillation under reduced pressure were attempted mixtures of **15** and

---

[23] Analyses were by Mrs. E. H. Klotz in 1949.

16 were obtained. By chromatography over silica gel the first fraction eluted (2:1 hexane–benzene) was distilled to yield 8.5 g (51%) of pure **15**, bp 58–60° (1.5 mm).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.5; H, 10.9. Found: C, 79.4; H, 10.9.

The second fraction eluted (1:1 hexane–benzene) yielded 1.8 g (11%) of **16**, bp 68–70° (1.5 mm). This aldehyde was not analyzed but gave infrared and nmr spectra consistent with such a structure. The 2,4-dinitrophenylhydrazone, mp 141–142°, and semicarbazone, mp 195–196°, were prepared.

Anal. Calcd for $C_{17}H_{22}N_4O_4$: C, 58.9; H, 6.4; N, 16.2. Found: C, 58.8; H, 6.5; N, 16.1. Calcd for $C_{12}H_{21}N_3O$: C, 64.5; H, 9.5; N, 18.8. Found: C, 64.6; H, 9.7; N, 18.6.

On pyrolysis neat at 145–165° for 3 hr **15** was quantitatively converted into **16**.

9-Methoxy-9-(1-methoxyethyl)fluorene (**10**).—To a stirred suspension of 19 g of **7** in 125 ml of dry methanol at 5–10° was added a solution of sodium methoxide (prepared from 10 g of sodium and 115 g of methanol) until a slight excess had been added. The mixture was stirred for 30 min and poured into ice water. The product was isolated in high yield as usual using ether. Care was taken not to heat the product above room temperature. After drying *in vacuo* over $CaSO_4$, the product melted in the 110–115° range. This product had no ir absorption in the carbonyl region. The nmr spectrum showed a mixture of two compounds in a ratio of about 19:1. On crystallization from Skellysolve B using care not to overheat, a purer sample of the major component was obtained which gave an nmr spectrum consistent with the structure **10**, *e.g.*, a doublet at τ 9.08, (8 cps, 3 H, $CHCH_3$), two singlets at 7.23 and 6.58 (3 H, each $-OCH_3$), a quartet at 6.74 (8 cps, 1 H, $-CHCH_3$ partly obscured by the singlet at 6.58), in addition to aromatic H.

On warming in Skellysolve B for longer times or on heating **10** was converted mainly into **11** which was purified by crystallization to yield **11**, mp 136–137°, whose nmr spectrum had three singlets at τ 7.42 ($=CCH_3$), 6.68 (CH_3OH),[24] and 6.20 ($=COCH_3$) in addition to aromatic H.

Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.3; H, 7.1. Found: C, 80.3; H, 7.3.

In order to remove the last traces of methanol from **11** slow heating to 165° at atmospheric pressure followed by vacuum distillation was needed to obtain **12** as an oil, bp ~150° (0.4 mm). We were unable to obtain **12** in solid form. However, a picrate, mp 175–176.5°, was prepared.

Anal. Calcd for $C_{22}H_{17}N_3O_8$: C, 58.6; H, 3.8; N, 9.3. Found: C, 58.3; H, 3.9; N, 9.5.

The nmr spectrum of **12** had a singlet (3 H) at τ 7.46 ($=CCH_3$), a singlet (3 H) at 6.23 ($=COCH_3$), and a multiplet (8 H) of aromatic hydrogens centered at 2.2.

Bicyclo[4.1.0]hept-7-ylidenecyclohexane (**2**).—A suspension of 3.9 g of lithium ethoxide[9] in 15 ml of freshly distilled cyclohexene was added under nitrogen to a stirred suspension of **1** in 25 ml of cyclohexene at room temperature. The reaction was exothermic and was kept at about 45° by cooling. Nitrogen evolution was quantitative. After stirring for 2 hr the mixture was worked up as usual. Distillation on a spinning-band column yielded 4.6 g (65%) of **2**: bp 68–70° (0.3 mm); $n^{25}\mathrm{D}$ 1.5065 (lit.[10] 1.5070); mol wt, 176 (mass spectrograph[25]); ir band at 5.5 μ (1818 cm^{-1}, strong) characteristic of a double bond exocyclic to a cyclopropane ring.[26] The analytical sample was obtained by preparative vpc using a 5-ft column of 20% silicon rubber SE30 on 60–80 mesh Chromosorb P 609 at 125°.

Anal. Calcd for $C_{13}H_{20}$: C, 88.6; H, 11.4. Found: C, 88.6; H, 11.4.

The nmr spectrum was not sufficiently characteristic to be used as proof of structure (three unresolved peaks between τ 7.5 and 9.0). In different runs the yields varied from 40 to 65%, yields being lower when potassium *t*-butoxide was used.

2-Isobutoxycyclohexylidenecyclopropane (**3**).—A suspension of 7.36 g of **1** in freshly distilled isobutyl vinyl ether[27] was treated as in the preparation of **2** with 2.4 g of lithium ethoxide.[9] After the usual work-up distillation on a spinning-band column afforded 5.8 g (74%)[28] of **3**: bp 58–60° (0.4 mm); $n^{25}\mathrm{D}$ 1.4725; ir band at 5.6 μ. The analytical sample was obtained by preparative vpc (at 140°) as for **2**. The nmr spectrum was in good agreement with the postulated structure.

Anal. Calcd for $C_{13}H_{22}O$: C, 80.4; H, 11.4. Found: C, 80.4; H, 11.4.

2-Isopropoxycyclohexylidenecyclopropane (**4**).—On treatment of **1** as in the case of **2**, except that isopropyl vinyl ether[27] was used, there was obtained 5.8 g (85%)[28] of **4**, bp 100° (8 mm), $n^{22}\mathrm{D}$ 1.4765, on the analytical sample obtained by preparative vpc as above. The nmr spectra showed excellent agreement with the postulated structure.

Anal. Calcd for $C_{12}H_{20}O$: C, 79.9; H, 11.2. Found: C, 79.7; H, 11.2.

Competition between Cyclohexene and Ethanol for Unsaturated Carbene.—Suspension of **1** in a mixture of equimolar amounts of cyclohexene and ethanol with lithium ethoxide at temperatures from 3 to 30° resulted in vigorous reaction which caused the final temperatures to be in the 30–65° range. The products were worked up as usual and distilled at atmospheric pressure. By vpc analyses using a 2-ft column of silicon rubber SE-30 on 60–80 W 609 which had been standardized with known mixtures of ethoxymethylenecyclohexene and **2**, the mixtures were found to consist of these compounds in ratios of 4.7:1 to 6.8:1, the higher ratios being found when the final temperatures were higher.

Deuterium Experiments.—To an ice-cooled mixture of 1.84 g of **1**, 6 ml of CH_3OD,[29] and 5 ml of glyme (1,2-dimethoxyethane) was added 0.6 g of alcohol-free sodium methoxide. The reaction mixture (cooling bath removed) was stirred for 1 hr during the first 15 min of which gas evolution was complete and quantitative. After dilution with water and the usual work-up there was obtained 0.83 g (65%) of **5a**, bp 84–85° (55 mm). A part of this material was purified by preparative vpc and submitted to nmr analysis. The presence of a very small peak at τ 4.4 showed that only a very small amount of vinylic hydrogen was present. When the corresponding nondeuterated vinyl ether was treated with sodium methoxide in CH_3OD, the ratio of the peaks at τ 4.4 and 6.6 (OCH_3) was 1:3 as in the case of the untreated vinyl ether.

When a suspension of **1** in D_2O and glyme was treated under N_2 with a small excess of aqueous NaOD in D_2O nitrogen was evolved rapidly. After the usual work-up, which included washing with dilute H_3O^+ (loss of α deuterium), the aldehyde **6** was obtained in 45–50% yield. The nmr showed the absence of the aldehyde hydrogen (τ 0.6). In addition the ir band at 3.68 μ, characteristic of the aldehydic hydrogen, was absent in the product obtained from the reaction of **1** in D_2O.

Registry No. –**2**, 19690-02-9; **3**, 19690-03-0; **4**, 19690-04-1; **7**, 19713-85-0; **10**, 19684-42-5; **11**, 19684-43-6; **12** (picrate), 19684-44-7; **14**, 19684-45-8; **16**, 19684-46-9; **16** (2,4-dinitrophenylhydrazone derivative), 19713-86-1; **16** (semicarbazone), 19684-47-0; 2-(9-hydroxy-9-fluorenyl)propionic acid hydrazide, 19684-56-1; 4-methylspiro[fluorene-9′,5-oxazolidin]-2-one, 19684-57-2; 1-hydroxycyclopentylacetic acid hydrazide, 19684-58-3; 1-oxa-3-azaspiro[4.4]nonan-2-one 19684-59-4.

---

[24] For pure CH_3OH, τ is 6.62: L. M. Jackman, "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," The Macmillan Co., New York, 1959, p. 55.

[25] We thank Dr. Ralph Dougherty for this determination.

[26] H. E. Simmons, E. P. Blanchard, and H. D. Hartzler, *J. Org. Chem.*, **31**, 295 (1966).

[27] We thank the General Aniline and Film Corp. for a generous gift of this vinyl ether.

[28] Repetition of the preparations of **2** and **4** by Dr. T. Patrick gave somewhat lower yields (50–57% **2** and 41% **4**). These results may be due to unfamiliarity with the procedure used by D. Okorodudu or to unknown variations in procedure.

[29] CH_3OD (99+%) was obtained from Brinkmann Instruments Inc., Westbury, N. J.