247°. Recrystallization from ethanol gave the analytical sample: mp 246–247°; ir ($CHCl_3$) 3450–2380, 1610, 1580, 1510, 1460, 1440, 1360, 1310, 1260, 1160, 1140, 1040, 1025, 833, and 823 cm^{-1}; nmr δ ($CDCl_3$) 1.57–2.2 (m, 10 H), 2.7–3.4 [m, 5 H, after the N^+H_2 protons are exchanged with D_2O, the multiplet resolved into 2.7–3.2 (m, 3 H), 3.32 (d, J = 3 Hz, 2 H)], 3.77 (s, 3 H), 3.88 (s, 3 H), 6.3–6.5 (m, 2 H), 7.35 (d, J = 8 Hz, 1 H), and 8.67–8.92 (b, 2 H, N^+H_2, absent after exchange with D_2O).

Anal. Calcd for $C_{18}H_{26}ClNO_2$: C, 66.74; H, 8.09; Cl, 10.94; N, 4.34. Found: C, 66.55; H, 8.06; Cl, 11.09; N, 4.24.

The free base was isolated by treatment of the hydrochloride with aqueous ethanolic sodium hydroxide, extraction with ether, drying, solvent evaporation, and crystallization from ethanol, mp 136–138°. The analytical sample resulted from two crystallizations from ethanol–water: mp 136–137°; ir($CHCl_3$) 3390, 1600, 1580, 1490, 1460, 1450, 1150, 1130, 1070, 1030, and 990 cm^{-1}; nmr δ ($CDCl_3$) 1.4–2.7 (m, 14 H, after exchange with D_2O, 13 H), 3.12 (d, J = 3 Hz, CH_2N, 2H), 3.75 (s, 3 H, $ArOCH_3$), 3.80 (s, 3 H, $ArOCH_3$), 6.35–6.55 (m, 2 H), 7.55 (d, J = 8 Hz, 1 H); mass spectrum, *m/e* (rel intensity), 287 (100), 272 (28), 258 (43), 257 (3), 256 (10), 244 (42), 230 (96), 216 (27), 215 (14), 204 (80), 203 (17), 193 (24), 192 (23), 178 (20), 164 (24), 163 (27), 151 (14), 91 (13), 79 (13), 77 (12), 32 (20), and 30 (13).

Anal. Calcd for $C_{18}H_{25}NO_2$: C, 75.22; H, 8.77; N, 4.87. Found: C, 75.25; H, 8.67; N, 4.91.

6d from 7. A mixture of **7** (0.5 g, 3 mmol), aluminum chloride (1 g, 7.5 mmol), and 1,3-dimethoxybenzene (6 g, 43.5 mmol) in methylene chloride (10 ml) was refluxed for 17 hr. Then 18% hydrochloric acid (25 ml) was added at 0–5°. The organic layer was separated and extracted with three small portions of 18% hydrochloric acid. The combined acidic solution was washed with three small portions of Skelly C, and then slowly added to 50 ml of 25% sodium hydroxide at 0° with good stirring. The fine white precipitate was collected and washed with water, giving 29% of crude **6d** (0.25 g). Two recrystallizations from ethanol–water gave an 81% recovery of pure product; the melting point, mixture melting point, and ir spectrum (Nujol) demonstrated identity with the material prepared from **2**.

Acknowledgment. We are grateful to the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work. Contributions of Mr. T. A. Wnuk to the experimental work are appreciated. We thank Dr. Peter Yates for the mass spectral data, Dr. V. L. Narayanan for spectral data on 4-azahomoadamantane, and Mr. A. Gasiecki for some of the microanalyses. We express our appreciation to one of the referees for bringing ref 23a to our attention.

Rearrangements of 2,5-Dimethyl-2-vinyl-2,3-dihydrofuran and Related Isomers[1,2]

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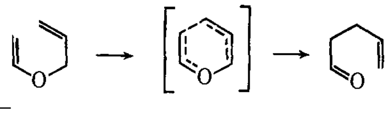
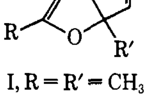
Contribution from the Department of Chemistry, University of Wyoming, Laramie, Wyoming 82070. *Received December 18, 1970*

Abstract: The rearrangement of 2,5-dimethyl-2-vinyl-2,3-dihydrofuran (I) to 4-methyl-4-cycloheptenone (III) in the temperature range 140–200° has been demonstrated to occur through the intermediacy of 2-methyl-2-vinyl-5-methylenetetrahydrofuran (VII). Interconversion of I and VII occurs rapidly at active sites on a glass surface but may be arrested in sodium hydroxide coated tubes. At higher temperatures and lower pressures, I rearranges to produce a mixture of III, 1-methyl-4-acetylcyclopentene (IV), and 5-methylene-6-hepten-2-one (X). The isomeric cyclopropane derivatives *cis*- and *trans*-1-acetyl-2-vinyl-2-methylcyclopropane (V and VI) and *cis*- and *trans*-1-acetyl-2-isopropenylcyclopropane (VIII and IX) have been prepared and their thermal behaviors studied. Rearrangement of V and of VIII produces III as well as I, IV, and X, in relative amounts which depend on the rearrangement conditions imposed. A facile enolene rearrangement of VI leads to the formation of X. *trans*-1-Acetyl-2-isopropenylcyclopropane (IX) survives heating at 215°. The results are explained in terms of wall reactions of I and V giving rise to III, and the intermediacy of a common bisallylic diradical which can partition to I, IV, V, and VI (X).

Thermal lability in unconstrained vinyl allyl ethers (Claisen rearrangement) is a familiar phenomenon, attributable to the concerted nature of the electron reorganization leading to the thermodynamically favored homallylic carbonyl isomer.[4] It has been of interest to us to explore the consequences of geometric restraint in such systems and, to this end, we have examined vinyl derivatives of dihydrofurans in which the first and fourth atoms of the vinyl allyl ether are bridged by a methylene group,[5] *i.e.*





I, R = R′ = CH_3

Models suggested that in such systems achievement of the orientations required for a concerted rearrangement[4] would be difficult, if not impossible, and that alternative isomerization pathways might be observed.[6]

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[1] A preliminary account of a portion of this work has appeared: S. J. Rhoads and C. F. Brandenburg, *J. Amer. Chem. Soc.*, **88**, 4294 (1966).

[2] Taken from the Ph.D. Dissertation of C. F. B., University of Wyoming, 1969.

[3] U. S. Bureau of Mines Fellow of the Laramie Petroleum Research Center, 1967–1969.

[4] See A. Jefferson and F. Scheinmann, *Quart. Rev., Chem. Soc.*, 22, 391 (1968), for a recent and excellent review of Claisen and related rearrangements.

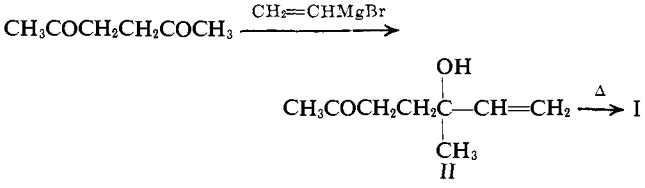
[5] That bridging of these atoms by two methylene groups does not impede the normal Claisen rearrangement recently has been demonstrated in vinyl dihydropyran systems by G. Büchi and J. E. Powell, Jr., *J. Amer. Chem. Soc.*, **89**, 4559 (1967); **92**, 3126 (1970).

[6] Under a variety of conditions, 2-vinylic-2,3-dihydrofuran systems have been reported to rearrange to acyl cyclopentenes, acyl vinylic

In this paper we report on the thermal behavior of 2,5-dimethyl-2-vinyl-2,3-dihydrofuran (I) and its valence isomeric species, *cis*- and *trans*-1-acetyl-2-vinyl-2-methylcyclopropane (V and VI).

Results and Discussion

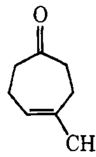
Synthesis and Rearrangement of I. The preparation of I was accomplished by treatment of 2,5-hexanedione with 1 equiv of vinylmagnesium bromide followed by cyclodehydration of the monoaddition product, 5-methyl-5-hydroxy-6-hepten-2-one (II). The structure of I follows unequivocally from its spectral properties (detailed in the Experimental Section and Table I). Notable among these are the presence of strong absorption at 1680 cm^{-1} in the infrared and a $\pi \rightarrow \pi^*$ band at 208 nm (ϵ 2880) in the ultraviolet, characteristics of vinyl ethers.[7]



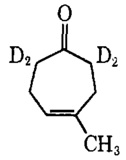
$$CH_3COCH_2CH_2COCH_3 \xrightarrow{CH_2{=}CHMgBr} CH_3COCH_2CH_2\overset{OH}{\underset{CH_3}{C}}—CH{=}CH_2 \xrightarrow{\Delta} I$$

II

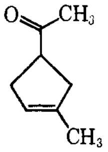
When I, neat or in decane solution, was held at 175° for 24 hr, it rearranged in high yield to a single compound which proved to be 4-methyl-4-cycloheptenone (III). Glpc monitoring throughout the rearrangement established the absence of the Claisen rearrangement product, 1-methyl-4-acetylcyclopentene (IV), and of the cyclopropane isomers V and VI.



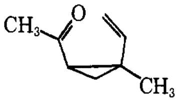
III



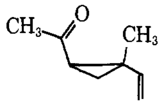
III-d_4



IV



V

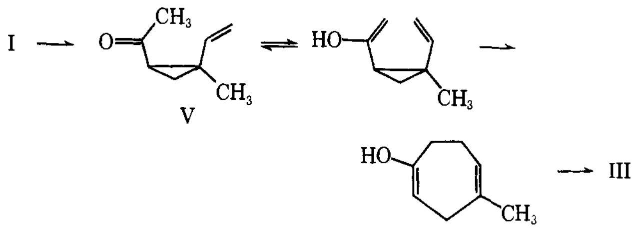


VI

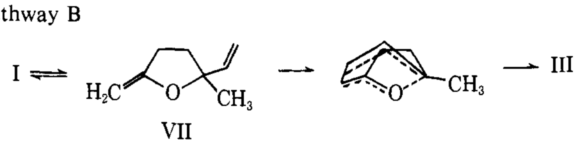
The structure of III is supported by spectral and chemical evidence (Table I and the Experimental Section). The location of the double bond at the 4 position and the assignment of the two groups of methylene protons in the nmr spectrum of III follow from the nmr spectrum of III-d_4, prepared by base-catalyzed deuterium exchange. In the spectrum of III-d_4, the multiplet at δ 2.3 ppm has disappeared and the signals of the four allylic methylene protons show a much simplified pattern at δ 1.9 ppm. The splitting patterns of the vinyl and methyl protons remain unchanged in the deuterated material, confirming the position of the double bond. The carbon skeleton of III was verified by catalytic reduction to 4-methylcycloheptanone, identical in all respects with an authentic sample.[8]

In order to rationalize this unexpected rearrangement, two possibilities have been considered: pathway A, rearrangement of the dihydrofuran system to (*cis*-1-acetyl-2-vinyl)-2-methylcyclopropane (V)[9] followed by enolization toward the methyl group[10] and a rapid cis divinylcyclopropane rearrangement[11] leading to the enol of III; and pathway B, endo-exo isomerization of I to form 2-methyl-2-vinyl-5-methylenetetrahydrofuran (VII),[12] and subsequent Claisen rearrangement of the new and less constrained vinyl allyl ether system in VII.

Pathway A

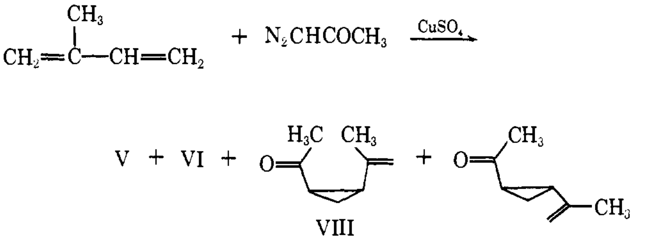


Pathway B



VII

Synthesis and Rearrangement of V and VI. The possible intervention of V as a transient intermediate in the rearrangement of I necessitated its preparation and study of its thermal behavior. Our first approach to its synthesis employed the copper sulfate catalyzed addition of diazoacetone to isoprene.[13] This reaction produced, in poor yield, a mixture of the four possible addition products, *i.e.*, V, its trans isomer VI, and the corresponding isopropenyl derivatives, VIII and IX, in a ratio of *ca.* 5:3:1:3.5. Preparative glpc permitted the isolation of pure samples of each of the four isomers. A more convenient preparation of the cis isomer V was found in the photoisomerization of I.[14] When irradiated in pentane solution at 254 nm, I is



VIII

IX

$$\underset{CH_2=C—CH=CH_2}{\overset{CH_3}{|}} + N_2CHCOCH_3 \xrightarrow{CuSO_4}$$

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cyclopropanes, and acyclic dienic carbonyl compounds. *Cf.* J. Wiemann and S. T. Thuan, *Bull. Soc. Chim. Fr.*, 199 (1958); J. Wiemann, P. Casals, and N. Lefebvre, *ibid.*, 319 (1962); N. Thoai, *ibid.*, 225 (1964); J. Wiemann, N. Thoai, and F. Weisbuch, *ibid.*, 2187 (1964). It is not clear, in any of these cases, however, that a purely thermal process was being observed.

[7] S. J. Rhoads, J. K. Chattopadyay, and E. E. Waali, *J. Org. Chem.*, **35**, 3352 (1970).

[8] C. Djerassi, B. F. Burrows, C. G. Overberger, T. Takekoshi, C. D. Gutsche, and C. T. Chang, *J. Amer. Chem. Soc.*, **85**, 949 (1963).

[9] See C. L. Wilson (*ibid.*, **69**, 3002 (1947)), D. M. A. Armitage and C. L. Wilson (*ibid.*, **81**, 2437 (1959)), and ref 6 for examples of such ring contractions.

[10] C. Rappe and W. H. Sachs (*Tetrahedron*, **24**, 6287 (1968)) have shown in the case of methyl cyclopropyl ketone that enolization toward the methyl group is strongly favored over enolization toward the ring.

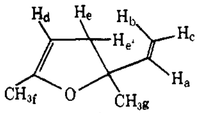
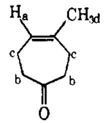
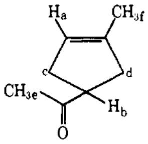
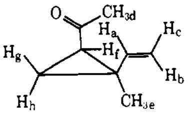
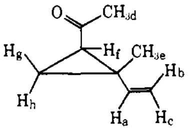
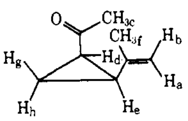
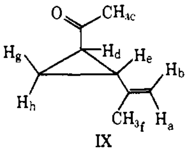
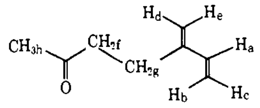
[11] W. von E. Doering and W. R. Roth, *ibid.*, **19**, 715 (1963).

[12] A. Kankkaanpera, E. Taskinen, and P. Salomaa, *Acta Chem. Scand.*, **21**, 2487 (1967).

[13] See W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964, p 132, for reactions of this type and leading references.

[14] Similar photoisomerizations have been reported by J. Wiemann, N. Thoai, and F. Weisbuch, *Bull. Soc. Chim. Fr.*, 575 (1966), and W. G. Dauben and G. W. Shaffer, *J. Org. Chem.*, **34**, 2301 (1969).

Table I. Nuclear Magnetic Resonance Spectral Data for $C_8H_{10}O$ Isomers[a]

Compd	Proton, chemical shift, multiplicity, coupling constants
 I	abc, 5.89, 5.12, 4.92, ABX pattern, $J_t = 17.1$, $J_c = 10.7$, $J_{gem} = 1.5$ Hz; d, 4.29, m, $J_{e.d} = J_{e'.d} = 2.3$, $J_{d,f} = 1.2$ Hz; e and e′, 2.52 and 2.38, m, $J_{e.e'} = 14.4$, $J_{e.f} = J_{e'.f} = 2.0$ Hz; f, 1.71, t of d's, split by $J_{d,f}$, $J_{e.f}$, and $J_{e'.f}$; g, 1.40, s
 III[b]	a, 5.26, m with fine splittings; b, 2.26, complex envelope; c, 1.90, complex envelope; d, 1.47, m with fine splitting
 IV[c]	a, 5.17, m with fine splittings; b, 3.24, five-line m with 8-Hz spacings and further fine splitting; cd, 2.5, complex envelope; e, 2.12, s; f, 1.68, m with fine splitting
 V	abc, 5.72, 5.01, 4.92, ABX pattern, $J_t = 17.0$, $J_c = 10.0$, $J_{gem} = 2.0$ Hz; d, 2.11, s; e, 1.29, s; f, 2.01, d of d's, $J_{f.g} = 6$, $J_{f.h} = 8$ Hz; g, 1.52, d of d's, split by $J_{f.g}$ and $J_{g.h} = 4$ Hz; h, 0.92, d of d's, split by $J_{f.h}$ and $J_{g.h}$
 VI	abc, 5.45, 5.00, 4.92, ABX pattern, $J_t = 16.0$, $J_c = 10.0$, $J_{gem} = 2.0$ Hz; d, 2.14, s; e, 1.16, s; f, 1.97, d of d's, $J_{f.g} = 6$, $J_{f.h} = 8$ Hz; g, 1.42, d of d's, split by $J_{f.g}$ and $J_{g.h} = 4$ Hz; h, 0.94, d of d's, split by $J_{f.h}$ and $J_{g.h}$
 VIII	ab, 4.95, complex m; c, 2.08, s; de, 2.1–1.7, complex overlapping m's; f, 1.65, m with fine splitting; g, 1.46, t of d's, $J_{g.d} = J_{g.e} = 6$, $J_{g.h} = 4$ Hz; h, 0.98, t of d's, $J_{h.d} = J_{h,e} = 8$, $J_{g.h} = 4$ Hz.
 IX	ab, 4.70, complex m; c, 2.16, s; de, 2.1–1.7, complex overlapping m's; f, 1.65, m with fine splitting; g, 1.25, d of d's of d's, $J_{g.d} = 6.5$, $J_{g.e} = 8$, $J_{g.h} = 4$ Hz; h, 0.99, d of d's of d's, $J_{h.d} = 8$, $J_{h.e} = 6.5$, $J_{g.h} = 4$ Hz
 X	a, 6.30, d of d's, $J_{a,b} = 9$, $J_{a,c} = 5$ Hz; bcde, 5.08–4.96, overlapping m's; fg, 2.51, complex m; h, 2.08, s

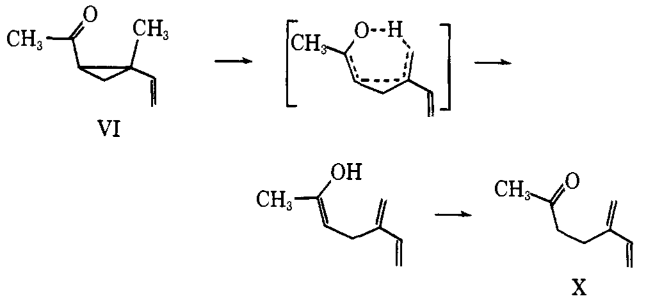
[a] Spectra were measured in carbon tetrachloride and with a Varian HA-100 instrument unless stated otherwise. All signals gave the proper integrals for the proton assignments. Chemical shifts are in δ units relative to an internal TMS standard. [b] In benzene-d_6. [c] In chloroform-d_1.

transformed to a mixture consisting largely of V and VI, in a 2:3 ratio, accompanied by a small amount of the Claisen product IV. Separation of these isomers may be facilitated by a short preliminary heating of the photoreaction mixture at 150°, a procedure which induces the facile enolene rearrangement of VI to X (see below) but leaves V and IV unchanged. The retention time of V is sufficiently different from those of IV and X to permit its separation in good purity by preparative glpc. The minor product of the photoreaction, IV, was also isolated and its structure confirmed by its spectral characteristics (Table I and Experimental Section).

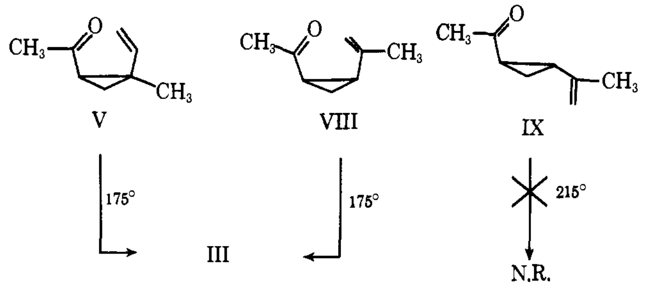
Structural assignments for the four cyclopropane isomers V, VI, VIII, and IX are based on the differences in their nmr spectra and in their thermal behavior. The nmr data (Table I) readily distinguish the sets of cyclopropane isomers carrying vinyl and isopropenyl side chains by the appearance of the familiar ABX pattern of the vinyl group in the spectra of V and VI. The cis disposition of the acetyl and isopropenyl groups in VIII and the trans nature of these groups in IX follow from consideration of the couplings of the ring protons. In the spectrum of VIII, the two protons of the methylene group produce signals at δ 1.46 and 0.98 ppm. Each of these is a well-defined triplet of doublets, revealing the couplings with the methinyl protons at C-1 and C-2 as well as a geminal coupling of 4 Hz. The signal of the more deshielded proton (δ 1.46 ppm) yields couplings of 6 Hz, requiring that this proton be trans[15] to the methinyl protons at C-1 and C-2, whereas cis couplings of 8 Hz[15] characterize the signal at 0.98 ppm. In the trans isomer, IX, the corresponding methylene signals are found at δ 1.25 and 0.99 ppm as doublets of doublets of doublets; each signal reveals a cis (8 Hz) and a trans (6.5 Hz) coupling with the methinyl protons as well as a geminal coupling of 4 Hz. In each case, the more deshielded of the two methylene protons is identified with that one which is cis to the acetyl group.

A clear-cut distinction between the cis and trans isomers, V and VI, is not immediately forthcoming from their nmr spectra since the splitting patterns of the methylene protons are the same, i.e., both isomers have one methylene proton showing a cis coupling with the C-1 proton and the other methylene proton showing a trans coupling. The assignment of the cis geometry to V and the trans to VI rests upon the parallelisms in chemical-shift values for corresponding groups of protons in V and VIII *vs.* VI and IX and upon identification of the more deshielded of the two methylene protons in the four isomers as being that one which is cis to the acetyl function. Confirmation of the structural assignments is found in the contrasting thermal behavior of the four isomers.

Easily the most labile of the isomers is (*trans*-1-acetyl-2-vinyl)-2-methylcyclopropane (VI). When held at 125° for 5 hr, VI is completely converted to the acyclic dienic ketone, 5-methylene-6-hepten-2-one (X), in a facile enolene rearrangement.[16] The structure of X is supported by its spectral characteristics, *i.e.*, a molecular ion with *m/e* 124,[17] strong carbonyl absorption at 1720 cm^{-1}, characteristic conjugated diene absorption at 1640 and 1600 cm^{-1}, and a vinylic proton pattern in its nmr spectrum (Table I) which closely matches that of isoprene.



Both of the cis isomers, V and VIII, undergo rearrangement when held at 175° for 24 hr in good overall conversion to produce 4-methyl-4-cycloheptenone (III), identical with that obtained from I. The trans isomer, IX, on the other hand, is markedly more stable and survives virtually unchanged after 30 hr at 215°. Because of limited supply, the isomers VIII and IX were not further investigated.



Elimination of the Intermediacy of V in the Rearrangement of I. At first glance, the fact that V (as well as VIII) does, indeed, produce the rearrangement product, III, appears to support pathway A for the rearrangement of I. However, closer examination of the thermal behavior of I and V reveals that this is not the case. Several lines of evidence point to the conclusion that I rearranges to III quite independently of V.

Qualitative comparison of the extent of rearrangement of I and V under identical conditions showed the rearrangement of I to III to be almost twice as fast as the conversion of V to III in the temperature range 160–200° (see Table II). In these experiments, the starting materials were heated, neat or in decane, in evacuated, sealed capillary tubes of Pyrex glass, and it may be assumed that the rearrangements were occurring largely in the liquid phase. The absence of any detectable amount of V in the glpc-monitored rearrangement of I establishes that the more slowly rearranging V cannot be involved.

When efforts were made to evaluate rate constants for the rearrangements of I and V, it quickly became apparent from the erratic behavior of the rate data that the processes in both cases were complex ones and surface phenomena seemed implicated. Thus, the rates of rearrangement of both I and V were retarded in soft glass or "base-washed" Pyrex tubing (tubing which had been cleaned by washing with dilute sodium hydroxide solution and then with distilled water). This effect was particularly striking in the case of the dihydrofuran system I; indeed, in one set of experiments in "unwashed" soft glass, the rearrangement of I was completely arrested after 7% reaction. In other runs in soft glass, the rearrangement of I could not be completely inhibited but still showed a marked retardation after the first 6–8% rearrangement.

It was further observed that although the overall conversions of both I and V to III were quite good, the rearrangement of I was actually much cleaner than that of V. This contrast was especially pronounced when the rearrangements were conducted in soft glass at 140–180°. Under these conditions, extraneous, small peaks (accounting for *ca.* 15% of all volatile materials) appeared in glpc traces of rearranging V, while I showed only a much slower conversion to the single substance III (*cf.* experiments 8, 9, and 10 of Table II and Table IV). Although the minor products in these rearrangements of V were too small to be isolated and positively identified, it is significant that the retention times of the dominant ones corresponded to those of X, I, and IV, suggesting that V was slowly isomerizing to its geometric isomer VI (giving rise to X), as well as to its structural isomers, I and IV, while pursuing its main

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[15] D. J. Patel, M. E. H. Howden, and J. D. Roberts, *J. Amer. Chem. Soc.*, **85**, 3218 (1963).

[16] R. M. Roberts, R. G. Landolt, R. N. Greene, and E. W. Heyer, *ibid.*, **89**, 1404 (1967).

[17] It is noteworthy that when the inlet system of the mass spectrometer is maintained at 250°, the high ionizing voltage spectral fragmentation patterns of VI and X are identical, a fact which implies that the rearrangement of VI to X occurs in the inlet system at 10^{-6} mm and supports the intramolecular nature of the rearrangement.

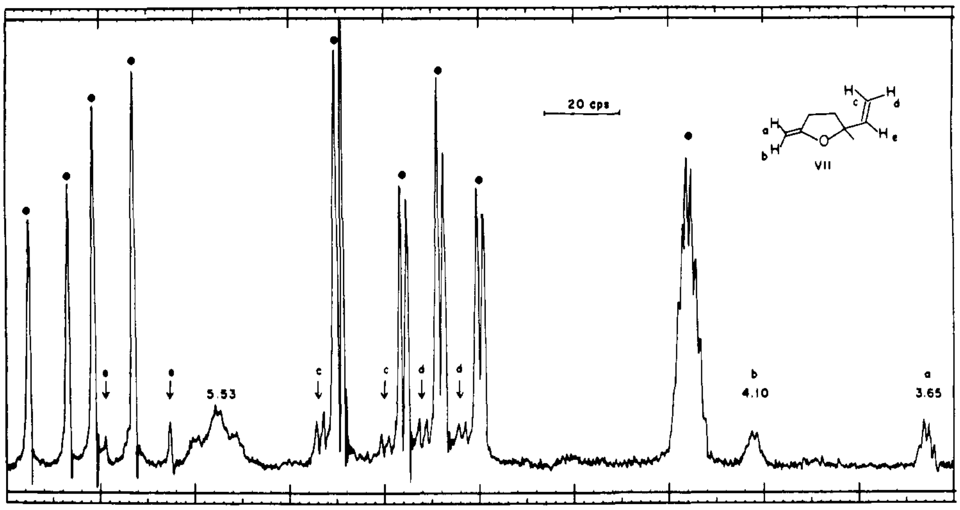

Figure 1. Vinyl region of 100-MHz nmr spectrum of I in cyclohexane showing the presence of VII.

rearrangement course to III. Support for this interpretation is found in the thermal behavior of V at higher temperatures (see below).

Demonstration of the Intermediacy of VII in the Rearrangement of I. With the elimination of V as an intermediate in the rearrangement of I to III, the possibility of endo-exo isomerization and Claisen rearrangement of VII (pathway B) remained for consideration. The marked effect of the soft glass surface in retarding the otherwise facile conversion of I to III suggested that active sites in Pyrex glass were probably responsible for the funneling of I to its exo isomer and then to III. In order to test this hypothesis, soft glass tubing was coated with sodium hydroxide to provide a uniform, basic surface. In such reaction tubes, the rearrangement of I could be completely arrested and the intermediacy of the exo methylene isomer demonstrated as described below. It is noteworthy that heating of V in such reaction tubes resulted only in extensive polymerization—another indication of the lack of involvement of that species in the rearrangement of I to III.

The earlier observation that rearrangement of samples of I in soft glass showed a marked drop-off in rate after about 6–8% reaction seemed to imply that an equilibrium mixture of I and VII preexisted in samples of I and that the initial, rapid rearrangement was simply that of the equilibrated VII. Careful nmr analysis of samples of "pure" I did indeed reveal the presence of "impurity" signals which corresponded very well to those expected for the exo methylene protons and the vinyl side-chain protons of VII.[18] Figure 1 shows the vinyl region of interest in the high-gain 100-MHz spectrum of a sample of I in cyclohexane. (This sample had been heated at 150° for short periods in a Pyrex tube to assure equilibration with the exo isomer VII and contained about 10% of the concurrently formed rearrangement product, III.) The signals marked with filled circles are those of the vinyl protons of I and the signal at $\delta = 5.53$ ppm is that of the vinyl proton of III. Of particular interest are the signals at δ 3.65 and 4.10 ppm, assigned to the two vinylic protons a and b, respectively, of the exocyclic double bond of VII. The four sets of doublets at δ 4.88, 4.99, 5.08, and 5.26 ppm are attributed to the terminal vinyl protons d and c and show a pattern paralleling that of the corresponding signals in I. The lines at δ 5.65 and 5.82 ppm represent two of the four lines expected for the vinyl proton e of VII; the other two are obscured by overlapping signals of I.[18]

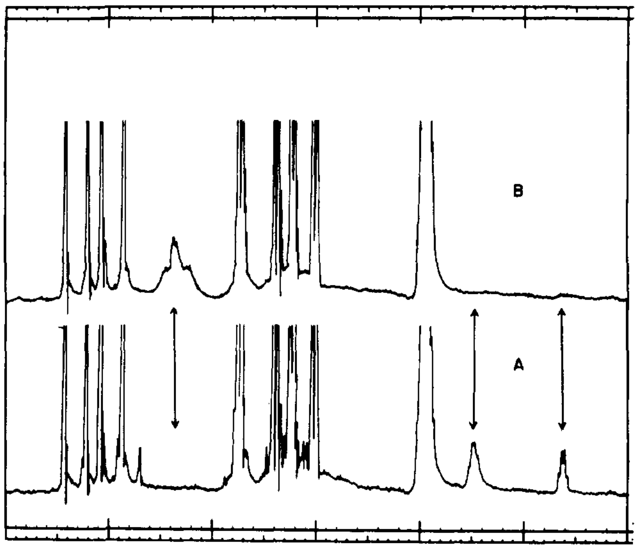

Figure 2. Vinyl region of nmr spectrum of I in sodium hydroxide coated tubes: A, before heating; B, after 3 days at 140°.

When samples of I containing the equilibrium amount of VII (~7%) were sealed neat in sodium hydroxide coated tubes and heated at 140°, the vinyl signals identified with VII had completely disappeared at the end of 72 hr and were matched by the appearance of the vinyl proton signal of III as shown in Figure 2. Continued heating of the samples at this temperature for 9 days produced no further change in

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[18] At the time of these experiments, a successful synthesis of VII had not been achieved. Therefore, it was necessary to "synthesize" a spectrum of VII by a combination of the pertinent signals in the spectra of I and 2-methylenetetrahydrofuran. In the latter, the protons of the exocyclic double bond corresponding to a and b of VII produce signals at 4.08 and 3.75 ppm, respectively. The assignments made on this basis are fully substantiated by the spectrum of pure VII, prepared by independent synthesis.[19]

[19] S. J. Rhoads and J. M. Watson, *J. Amer. Chem. Soc.*, **93**, 5813 (1971).

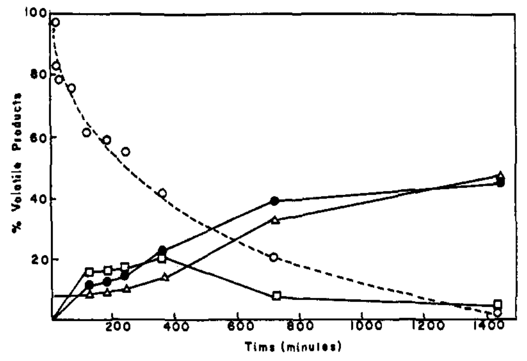
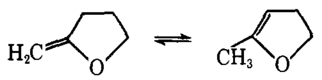


Figure 3. Isomerization of I in soft glass at 278°: ○, I; △, III; □, X; ●, IV.

this spectrum. In contrast, when the same experiment was performed in uncoated glass tubes, the signals of VII persisted with the same relative intensity to the signals of I throughout the rearrangement while the vinyl proton signal of III continued to grow. These experiments serve to confirm the hypothesis that I rearranges to III through the intermediacy of VII and that a preliminary endo–exo interconversion of I and VII is occurring at active, presumably acidic, sites on the glass surface.

The thermal interconversion of I and VII which formally involves a 1,3-hydrogen shift is forbidden as a concerted process on orbital symmetry grounds.[20] Such double bond isomerizations are very common in vinyl ethers, however, and are recognized to be extremely susceptible to trace amounts of acidic catalysts.[7] Recently, Salomaa and coworkers[12] carried out a quantitative investigation of the acid-catalyzed equilibration of 2-methylenetetrahydrofuran (XII) and 5-methyl-2,3-dihydrofuran (XIII) and reported an



XII XIII

equilibrium composition at 25° of 5.9% XII and 94.1% XIII. This value agrees well with the value of ~7% of VII in equilibrium with I deduced in this work and confirmed by the independent measurement reported in the accompanying paper.[19]

Thermal Behavior of I and V at 278°. Examination of the thermal behavior of both I and V at higher temperatures and lower pressures reveals some significant contrasts with the liquid-phase behavior of these substances in the lower temperature range. In these experiments, 5–7-μl samples of starting material were vapor transferred to soft glass tubes of *ca.* 1 ml volume, thoroughly degassed, and finally sealed under high vacuum. Such conditions should assure that the reactions observed were occurring largely in the gas phase at the reaction temperature of 278° (estimated pressure, 2–3 atm).

Under these conditions, the rearrangement of I proceeded to completion in 24 hr with a material balance of 60% of volatile products as judged by glpc analysis. In addition to III, two other major isomerization products were formed, the Claisen rearrangement product, IV, and the enolene rearrangement product, X. Besides the three major products, there were minor amounts (~0.1%) of two other components with glpc retention times corresponding to V and VI.

$$\underset{1.5\%}{\text{I}} \xrightarrow{278°,\ 24\ \text{hr}} \underset{47.5\%}{\text{IV}} + \underset{3.2\%}{\text{X}} + \underset{47.8\%}{\text{III}}$$

The complexity of this rearrangement process is illustrated by glpc monitoring of the volatile components of the reaction shown in Figure 3 and Table III. At the outset, the appearance of III is quite rapid, rising in the first few minutes to a level of *ca.* 8%, which then remains fairly constant over the next 200 min, a result which accords with the presence of about 8% of VII in the sample of I. In this same period, the production of IV and X proceeds at relative rates of about 1.5:1. Shortly thereafter, the concentration of III begins to build up again and the relative amounts of IV and X come closer together. We interpret these phenomena as manifestations of the onset of polymerization of X. The rapid buildup of III, coincident with extensive polymerization of X, may be attributed to the formation of water in the polymerization; the water, by etching the soft glass surface, may activate sites at which the isomerization of I to VII is accelerated. Under the same conditions, the rearrangement of V was 95% complete in 1 hr. The reaction mixture, in this case, consisted predominantly of the isomers I, IV, and X. The last, together with its precursor, VI, accounted for over 60% of the total volatile products. Formation of the cycloheptenone, III, is a relatively

$$\underset{5.1\%}{\text{V}} \xrightarrow{278°,\ 60\ \text{min}} \underset{17.1\%}{\text{I}} + \underset{15.1\%}{\text{IV}} + \underset{57.3\%}{\text{X}} + \underset{1.1\%}{\text{VI}} + \underset{4\%}{\text{III}}$$

minor process (4%) under these conditions. Continued heating of the reaction mixture at this temperature, however, produced a composition similar to that obtained from I after 24 hr. At the end of 7.5 hr, for example, the product composition was 61% IV, 36% III, and a small residue of unpolymerized X. Independent experiments indicated that the end products, IV and III, are stable toward these experimental conditions. The enolene rearrangement product, X, however, undergoes rapid and irreversible polymerization under these conditions.

The results of these high-temperature experiments are notable in two respects. First, under conditions at which the endo–exo isomerization is inactive (or at least strongly inhibited), the rearrangement of the cyclopropane isomer, V, is appreciably *faster* than that of the dihydrofuran isomer, I, in contrast to the reverse order of reactivity observed in the liquid phase at lower temperatures in Pyrex glass. This order of reactivity is more in accord with chemical intuition as well as results obtained recently in our laboratories for the related systems, 2-vinyl-2,3-dihydrofuran (XIV) and *cis*-2-vinylcyclopropanecarboxaldehyde (XV), in which the complicating endo–exo isomerization possibility has been eliminated. The relative rates of rearrangement of XIV and XV are *ca.* 1:4.[21] Secondly, the product distribution found in the rearrangement of V

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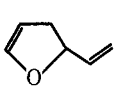
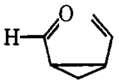
[20] R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, GmbH, Weinheim/Bergstr., 1970, p 114.

[21] Unpublished experiments, R. D. Cockroft, Ph.D. Dissertation, University of Wyoming, 1969.



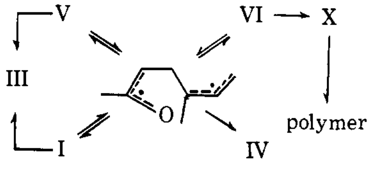
XIV



XV

suggests that geometric isomerization of V to VI and subsequent diversion of VI to X is at least three times as fast as structural isomerization to the dihydrofuran, I. This fact bears upon the question of the pathway for the conversion of V to III in the lower temperature, liquid-phase reactions and appears to rule out the possibility that V gives rise to III in good yield by funneling through the sequence V → I → VII → III. If that were indeed the case, considerably more diversion of V to X would have been observed. We conclude that V rearranges to III quite independently of I under the conditions cited and are left with the explanation of enolization of V followed by a Cope rearrangement of the *cis*-divinylcyclopropane system (pathway A of the original scheme). Enolization of V poses the same problem as the endo–exo isomerization of I in that it, too, involves a 1,3-hydrogen migration and cannot be a concerted, thermal process. The simplest explanation appears to be that enolization of V, like the interconversion of I and VII, is a surface phenomenon.

The mechanistic picture which emerges from the experiments described is one involving a bisallylic diradical intermediate (or intermediates[22]) which, through appropriate rotameric versions, may first partition among the various valence isomers I, V, VI, and IV. Diversion of VI by an enolene rearrangement to X and of I and V by wall reactions to III complicate and obscure this basic system.



Experimental Section

Infrared spectra were obtained as thin films with either a Beckman IR-1000 or a Perkin-Elmer Model 621 spectrophotometer. Ultraviolet spectra were measured with a Beckman DB spectrophotometer in matched 1-cm silica cells at 25°. A modified Consolidated Electrodynamics Corporation Model 21-103 C instrument was employed for the mass spectra. Nmr spectra were obtained with either a Varian A-60 or HA-100 instrument. Elemental analyses were performed by the Galbraith Laboratories, Inc., Knoxville, Tenn.

Glpc Analyses and Preparative Separations. Analyses of reaction mixtures were carried out with a variety of column materials in an Aerograph A-90P instrument equipped with a Model 328 temperature controller. The carrier gas was helium in all cases. Descriptions of the analytical columns follow: A, 30 ft × $^3/_8$ in. 15% SE-30 on 60–80 mesh Gas-Chrom P; B, 30 ft × $^3/_8$ in. 15% Carbowax 20M on 60–80 mesh Gas-Chrom P; C, 30 ft × $^3/_8$ in. 15% Reoplex 400 on 60–80 mesh Gas Chrom P; D, 8 ft × $^1/_4$ in. 25% SE-52 on 60–80 mesh Gas Chrom P; E, 25 ft × $^1/_4$ in. 15% Triton X-305 on 60–80 mesh Gas Chrom P. Larger scale preparative separations were carried out with a Nester/Faust Model 850 Prepkromatic instrument equipped with a Model 855 peak selector computer. In these separations, the column consisted of 3-ft sections of Nester/Faust $^3/_4$ in. BiWall column connected in series: column P-A, 6 ft of 25% SE-30 on 60–80 mesh Chromosorb W, 3 ft of 6% SE-30 on 60–80 mesh Gas-Chrom P, and 3 ft of 25% Reoplex 400 on Chromosorb W.

Reaction of Vinylmagnesium Bromide with 2,5-Hexanedione. Preparation of the Grignard reagent was carried out in a three-necked, 5-l. flask with a bottom outlet tube lightly packed with glass wool to act as a filter. The flask was equipped with a Tru-Bore stirrer, a Dry Ice cooled condenser, a pressure equalizing dropping funnel, and a dry nitrogen bleed vented through a mercury bubbler. To the flask was added 43.5 g (1.78 mol) of hot magnesium turnings, 50 mg of iodine, 50 ml of tetrahydrofuran (dried and distilled from lithium aluminum hydride), and 25 ml of anhydrous, purified vinyl bromide (Aldrich). The formation of the Grignard reagent commenced immediately. Addition of the remaining vinyl bromide as a 25% solution in tetrahydrofuran was regulated to maintain a gentle reflux of the flask contents. A total of 1.81 mol of vinyl bromide was added in this manner and the final solution was diluted to a volume of 1500 ml with tetrahydrofuran. The resulting solution of vinylmagnesium bromide was transferred under nitrogen pressure through the outlet tube to a solution of 250 g (2.20 mol) of redistilled Eastman 2,5-hexanedione in 1250 ml of tetrahydrofuran over a 2-hr period during which time vigorous magnetic stirring was maintained. The reaction product was hydrolyzed with 260 ml of saturated ammonium chloride solution and the supernatant solution was decanted from the solid salts. The solid was washed well with ether and the combined ether washes and tetrahydrofuran solution were dried ($MgSO_4$). Removal of the solvents left 276 g of crude product. Glpc analysis (column A, 130°) of this mixture showed the volatile components to be 31% I (formed by cyclodehydration of II in the injector block), 27% II, 31% unreacted 2,5-hexanedione, and 11% of the diaddition product, 3,6-dimethylocta-1,7-diene-3,6-diol. Samples of these components were trapped (column A, 130°) for spectral identification.

5-Methyl-5-hydroxy-6-hepten-2-one (II). Purified by glpc trapping (column B, 180°), II showed the following properties: ir 3450 (s), 3090, 1710 (s), 1640, 990 (s), 910 cm^{-1} (s); uv max (ethanol) 270 nm (ϵ 95); max (cyclohexane) 264 nm (ϵ 88); nmr ($CDCl_3$) δ 5.90 (1, d of d, $\mathrm{H{-}\overset{|}{C}{=}C{<}}$), 5.4–5.8 (2, m, $\mathrm{{-}\overset{|}{C}{=}CH_2}$), 3.19 (1, br s, OH), 2.52 (2, m, $\mathrm{{-}CH_2{-}\overset{|}{C}{=}O}$), 2.12 (3, s, $\mathrm{CH_3\overset{|}{C}{=}O}$), 1.75 (2, m, $-CH_2C{<}OH$), 1.25 ppm (3, s, $CH_3C{<}OH$).

3,5-Dimethylocta-1,7-diene-3,6-diol. Identification of the minor component of the Grignard reaction was made by spectral analysis of the glpc-trapped sample: ir 3420 (vs), 1625, 1100, 1000, 920 cm^{-1}; nmr (CCl_4) δ 5.88 (2, d of d, $\mathrm{{>}C{=}\overset{|}{C}{-}H}$), 5.4–4.8 (4, m, $>C{=}CH_2$), 3.88 (2, br s, OH), 1.53 (4, s, $-CH_2CH_2-$), 1.23 ppm (6, s, $-CH_3$).

2,5-Dimethyl-2-vinyl-2,3-dihydrofuran (I). The crude Grignard reaction mixture was simply distilled at 20 mm and the heterogeneous distillate boiling up to 56° was collected in a receiver cooled with Dry Ice (reversion of I to II occurs very rapidly if the distillate is allowed to collect without this precaution). By alternate thawing and freezing, the organic layer was cleanly separated and could be decanted from the water formed in the thermal cyclodehydration of II. Redistillation of the dried ($CaSO_4$) organic layer afforded 49 g (22%) of I, bp 65–68° (100 mm). Further purification was accomplished by careful fractional distillation in a Nester/Faust annular still: ir 3095, 3015, 1677 (s), 1641, 1271, 990, 920 cm^{-1}; uv max (cyclohexane) 208 nm (ϵ 2880); mass spectrum (7 eV), *m/e* 124 (M^+); nmr see Table I.

Anal. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74. Found: C, 77.12; H, 10.06.

4-Methyl-4-cycloheptenone (III). The rearrangement of I at 150–200°, conducted on neat samples or in decane solution, at atmospheric pressure or in sealed tubes, produced only III in better than 95% conversion, judged by glpc analysis (column A at 150°, column D at 150°, column E at 175°) of samples containing a decane internal standard. The thermal stability of III was tested by heating a sample sealed in an evacuated tube for 30 hr at 175°; comparison with an unheated sample showed that no diversion of the starting material had occurred. Samples of III were purified by trapping (column G, 175°) for spectral analysis and structure determination: ir 3020, 1705 (vs), 1670, 865, 810 745 cm^{-1}; uv max (cyclohexane) 282 nm (ϵ 22); max (ethanol) 280 nm (ϵ 27); mass spectrum (70 eV) *m/e* 124 (M^+); nmr see Table I.

Anal. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74. Found: C, 77.43; H, 10.10.

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[22] It is quite possible that the cyclopropane isomers V and VI give rise to a diradical intermediate that differs in subtle ways from the diradical generated by C–O bond cleavage of I and is separated from it by a small but significant energy barrier. In that event, partitioning to the isomeric products from these diradicals might be slightly different. In the system studied here, the complicating side reactions make testing of this point appear hopeless.

Table II. Thermal Behavior of I and V in the Temperature Range 140–200°

Expt	Rearrangement process	*T*, °C	Time, hr	% rearrangement	% material balance	Conditions
1	I → III	159	18	64	*a*	Pyrex tubes, neat
			26	73		
2	V → III	159	18	35	*a*	Pyrex tubes, neat
			26	45		
3	I → III	195	16.5	80	*a*	Pyrex tubes, neat
4	V → III	195	16.5	57	*a*	Pyrex tubes, neat
5	I → III	167	20	78	99	Pyrex tubes
			30	90	98	$C_{10}H_{22}$:I::1:2
6	I → III	167	20	47	60	Base-washed Pyrex tubes $C_{10}H_{22}$:I::1:2
7	V → III	167	20	26	60	Base-washed Pyrex tubes $C_{10}H_{22}$:V::1:2
8	I → III	140	16	7	87	Soft glass tubes $C_{12}H_{26}$:I::1:30
9	I → III	180	5	6.6	99	Unwashed soft glass tubes
			20	7.0	97	$C_{10}H_{22}$:I::1:1
10	V → III	180	5	11	88	Unwashed soft glass tubes
			20	47	65	$C_{10}H_{22}$:V::1:1

[a] Not determined.

4-Methyl-4-cycloheptenone-*d*$_4$ (III-*d*$_4$). Prepared by base-catalyzed exchange,[23] III-*d*$_4$ was isolated in pure form by glpc trapping (column C, 165°). Nmr analysis of this sample in benzene revealed signals at δ 5.26 (1, m, H—$\overset{|}{C}$=C<), 1.90 (4, unresolved envelope, allylic CH_2's), and 1.47 (3, br s, CH_3). The envelope of signals at 2.26 ppm (CH_2's α to —$\overset{|}{C}$=O) present in nondeuterated III was barely detectable in this sample.

Hydrogenation of III. The reduction of 183.4 mg of III over Adams catalyst in ethanol was interrupted after the absorption of 1 equiv of hydrogen and the reduced product was isolated and separated from minor impurities by glpc trapping (column C, 165°). The purified material was identical (glpc retention times and infrared and nmr spectra) with a sample of 4-methylcycloheptanone prepared by the method of Djerassi.[8]

Reaction of Diazoacetone with Isoprene. Diazoacetone, prepared in the usual way,[24] from 0.085 mol of acetyl chloride and 0.189 mol of diazomethane[25] was added dropwise to a mixture of 15 ml of freshly distilled isoprene, 10 ml of cyclohexane, and 0.75 g of anhydrous copper sulfate over a period of 2 hr. Duing this time the diazoacetone was protected from the atmosphere by a layer of cyclohexane. The reaction mixture, filtered free of catalyst and some polymeric material, was distilled. After a forerun of isoprene and cyclohexane, 2 g of colorless material could be distilled away from a black, polymeric residue at a bath temperature of 90° and a pressure of 0.5 mm. Glpc analysis (column C, 145°) of the distillate revealed four major components, eluting in the order VI, V, VIII, and IX and with relative abundances 3:5:3.5:1. Each of the components was trapped in sufficient quantity for spectral analysis and examination of its thermal behavior.

(*cis*-1-Acetyl-2-vinyl)-2-methylcyclopropane (V). The most abundant of the four isomers, V, showed the following properties: ir 3100, 3050, 1700 (s), 1640, 990 (s), 900 (s) cm^{-1}; mass spectrum (7 eV) *m/e* 124 (M$^+$); nmr see Table I.

(*trans*-1-Acetyl-2-vinyl)-2-methylcyclopropane (VI) showed the following properties: ir, identical with that of V except for minor differences in the fine structure; mass spectrum (7 eV) *m/e* 124 (M$^+$); nmr see Table I. When heated in a sealed tube for 5 hr at 125° VI completely rearranged to X and polymeric material.

***cis*-1-Acetyl-2-isopropenylcyclopropane (VIII)** showed the following properties: ir 3090 3020, 1700 (s), 1650, 880 (s) cm^{-1}; mass spectrum (7 eV) *m/e* 124 (M$^+$); nmr, see Table I. When heated in a sealed tube at 175° for 24 hr, VIII rearranged almost completely to III.

***trans*-1-Acetyl-2-isopropenylcyclopropane (IX)** showed the following properties: ir identical with that of VIII except for minor differences in fine structure; mass spectrum (7 eV) *m/e* 124 (M$^+$); nmr, see Table I. When heated 30 hr at 215° in a sealed tube, IX showed no evidence of rearrangement or decomposition (glpc analysis).

Photoisomerization of I. A 10% (vol) solution of I in pentane was irradiated in a quartz tube 72 hr within a circular bank of 16 mercury resonance lamps (254 nm). At the end of this time, the reaction mixture (analyzed by glpc, column A, 150°) consisted mainly of V and VI, together with small amounts of I and IV. The solvent-free mixture of isomers was heated at 150° for 5 hr to induce the enolene rearrangement of VI. Distillation of the heated mixture afforded a colorless distillate, bp 45–75° (25 mm), which was separated into its components by preparative glpc (column P-A, 150°).

1-Methyl-4-acetylcyclopentene (IV). Glpc purified IV, isolated from the photoreaction of I, showed the following properties: ir 3040, 1705 (s), 1655, 785 cm^{-1}; mass spectrum (7 eV) *m/e* 124 (M$^+$); nmr, see Table I. The thermal stability of IV was established by the fact that it survived unchanged after heating in a sealed tube for 16 hr at 278°.

5-Methylene-6-hepten-2-one (X). Isolated by glpc trapping (column A, 130°) from the rearrangement of VI, X showed the following properties: ir 3100, 3020–2900, 1720 (s), 1640, 1600, 990, 900 cm^{-1}; mass spectrum (7 eV) *m/e* 124 (M$^+$); nmr, see Table I. The nmr spectrum of isoprene in carbon tetrachloride shows a pattern in the vinylic region practically identical with that of X, *i.e.*, a d of d's (J_c = 5, J_t = 9 Hz) at δ 6.30 ppm due to the nonterminal vinyl hydrogen and a complex of signals at δ 5.15–4.90 ppm due to the four terminal hydrogens. X was also identified as a minor component of the dehydration of II when it was subjected to glpc analysis (column A, at 130° and higher). When X was heated in the presence of a dodecane marker in soft glass tubes at 278° it gave evidence of rapid diversion to nonvolatile polymers. At the end of 90 min at this temperature, the polymerization to nonvolatiles was *ca.* 70% complete.

Isomerization Studies. Samples of I were purified for isomerization studies by repeated glpc trapping, drying over lithium aluminum hydride, and a final vapor transfer from that reagent. Samples of V were subjected to repeated glpc trapping, dried over barium oxide, and finally vapor transferred to reaction tubes. Prior to sealing, the samples were degassed by alternate freezing and thawing under the vacuum of an oil diffusion pump. Decane or dodecane was included as a solvent and/or internal standard in most cases.

Reaction tubes were fashioned from capillary Pyrex tubing (2 mm bore) or from soft glass tubing (5 mm o.d.). In the latter case, the tubes were made with a finely constricted neck and were carefully annealed. Before use, the reaction tubes were cleaned in various ways: (a) Pyrex tubes were cleaned with acid dichromate solution, rinsed with distilled water, soaked in dilute ammonia solution overnight, rinsed again with distilled water, and flame-dried; (b) "base-washed" Pyrex tubes were washed with dilute sodium hydroxide solution, rinsed with distilled water, and flame-dried; (c) soft glass tubes were rinsed with distilled water and oven-dried. In some cases, soft glass was used as it came from stock (unwashed

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(23) A. Murray and D. L. Williams, "Organic Syntheses with Isotopes," Part II, Interscience Publishers, New York, N. Y., 1958, p 1511.

(24) W. E. Bachmann and W. S. Struve, *Org. React.*, **1**, 47 (1962).

(25) A. Moore and D. E. Reed, *Org. Syn.*, **41**, 16 (1961).

Table III. Isomerization of I in Soft Glass at 278°

	% volatile components					
Time, hr	I	X	IV	III	$C_{12}H_{26}$ (internal std)	V + VI[a]
0.0	96.7	0.0	0.0	0.0	3.3	0.0
0.25	83.8	2.5	1.7	7.7	3.6	0.6
0.50	79.2	5.3	3.5	8.1	3.2	0.7
1.0	76.7	6.9	4.7	8.0	3.0	0.6
2.0	61.6	14.7	10.4	9.8	3.0	0.5
3.0	59.7	15.2	11.5	10.3	3.1	0.5
4.0	54.7	16.1	15.1	10.4	3.1	0.4
6.0	40.3	19.4	22.4	14.0	3.5	0.4
12.0	19.9	6.8	37.5	32.0	3.6	0.2
24.0	1.4	3.0	45.0	45.1	5.4	0.1

[a] Identified by retention times only.

soft glass). Sodium hydroxide coated tubes were prepared by filling soft glass tubes with a 1% solution of base up to the constriction, withdrawing the excess solution with a syringe, and baking the wet tubes at 150° for 48 hr.

Isomerizations in the temperature range 140–200° were carried out on samples ranging in size from 30 to 50 μl. The isomerizations at 278° were conducted in soft glass tubes of about 1 ml volume and the sample size was reduced to 5–7 μl. Temperature control in the lower range was provided by a silicon oil bath equipped with an immersion heater and a temperature controller which maintained a desired temperature within ±0.1°. The higher temperature isomerizations were carried out in the air furnace of an Aerograph 90-P gas chromatograph equipped with a temperature controller.

Table IV. Isomerization of V in Soft Glass at 140 and 278°

Time, hr	V	I	X	IV	III	VI	% material balance
			T = 140°				
0.0	100	0	0	0	0	0	100
1.0	87	0	8.3[a]	3.5[a]	1.2	0	98
17.6	49.7	0.7[a]	10.7[a]	5.4[a]	34.1	0	80
			T = 278°				
1.0	5.1	17.1	57.3	15.1	4.0	1.1[a]	b
7.5	Trace	Trace	2.5	61.0	36.5	0	b

[a] Identified by retention times only. [b] Not determined.

Analyses of isomerization mixtures were performed on column D at 150°; integrations were made with either a Perkin-Elmer D-2 integrator or a Nester/Faust summatic integrator. The analytical method was tested with synthetic mixtures of the reaction components and showed a much higher reproducibility than that observed in the isomerization experiments themselves. Representative data showing the isomerization results are reproduced in Tables II, III, and IV.

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The Claisen Rearrangement of 2-Methyl-2-vinyl-5-methylenetetrahydrofuran[1]

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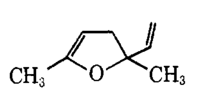
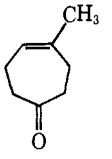
Abstract: 2-Methyl-2-vinyl-5-(bromomethyl)tetrahydrofuran, prepared by brominative cyclization of 3-methylhepta-1,6-dien-3-ol with *N*-bromosuccinimide, undergoes base-catalyzed dehydrohalogenation to form 2-methyl-2-vinyl-5-methylenetetrahydrofuran (III). The Claisen rearrangement of III to 4-methyl-4-cycloheptenone (II), studied over the temperature range 155–185°, is a first-order process with $k_{170°} = 4.13 \times 10^{-5}\ \text{sec}^{-1}$, $\Delta H^{\ddagger} = 32.7$ kcal/mol, and $\Delta S^{\ddagger} = -5.6$ eu. In the absence of basic inhibitors, III rapidly interconverts with 2,5-dimethyl-2-vinyl-2,3-dihydrofuran (I) to give an equilibrium mixture consisting of 6.6% III and 93.4% I at ambient temperatures.

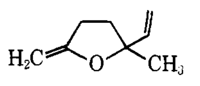
In the preceding paper,[2] the responsible intermediate species in the rearrangement of 2,5-dimethyl-2-vinyl-2,3-dihydrofuran (I) to 4-methyl-4-cycloheptenone (II) was identified as 2-methyl-2-vinyl-5-methylenetetrahydrofuran (III). With this finding, the synthesis and direct study of III became a major objective. In this paper, we report the successful synthesis of the tetrahydrofuran derivative and a kinetic study of its thermal rearrangement to II.



I



II



III

Results

After several unsuccessful synthetic approaches, III was prepared in an amazingly simple series of reactions (Scheme I). This method was brought to our attention by recent work of Demole and Enggist[3] who applied

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(2) S. J. Rhoads and C. F. Brandenburg, *J. Amer. Chem. Soc.*, **93**, 5805 (1971).

(3) E. Demole and P. Enggist, *Chem. Commun.*, 264 (1969).