were assigned using a series of free-radical polymers which are known to follow Bernoullian statistics and are therefore predicable.[16,39,51] The consistency relationships between the peak intensities were checked[39] and found to hold. The tetrad ratios were used to calculate the triad ratios in poly(ethyl *cis*-β-d_1-methacrylate).[39] Because the tetrad chemical shift differences were small in the deuterated poly(isopropyl acrylate), it was not possible to calculate tetrad–triad relationships. The reported ratio of *threo–meso* to *meso* has been corrected for the 10% undeuterated monomer in the two methacrylate ester polymer.

(51) These assignments have been confirmed using a Varian HA-100 and computed average transients on a DP-60 on model compounds. The assignments plus a statistical evaluation of the data to verify the foregoing mechanism will be reported.

Acknowledgment. The authors gratefully acknowledge the interest and assistance of T. E. Hogen-Esch, J. Smid, and M. Szwarc in the use of special techniques devised and used previously by them in similar systems.

Enolene Rearrangements. Relationship to the "Abnormal Claisen Rearrangement" and Other 1,5-Hydrogen Shift Processes[1]

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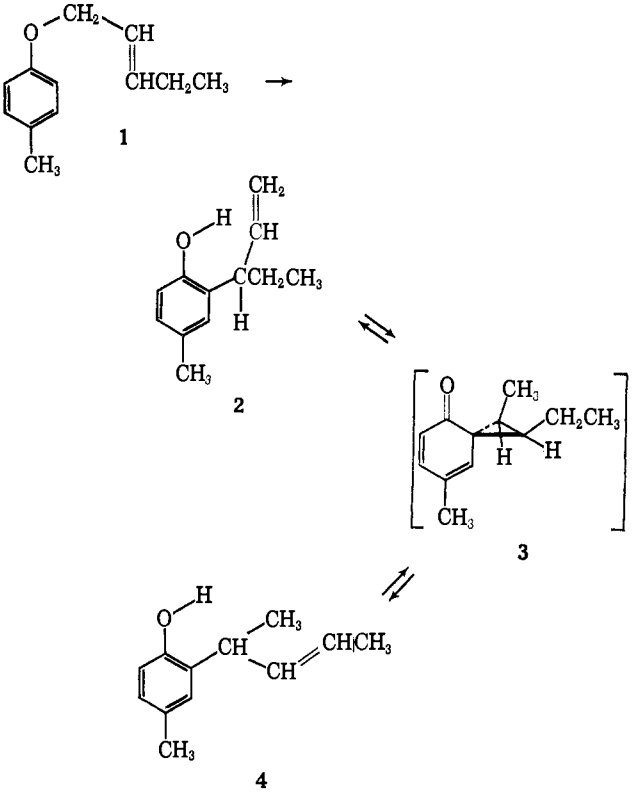
Abstract: Acylalkylcyclopropanes have been shown to undergo clean, facile ring opening upon heating, to produce homoallylic ketones when the acyl and alkyl groups are *cis* (1-acetyl-2,2-dimethylcyclopropane, *cis*-1-acetyl-2-methylcyclopropane), but not when they are *trans* (*trans*-1-acetyl-2-methylcyclopropane). First-order rate constants and the heat of activation of the rearrangement of 1-acetyl-2,2-dimethylcyclopropane to 5-methyl-5-hexen-2-one have been determined. The ring opening and the concerted 1,5-hydrogen shift have been demonstrated to be reversible by following intramolecular deuterium transfers in three homoallylic ketones, 4-pentenophenone, 3-methyl-4-pentenophenone, and 4-methyl-4-pentenophenone, by means of nmr spectroscopy. The lack of deuterium incorporation into the 4-methyl group of the last compound confirmed the intramolecular nature of the transfer of hydrogen to the terminal methylene groups of all three homoallylic ketones. The mechanism of these rearrangements *via* "enolene" intermediates represents an aliphatic analog of the rearrangement of allylic phenols responsible for the "abnormal Claisen rearrangement." The scope of enolene rearrangements and their relationship to other thermal intramolecular rearrangements are discussed.

The "abnormal Claisen rearrangement"[3] has now been clearly identified as the result of two consecutive processes: normal *ortho* Claisen rearrangement of a γ-alkylallyl aryl ether (*e.g.*, **1**) to an *o*-(α-alkylallyl)-phenol (*e.g.*, **2**), followed by rearrangement of the side chain of this phenol to produce an isomeric phenol **4**.[4] The mechanism of the secondary rearrangement was formulated as involving a substituted spiro[2.5]-octa-4,6-dien-3-one intermediate **3**;[4] recent work has provided strong support for this mechanism.[5,6]

In the present paper we demonstrate that this mechanism is not restricted to allylic phenols but that this



(1) Preliminary descriptions of this research were given by (a) R. M. Roberts and R. G. Landolt, *J. Am. Chem. Soc.*, 87, 2281 (1965); (b) R. M. Roberts, R. N. Greene, R. G. Landolt, and E. W. Heyer, *ibid.*, 87, 2282 (1965); (c) R. M. Roberts and R. G. Landolt, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965, Abstracts, p 56S. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society; to the Robert A. Welch Foundation; to the National Science Foundation; and to The University of Texas Research Institute for support of this research.

(2) University of Texas Fellow, 1964–1965.

(3) (a) W. M. Lauer and W. F. Filbert, *J. Am. Chem. Soc.*, 58, 1388 (1936); (b) W. M. Lauer, G. A. Doldouras, R. E. Hileman, and R. Liepins, *J. Org. Chem.*, 26, 4785 (1961); (c) A. Habich, R. Barner, W. von Philipsborn, and H. Schmid, *Helv. Chim. Acta*, 45, 1943 (1962).

(4) E. N. Marvell, D. R. Anderson, and J. Ong, *J. Org. Chem.*, 27, 1109 (1962).

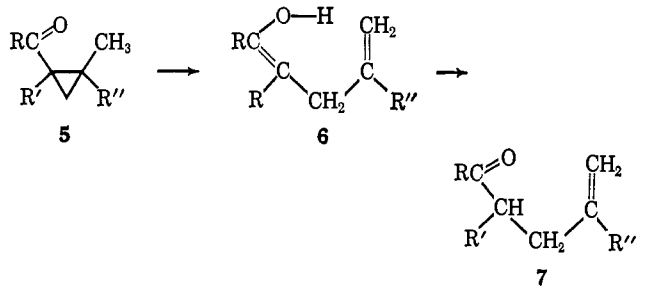
(5) W. M. Lauer and T. A. Johnson, *ibid.*, 28, 2913 (1963).

(6) A. Habich, R. Barner, W. von Philipsborn, and H. Schmid, *Helv. Chim. Acta*, 48, 1297 (1965).

phase of the "abnormal Claisen rearrangement" is only one example of a general thermal molecular reorganization process.

Discussion of Results

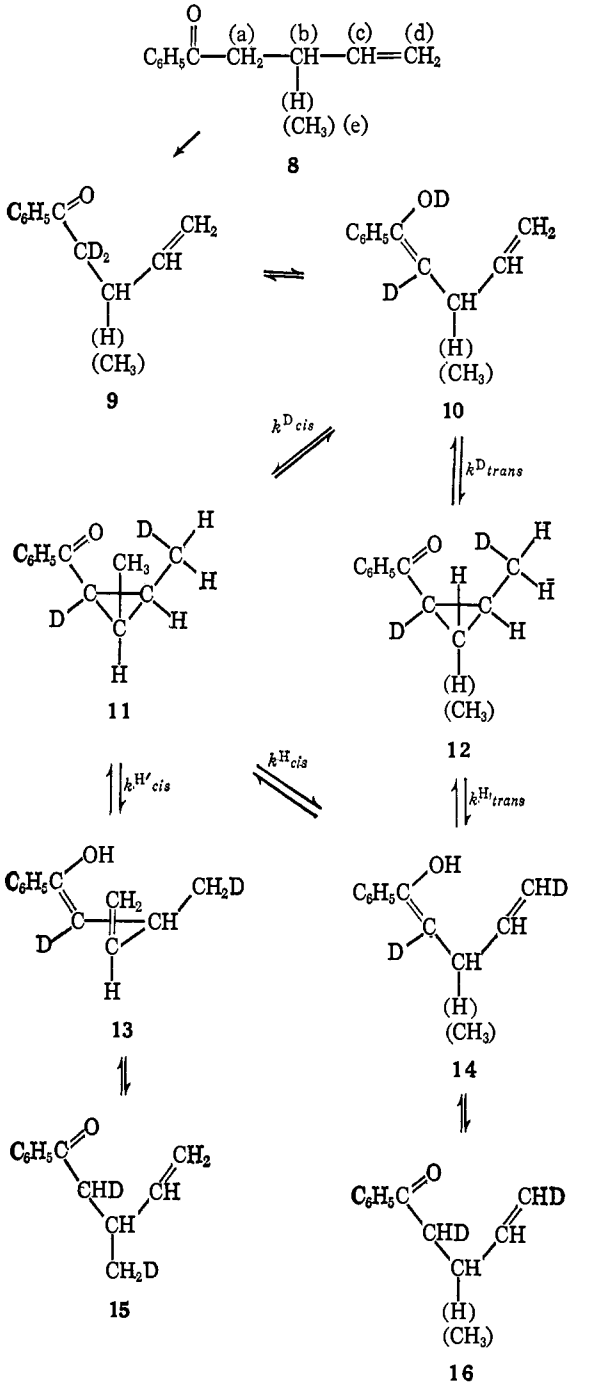
Ring Opening of Acylalkylcyclopropanes. The mechanism of the rearrangement of **2** to **4** is fundamentally a 1,5-hydrogen shift[7] concerted with the closing and opening of a cyclopropane ring. As the first step in ascertaining whether this kind of rearrangement is restricted to allylic phenols or may also extend to enols of aliphatic carbonyl compounds, we examined the thermal stability of one of the simplest types of molecules capable of undergoing an analogous reaction, an acylalkylcyclopropane **5**. In order to avoid geometrical problems, 1-acetyl-2,2-dimethylcyclopropane (**5**, R = R'' = CH_3, R' = H) was first synthesized; *i.e.*, the structure of this molecule is such that one of the methyl



groups must be *cis* to the carbonyl group and thus in a favorable position for the intramolecular 1,5-hydrogen shift. This compound was found to rearrange cleanly to 5-methyl-5-hexen-2-one (**7**, R = R'' = CH_3, R' = H) at temperatures above 150°. The reaction exhibited first-order kinetics with rate constants of 4.00×10^{-5} sec^{-1} at 152° and 9.83×10^{-5} sec^{-1} at 163°; the heat of activation was 30 kcal/mole,[9] and the entropy of activation was −10 eu.

The *cis* and *trans* isomers of 1-acetyl-2-methylcyclopropane (**5**, R = CH_3, R' = R'' = H) were next prepared and heated separately at 160° for 12 hr. The *cis* isomer was converted completely into 5-hexen-2-one (**5**, R = CH_3, R' = R'' = H), while the *trans* isomer was unchanged, confirming the requirement of a *cis* relationship between the carbonyl and methyl groups for the ring opening and the concerted 1,5-hydrogen shift.

1,5-Hydrogen Shifts in Enolenes[10] *via* Cyclopropane Intermediates. In order to demonstrate the reversibility of this ring opening, we chose a modification of the elegant deuterium tracer technique used by Schmid and co-workers[6] for the allylic phenols. 4-Pentenophenone [**8**(H)] is ideally suited for this study because of the clean separation of the nmr absorptions of its hydrogens. It was deuterated by base-catalyzed exchange with D_2O to yield 4-pentenophenone-2-*d*- [**9**(H)], with an nmr spectrum identical with that of **8**(H) except for disappearance of the CH_2(a) triplet at δ 2.9 and replacement of the CH_2(b) multiplet at δ 2.4 by a doublet. Intramolecular hydrogen shifts according to the scheme shown for **9**(H) ⇄ **16**(H) could be followed by appearance of proton nmr absorption at δ 2.9 and decrease at 5.0 [CH_2(d)]. If equilibrium were to be reached, absorption in these regions should become equal. 4-Pentenophenone-2-d_2 [**9**(H)] was heated at 202 ± 2° for the times shown in Table I with the resultant changes in deuterium distributions shown there. After heating, the samples were found to have unchanged vpc retention times and infrared and mass spectra characteristic of deuterated 4-pentenophenone only.



A similar experiment was carried out with 3-methyl-4-pentenophenone-2-d_2 [**9**(CH_3)]. Intramolecular 1,5-

(7) It is interesting to note that, strictly speaking, the hydrogen shifts from oxygen to carbon in the steps **2** → **3** and **4** → **3** are 1,6 shifts; however, the reverse steps (**3** → **2** and **3** → **4**) are 1,5 shifts. On the basis of the principle of microscopic reversibility, it is reasonable to describe the mechanism in both directions as involving 1,5-hydrogen shifts. The reversibility of the rearrangement has been demonstrated; the equilibrium proportions of **2** and **4** are about 4:96.[8]

(8) R. M. Roberts and R. G. Landolt, *J. Org. Chem.*, **31**, 2699 (1966).

(9) The kinetic values reported previously[1] have been corrected by applying the method of least squares.

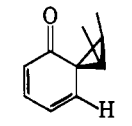
(10) This term is used to describe the enol forms of the γ,δ-unsaturated ketones (an *enol*, also an alk*ene*)—the forms conjugated to the cyclopropanes by the 1,5-hydrogen shift.

Table I. Deuterium Distributions in 4-Pentenophenone

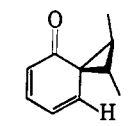
Time, hr	D, g-atom			
	CH_2(a)	CH_2(b)	CH(c)	CH_2(d)
17	1.73	0.00	0.00	0.20
41	1.37	0.00	0.00	0.56
72	1.23	0.00	0.00	0.74
145	0.97	0.00	0.00	0.90

hydrogen shifts in this molecule according to the scheme for **9**(CH_3) ⇄ **15** ⇄ **16**(CH_3) may be seen to correspond to the allylic phenol rearrangements demonstrated with deuterium labeling[6] and C^{14} labeling,[3b,c,5] and to be strictly analogous to those in which chemically different molecules are produced.[3a,4] The equilibrium distribution of the two deuterium atoms expected would be CH_2(a) 0.57, CH_2(d) 0.57, and CH_3(e) 0.86.

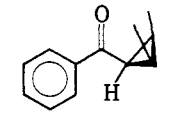
3-Methyl-4-pentenophenone-2-d_2 [**9**(CH_3)] was heated at 202 ± 2° for the times shown in Table II, with the resultant changes in deuterium distribution shown there. After heating, the samples were found to have unchanged vpc retention times and infrared and mass spectra characteristic of deuterated 3-methyl-4-pentenophenone only. It is clear that deuterium is transferred from the α-carbon methylene [CH_2(a)] exclusively to the terminal methylene group [CH_2(d)] and to the methyl group [CH_3(e)], and that the rate of incorporation of deuterium into CH_2(d) is much faster than into CH_3(e). These results are generally in accord with those in the aromatic system.[6] Although a quantitative comparison of our results with those of Schmid[6] cannot be made, owing to the difference in experimental conditions, it is interesting to note that there is apparently a greater difference in the rates of methylene-*d* and methyl-*d* incorporation in our aliphatic system than in the phenol system; *e.g.*, in our 48-hr experiment, with 59% migration of deuterium from the α carbon, $3n/2m$ = 1.82, while in the phenol system, with only 49% migration of deuterium, $3n/2m$ = 1.78.[11] A logical explanation of this finding can be given in terms of the relative potential energies of the geometric isomers of the acylcyclopropane intermediates in the two systems. In the phenol system there is not as much difference in the energies of the *cis* and *trans* isomers (**17c** and **17t**) as in the aliphatic system (**18c** and **18t**), because of the nonbonded interaction between the methyl group and the aromatic ring carbon in **17t**, which has no counterpart in the aliphatic system. Of course, there can be introduction of deuterium into a methyl group only when the cyclopropane ring closes in the higher energy *cis* forms **17c** and **18c**. Schmid[6] demonstrated clearly



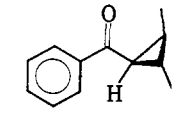
17c



17t



18c



18t

that a methyl group in the 3 position of the aromatic ring virtually precluded ring closure in the *trans* configuration, finding that $3n/2m$ = 1 for deuterium incorporation into the side chain of 2-α-methylallyl-3,5-dimethylphenol long before equilibrium was reached. Although much less effect is to be expected from *hydrogen* in the 3 position (as was found by Schmid), in the comparison of the unsubstituted phenol with our *aliphatic* compound (*i.e.*, **17t** *vs.* **18t**), the pertinent nonbonded oppositions of the methyl groups are those with the *3 carbon and its hydrogen* in **17t** and that with only hydrogen in **18t**.

A conformational factor may account for the slower rate of deuterium transfer from the α methylene of 4-pentenophenone-2-d_2 than in the case of 3-methyl-4-pentenophenone-2-d_2 (see Tables I and II). The methyl group of the latter compound probably serves to enhance the transfer of deuterium *via* ring closure by destabilizing the conformations in which the two ends of the molecules are far apart more than those in which they are near enough for concerted deuterium shift and ring closure, while in the former compound there is no such preferential factor.

Examination of the data from the thermolysis of **9**(H) brought to light one unsuspected process. Although the stereospecificity, the first-order kinetics, and the large negative entropy of activation characterized the ring-opening reaction as an intramolecular process, we found significant exchange of deuterium between molecules in the experiments with deuterated ketones. Mass spectral data indicated the presence of d_0, d_3, and d_4 molecules in the pyrolysis product of **9**(H) after 72 hr, whereas no d_3 or d_4 molecules were present

Table II. Deuterium Distributions in 3-Methyl-4-pentenophenone[a,b]

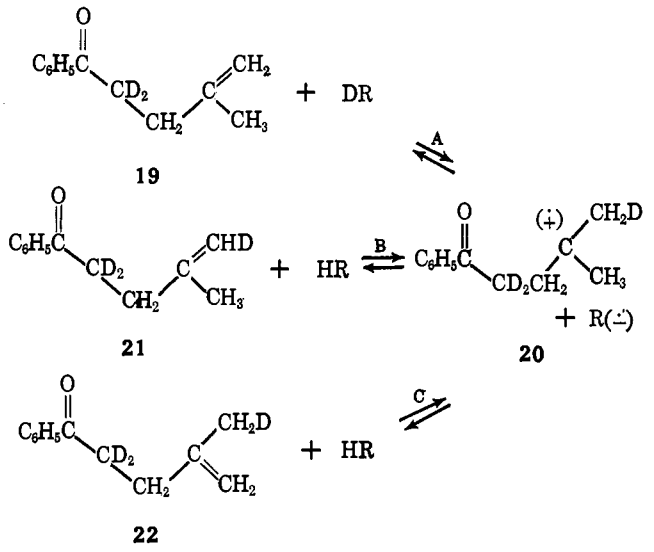
Time, hr	D, g-atom			
	CH_2(a)	CH(c)	CH_2(d)	CH_3(e)
12	1.27	0.00	0.60	0.12
48	0.83	0.00	0.63	0.52
121	0.58	0.00	0.63	0.66

[a] Since no D was found to migrate to the CH_2(b) in 4-pentenophenone, it was assumed that there was no migration to CH(b) in 3-methyl-4-pentenophenone; one H was subtracted from the integrated signal from the overlapping (a) and (b) multiplets to give the H integral for CH_2(a). [b] The numbers of D and H in various positions were calculated from nmr H integrals, using the aromatic hydrogens as internal standards. For simplicity, the values are corrected to those expected from starting material completely deuterated at the α carbon.

(11) (a) n = amount of D on the methylene carbon, m = amount of D on the methyl carbon. At equilibrium $3n/2m$ = 1; a large preequilibrium value of $3n/2m$ is indicative of more rapid incorporation of D into the methylene group than into the methyl group. (b) A referee pointed out that the experimental finding of no incorporation of deuterium into the methyl group of 4-methyl-4-pentenophenone does not necessarily "confirm the intramolecular character of hydrogen transfer," but only shows that the two groups attached to C-4 never become equivalent. This is indeed true in the strictest sense, since it is possible to conceive bimolecular mechanisms in which these two groups do not become equivalent. However, none of these alternatives is as plausible as the intramolecular mechanism. The demonstrated first-order kinetics and the entropy of activation of the ring opening reaction also speak against any significant contribution of an intermolecular mechanism to the 1,5-hydrogen shift. (c) Since a transfer of hydrogen from the α carbon to the oxygen of the ketone would be a 1,3 shift, it would not be expected to occur by a concerted thermal process [R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, 87, 2511 (1965)]. However, an intramolecular transfer of hydrogen from the oxygen of the enol form to the terminal methylene may be considered as a 1,5-sigmatropic shift in which the cyclopropane ring plays the part of a carbon–carbon double bond, and hence a concerted thermal process is to be expected.

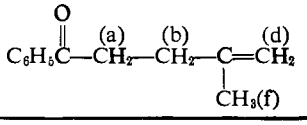
initially. A further experiment utilizing a 1:1 mixture of **9**(H) and **8**(CH_3) confirmed intermolecular hydrogen transfer. (Compound **8**(CH_3) was chosen as the undeuterated component in order to facilitate mass spectral analysis by virtue of its higher molecular weight.) After 17 hr at 202 ± 2°, 1.50 deuterons per molecule was incorporated into the 3-methyl-4-pentenophenone, while 0.30 deuteron remained in the 4-pentenophenone.

It thus remained to be demonstrated that hydrogen transfer to the terminal methylene in process **9** ⇄ **15** was indeed intramolecular. 4-Methyl-4-pentenophenone-2-d_2 (**19**) was selected as a reaction substrate, since deuterium transfer by either an ionic or radical intermolecular mechanism would render methyl and methylene carbons equivalent in **20**. The reverse process by path B would result in methylene deuterium incorporation into **21** and, by the chemically equivalent path C, deuterium would be incorporated into the methyl group of **22**.



4-Methyl-4-pentenophenone-2-d_2 was heated at 202 ± 2° and no detectable amount of deuterium was introduced into the 4-methyl group even after 159 hr, a period of time during which nearly half of the deuterium in the molecule shifted to the terminal methylene (Table III). Thus the intramolecular character of hydrogen transfer to the terminal methylene was confirmed.

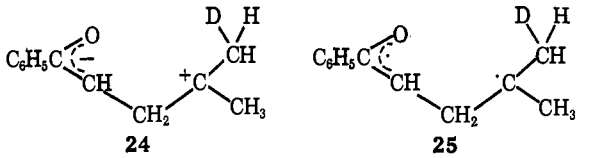
Table III. Deuterium Distributions in 4-Methyl-4-pentenophenone (**23**)



Time, hr	D, g-atom— CH_2(a)	CH_2(b)	CH_2(d)	CH_3(f)
0	1.93	0.00[a]	−0.06[b]	−0.10[b]
12	1.80	0.00[a]	0.04	−0.16[b]
41	1.47	0.00[a]	0.42	−0.10[b]
98[c]	1.14	0.00[a]	0.66	−0.14[b]
159[c]	0.86	0.00[a]	0.73	−0.10[b]

[a] The *protium* integrals were taken as 2.00 and used as internal standards, since deuterium incorporation into position b in rearrangements of 4-pentenophenone-2-d_2 were shown to be nil (see Table I). [b] Negative values resulted from protium integrals exceeding the number of protons possible at the respective positions. [c] Gross samples were vacuum distilled from a "kugelrohr" before analyses.

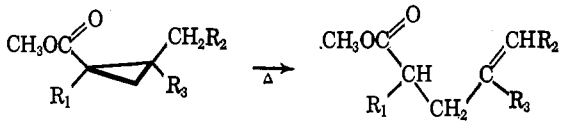
The failure of deuterium to enter the 4-methyl group also confirms the concerted nature of the transfer of the hydrogen to the methylene carbon and the formation of the cyclopropane ring, for if an intermediate dipolar ion **24** or diradical **25** had any significant lifetime, one might expect rotation about the C_3–C_4 bond, making the 4-CH_2D and 4-CH_3 groups chemically equivalent.



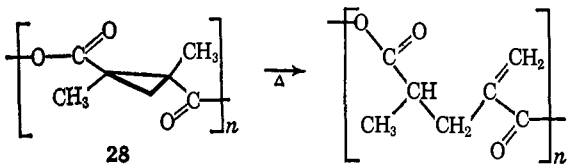
This would also lead to the formation of 4-methyl-4-pentenophenone containing deuterium in the 4-methyl group.[11b]

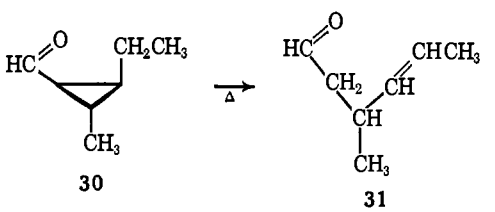
The formation of the d_0, d_3, and d_4 molecules may be explained in terms of intermolecular exchange of deuterium between the α carbons and the oxygens of the unsaturated ketones, preceded or followed by intramolecular shifts to the terminal methylene.[11c] Intermolecular processes may also initiate polymerization or decomposition, since 0.34 deuteron per molecule was "lost" to nmr analysis during the 159 hr of heating.

Other Examples of Enolene Rearrangements. Before the research described above was completed, the accidental observation of some closely related enolene-type rearrangements was reported.[12] Three carbomethoxycyclopropanes **26a**, **b**, and **c** were found to rearrange thermally to γ,δ-unsaturated esters **27a**, **b**, and **c**. The isomer of **26c** in which the 2-methyl group was *trans* to the carbomethoxy group was found to be thermally stable. Two other examples are in the older literature. In one of these,[13] the carbonyl function



	R_1	R_2	R_3
(a)	CN	H	CH_3
(b)	CN	CH_3	C_2H_5
(c)	CH_3	H	H



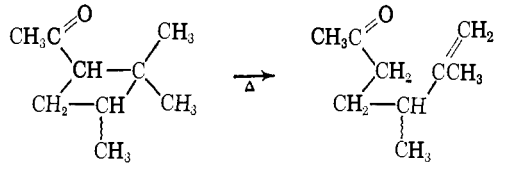


(12) D. E. McGreer, N. W. K. Chlu, and R. S. McDaniel, *Proc. Chem. Soc.*, 415 (1964).

(13) K. von Auwers and O. Ungemach, *Ann.*, 511, 152 (1934).

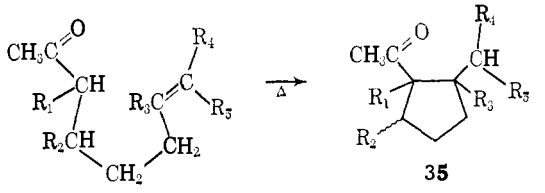
was present in a polymeric anhydride **28** and, in the other, in an aldehyde function **30**.[14] Since our preliminary publication,[1] several other examples of rearrangements of cyclopropyl aldehydes have been reported.[15]

Hydrogen Shifts Involving Enolenes and Larger Rings. We anticipated that enolenes in which the ene function was farther removed from the enol function might also undergo intramolecular hydrogen shifts. Preliminary evidence of the ring-opening rearrangement of an acylalkylcyclobutane had been obtained[16] before the recent publication by Conia and co-workers of their results on the same system. 1-Acetyl-2,2,3-trimethylcyclobutane (**32**) heated at 320° gave **33**.[17] In the



32 **33**

same laboratory it has also been shown[17,18] that enones having 4, 5, or 8 carbon atoms separating the C=C and C=O groups are actually cyclized by heating (*e.g.*, **34** → **35**). The yields of cyclized products (cyclopentyl and cyclohexyl ketones) from the first two types are reported to be good, while the yield of the

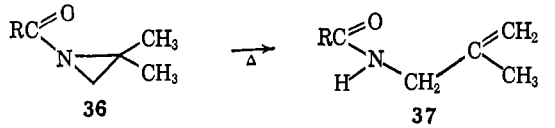


34 **35**

cyclononyl ketone is poor. Thus, the position of the thermal equilibrium between acyclic enones and cycloalkyl ketones is strongly dependent on ring size, as might be expected.

Related Thermal 1,5-Hydrogen Shifts in Other Systems

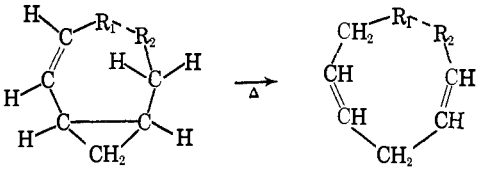
Acylaziridines. The thermal ring opening of a number of acylaziridines has been reported by Fanta and co-workers.[19] The kinetics of the thermolysis of



36 **37**

1-*p*-nitrobenzoyl-2,2-dimethylaziridine (**36**, R = *p*-$O_2NC_6H_4$) was studied and the reaction was found to be first order, with a heat of activation of 25.2 kcal/mole and an entropy of activation of −10.4 eu, in accord with a concerted cyclic process.[20] The reversibility of these reactions was not investigated; in fact, none of the N-allylic amides of type **37** obtained as thermolysis products was structurally capable of an isomerization analogous to the enolene rearrangement.

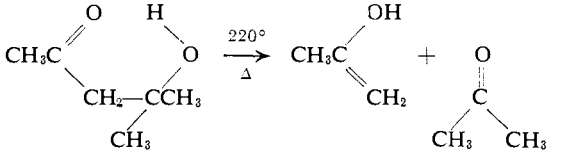
Vinylcyclopropanes. The rearrangement of *cis*-1-methyl-2-vinylcyclopropane (**38**, $R_1 = R_2 = H$) to *cis*-1,4-hexadiene (**39**, $R_1 = R_2 = H$)[21] may be seen



38 **39**

to be strictly analogous to the ring-opening step of the enolene rearrangement, with a carbon–carbon double bond involved in the 1,5-hydrogen shift rather than a carbon–oxygen double bond. This reaction was discovered in bicyclic systems in which R_1--R_2 was $(CH_2)_2$ and $(CH_2)_3$.[22] The stereospecificity, heat of activation, and entropy of activation in these systems show them to be closely related mechanistically to the enolene rearrangement.

Other Less Closely Related 1,5-Hydrogen Shift Thermolyses. Transannular 1,5-hydrogen shifts have been observed in cycloheptatrienes[23] and cyclooctatrienes;[24] in these cases a double bond functions in place of a cyclopropane ring. The 1,5 shifts of hydrogen from oxygen to carbon[25] or oxygen[26] demonstrated by Smith are formally related to the processes described above, but in all of these thermolyses, carbon–carbon σ bonds are cleaved. The most recent example[26] is actually quite similar to an enolene



rearrangement in that an enol is initially produced in the cleavage. Ester and xanthate pyrolyses[27] are also similar in that they involve intramolecular 1,5-hydrogen transfers concerted with σ bond cleavages.

Experimental Section[28]

I. Cyclopropyl Ketones. 1-Acetyl-2,2-dimethylcyclopropane. The procedure outlined by Corey and Chaykovsky[29] for the prep-

(14) C. D. Hurd and M. A. Pollack, *J. Org. Chem.*, 3, 550 (1939). In this earliest example of an aliphatic "abnormal Claisen rearrangement" the cyclopropane intermediate **30** was not isolated or recognized, of course. The starting material was γ-ethylallyl vinyl ether, which gave mainly the normal rearrangement product 3-ethyl-4-pentenal, but ozonolysis of this product indicated the presence of some **31**.

(15) G. Ohloff, *Tetrahedron Letters*, 3795 (1965).

(16) R. M. Roberts and P. B. Dennis, III, unpublished results. This work was interrupted by the accidental death of Mr. Dennis.

(17) J. M. Conia, F. Leyendecker, and C. Dubois-Faget, *Tetrahedron Letters*, 129 (1966).

(18) F. Rouessac and J. M. Conia, *ibid.*, 3313 (1965).

(19) D. V. Kashelikar and P. E. Fanta, *J. Am. Chem. Soc.*, 82, 4930 (1960), and previous papers referenced here.

(20) P. E. Fanta and M. K. Kathan, *J. Heterocyclic Chem.*, 1, 293 (1964).

(21) R. J. Ellis and H. M. Frey, *Proc. Chem. Soc.*, 221 (1964).

(22) (a) W. von E. Doering and W. Grimme, mentioned in W. von E. Doering and W. R. Roth, *Angew. Chem. Intern. Ed. Engl.*, 2, 119 (1963). For recent examples see (b) W. Grimme, *Chem. Ber.*, 98, 756 (1965); (c) W. R. Roth and J. König, *Ann.*, 688, 28 (1965); and (d) D. S. Glass, R. S. Boikess, and S. Winstein, *Tetrahedron Letters*, 999 (1966).

(23) A. P. ter Borg, H. Kloosterziel, and N. Van Meurs, *Proc. Chem. Soc.*, 359 (1962).

(24) D. S. Glass, J. Zirner, and S. Winstein, *ibid.*, 276 (1963).

(25) (a) G. G. Smith and R. Taylor, *Chem. Ind.* (London), 949 (1961); (b) G. G. Smith and S. E. Blau, *J. Phys. Chem.*, 68, 1231 (1964).

(26) G. G. Smith and B. L. Yates, *J. Org. Chem.*, 30, 2067 (1965).

(27) C. H. DePuy and R. W. King, *Chem. Rev.*, 60, 431 (1960)..

(28) Beckman IR-5A and Varian A-60 spectrometers were used for infrared and nmr measurements. Beckman GC-2A and Wilkens A-600 (Hy-Fi) and A-700 (Autoprep) instruments were used for vpc analyses and separations. Types of stationary-phase materials generally utilized included silicone gum rubber (SE-30), Carbowax (20M), and ethylene glycol succinate. Melting points are uncorrected.

(29) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, 84, 867 (1962).

aration of cyclopropyl ketones from α,β-unsaturated ketones was followed. Dried trimethylsulfoxonium iodide (39.0 g, 0.175 mole) was stirred into 130 ml of dimethyl sulfoxide. A nitrogen atmosphere was maintained as 8.2 g of a 52% suspension of sodium hydride (4.4 g, 0.175 mole) in mineral oil was added slowly. The temperature of the solution was kept below 40° by an ice bath. Mesityl oxide (16.7 g, 0.17 mole) was added over a period of 15 min, and again the ice bath was used to moderate the temperature of the mixture. Stirring at room temperature was continued for 3 hr, and the mixture was allowed to stand overnight. It was poured onto 150 g of ice, producing two layers. Skellysolve F (50 ml) was added, and, after separation, the aqueous portion was extracted twice with 100-ml portions of Skellysolve F. These extracts were combined with the original organic layer and washed with water. After drying over magnesium sulfate and rotary evaporation, vacuum distillation of the residue at 80–85 mm produced material boiling at 69–71°, 7.3 g (38%). The infrared spectrum of this material showed an absorption at 1690 cm^{-1} indicative of carbonyl in conjugation with a cyclopropane ring.[30] Analysis by vpc showed one large peak (only a trace of mesityl oxide was evident). An nmr spectrum (in δ) showed five distinct absorptions, and integration indicated one proton was obscured by overlap: multiplet at 0.7 (1 H), obscured multiplet at 1.1–1.2 (1 H), singlet at 1.1 (3 H), singlet at 1.2 (3 H), multiplet at 1.8 (1 H), and singlet at 2.2 (3 H).

The 2,4-dinitrophenylhydrazone was prepared, mp 161.5–162.5° (lit.[31] mp 159°).

trans-**1-Acetyl-2-methylcyclopropane. A. From** *trans*-**3-Penten-2-one.** The *trans*-α,β-unsaturated ketone was made by the method of Grignard[32] in yields varying from 20 to 40%, and in spite of careful distillation, mesityl oxide was found to contaminate the product; bp 120–124° (lit.[33] bp 124°).

trans-3-Penten-2-one and trimethylsulfoxonium iodide–sodium hydride were used in a procedure similar to that utilized in the preparation of 1-acetyl-2,2-dimethylcyclopropane. This resulted in a 13% yield of the desired compound; however, 30% of the distillate was 1-acetyl-2,2-dimethylcyclopropane derived from mesityl oxide present in the starting material.

B. From *cis*-**3-Penten-2-one.** The *cis*-α,β-unsaturated ketone was obtained from *trans*-3-penten-2-one by the method of Mecke and Noack.[33] Slow distillation of the *trans* ketone, to which one or two crystals of iodine had been added, through a Podbielniak distillation apparatus (no. 1050) produced *cis*-3-penten-2-one, bp 98–101° (lit.[33] bp 103°). Material produced this way was shown to be 94–98% *cis* isomer by vpc analysis.

With trimethylsulfoxonium iodide–sodium hydride, *cis*-3-penten-2-one produced 10% yields of material which had the same infrared spectrum as that produced from the *trans* ketone. Analysis by vpc showed the product from *cis* starting material to be free of 1-acetyl-2,2-dimethylcyclopropane and to have a retention time identical with that of the main product from the *trans* ketone. The nmr spectrum (in δ) showed the following absorptions: singlet at 2.2 (3 H), multiplet at 1.7 (1 H), overlapping singlet and multiplet centered at 1.2 (5 H), multiplet at 0.7 (1 H); $n^{22}D$ 1.4252 (lit.[31] $n^{18}D$ 1.4270). A sample of ketone submitted to mass spectral analysis showed a cracking pattern almost identical with that found for *cis*-1-acetyl-2-methylcyclopropane. The 2,4-dinitrophenylhydrazone of *trans*-1-acetyl-2-methylcyclopropane melted, after various recrystallizations, at 88–90°, 93–95°, and 88–95° (lit.[31,34] mp 87–88° and 93–95°). (The references did not specify *trans* geometry; that designation here is based on the considerably higher melting point of the *cis* derivative, the likelihood that the methods previously used would result in the more stable *trans* isomer, and upon the degradation data below.) The semicarbazone was prepared, mp 91.9–92.9°.

Anal. Calcd for $C_7H_{13}N_3O$ (semicarbazone): C, 54.16; H, 8.46. Found: C, 54.45; H, 8.40.

trans-**2-Methylcyclopropanecarboxylic acid** was derived from *trans*-1-acetyl-2-methylcyclopropane by a modification of the oxidative cleavage procedure developed by Newman and coworkers.[35,36] The ketone (0.8 g, 0.008 mole) was added with stirring to a solution of 0.05 mole of potassium hypochlorite. The temperature was raised to 49° briefly, and the mixture was stirred for about 15 hr at room temperature. Sodium bisulfite (0.8 g) was added to destroy the excess reagent, and the solution was acidified with concentrated hydrochloric acid. The organic material was recovered by continuous ether extraction. After removal of solvent by rotary evaporation, 0.6 g of crude material was subjected to "kugelrohr" distillation at 14 mm and 95–105° bath temperature. About 0.4 g of a clear liquid was obtained, and infrared analysis showed a spectrum corresponding with that reported for *trans*-2-methylcyclopropanecarboxylic acid.[37] There were also weak bands at positions where the *cis* isomer was reported to absorb; $n^{26}D$ 1.4356 (lit.[37] $n^{25}D$ 1.4348). The nmr spectrum showed only one absorption downfield from δ 2, a singlet for the acid proton at δ 11.8 (neat sample).

The *trans* acid (0.19 g) was heated for 0.5 hr at 75° with 0.6 ml of thionyl chloride (Matheson Coleman and Bell "Purified") in an adaptation of the general procedure of Cheronis and Entrikin.[38] Dry benzene (20 ml) was added, and the solution was saturated with ammonia gas. Ammonium chloride was removed by filtration, and benzene was evaporated, yielding a brownish solid. Sublimation at 50° (12 mm) produced white crystals which were recrystallized from pentane–methylene chloride, mp 110–111° (lit.[37] for *trans*-2-methylcyclopropanecarboxamide, mp 111.3–112.0°).

cis-**1-Acetyl-2-methylcyclopropane.** The Simmons–Smith reaction, as outlined by Shank and Shechter[39] in their preparation of 2-oxabicyclo[4.1.0]heptane, was carried out with *cis*-3-penten-2-one (21.0 g, 0.025 mole). The resulting black oil yielded 5 g (20%) of material upon "kugelrohr" distillation at 80° (90 mm) which proved to be a 56:44 mixture of *cis*- and *trans*-1-acetyl-2-methylcyclopropane. Analytical and preparative scale vpc separation was effected with a 10 ft × 3/8 in., 10% silver fluoroborate–20% Carbowax 20M column, which gave the best separation of the *cis*–*trans* pair. The infrared spectrum of *cis*-1-acetyl-2-methylcyclopropane was similar to that of the *trans* isomer in many respects; however, a medium absorption at 1322 cm^{-1} in the *trans* isomer was absent in the *cis*, and the *cis* isomer showed a medium band at 1128 cm^{-1} not seen in the *trans* compound. The nmr absorptions (in δ) of the *cis* isomer were: overlapping singlet and multiplet at 0.8–1.5 (6 H), multiplet at 1.9 (1 H), and singlet at 2.2 (3 H); $n^{25}D$ 1.4252. The 2,4-dinitrophenylhydrazone was prepared, mp 150–153°. The semicarbazone was prepared, mp 137.5–137.6°.

Anal. Calcd for $C_7H_{13}N_3O$ (semicarbazone): C, 54.16; H, 8.46. Found: C, 54.64; H, 8.48.

cis-**2-Methylcyclopropanecarboxylic acid** was prepared from 0.74 g of *cis*-1-acetyl-2-methylcyclopropane using a procedure identical with that for the *trans* acid. "Kugelrohr" distillation of the extracted oxidation product yielded 0.42 g of material whose infrared spectrum matched that reported[37] for *cis*-2-methylcyclopropanecarboxylic acid; $n^{25}D$ 1.4385 (lit.[37] $n^{25}D$ 1.4389). The nmr spectrum showed only one absorption downfield from δ 2 at δ 12 (sample was dissolved in carbon tetrachloride solution).

The amide of *cis*-2-methylcyclopropanecarboxylic acid was prepared by the same procedure used to make the amide of the *trans* acid. Crystals obtained from the benzene solution melted at 126.5–127.5° after several recrystallizations from pentane–methylene chloride (lit.[37] for *cis*-2-methylcyclopropanecarboxamide, mp 128–128.5°).

II. Homoallylic Ketones. Allyl Benzoylacetate. The following transesterifications and rearrangements to homoallylic ketones are adaptations of the procedures of Kimel and Cope.[40] Sodium (0.50 g) was dissolved in allyl alcohol (174.0 g, 3.00 moles), and 150.0 g (0.78 mole) of ethyl benzoylacetate was added. The mixture was heated to reflux, and 42 ml of material boiling lower than 80° was distilled slowly (reflux ratio, 98:2) over a period of 28 hr. The residue was diluted with 400 ml of ether and washed successively with 100 ml of 5% hydrochloric acid and 100 ml of water. After drying over sodium sulfate, most of the ether and residual allyl alcohol were removed by rotary evaporation. Vacuum distillation at 112–118° (0.5 mm) yielded 112 g of crude ester.

(30) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962, pp 24 and 42.
(31) M. Julia, S. Julia, and J. A. du Chaffaute, *Bull. Soc. Chim. France*, 1735 (1960).
(32) V. Grignard and M. Fluchaire, *Ann. Chim.*, [10] **9**, 5 (1928).
(33) R. Mecke and K. Noack, *Chem. Ber.*, **93**, 210 (1960).
(34) G. W. Cannon, A. A. Santilli, and P. Shenlan, *J. Am. Chem. Soc.*, **81**, 1660 (1959).
(35) M. S. Newman and H. L. Holmes, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p 429.
(36) S. Sarel and M. S. Newman, *J. Am. Chem. Soc.*, **78**, 5416 (1956).
(37) D. E. Applequist and A. H. Peterson, *ibid.*, **82**, 2372 (1960).
(38) N. D. Cheronis and J. B. Entrikin, "Semimicro Qualitative Organic Analysis," 2nd ed, Interscience Publishers, Inc., New York, N. Y., 1957, p 352.
(39) R. S. Shank and H. Shechter, *J. Org. Chem.*, **24**, 1825 (1959).
(40) W. Kimel and A. C. Cope, *J. Am. Chem. Soc.*, **65**, 1992 (1943).

Infrared analysis showed terminal unsaturation absorptions[30] at 935 and 990 cm^{-1}. This material was used without further purification for preparation of 4-pentenophenone.

4-Pentenophenone. The Kimel and Cope rearrangement method[40] was used; crude allyl benzoylacetate (110 g) was heated at 225–235° for 7.5 hr with a Wood's metal bath. The mixture refluxed gently and gas was evolved. Distillation (1.5 mm) yielded material boiling at 72–78°, which was shown to be essentially pure by vpc analysis; yield, 36.8 g (30.8%). The semicarbazone was prepared, mp 159–160° (lit.[41] mp 157.0–157.5°). Nmr absorptions (in δ) were: multiplet at 7.9 (2 H), multiplet at 7.4 (3 H), multiplet at 5.9 (1 H), triplet at 5.0 (2 H), triplet at 2.9 (2 H), and multiplet at 2.4 (2 H).

4-Pentenophenone-2-d_2. A mixture was made of freshly distilled triethylamine (46.5 g, 0.46 mole), deuterium oxide (98%, 14 g, 0.7 mole), 4-pentenophenone (36.8 g, 0.23 mole), and 50 ml of dry *p*-dioxane, for a deuteration procedure similar to that outlined by Greene.[42] A gentle reflux was maintained for 25 hr, after which the amine, water, and *p*-dioxane were distilled until the temperature rose to 90° and the distillate was clear. Fresh deuterium oxide, amine, and *p*-dioxane in the amounts given above were added, and the stirred reflux was repeated, followed by removal of amine, water, and *p*-dioxane as before. The process was repeated for a third time, and after the amine–water–*p*-dioxane portion was distilled out, a vacuum distillation produced the deuterated compound at 74° (1.0 mm). Analysis by vpc indicated the distillate to be pure. Mass spectral analysis showed parent peaks at *m/e* 160 for the undeuterated material and at *m/e* 162 for the deuterated compound. Calculations on the basis of pertinent *m/e* values in the mass spectrogram of the deuterated material also indicated the presence of 1.94 deuterons per molecule, 96.4% dideuterated and 5.6% monodeuterated. The absorption seen at δ 2.9 in the nmr spectrum of 4-pentenophenone decreased upon deuteration to an integral of 0.04 H, indicating 1.96 deuterons per molecule, and the triplet assigned to the β position (b), at δ 2.4, collapsed into a doublet.

3-Methyl-4-pentenophenone. Crotyl Benzoylacetate. Sodium (0.3 g) was added to pure crotyl alcohol (75.5 g, 1.05 moles) and ethyl benzoylacetate (100 g, 0.524 mole), and the mixture was slowly distilled under reduced pressure (191 mm). Over a period of 19 hr, a 50-ml distillate boiling up to 61° was collected. The residue was diluted with ether, washed with 5% hydrochloric acid and water, and dried over sodium sulfate. Vacuum distillation yielded a fraction boiling at 115–135° (0.28–0.67 mm), which was contaminated on the order of 1% by ethyl benzoylacetate (vpc analysis). Infrared analysis of this material showed a very strong absorption at 972 cm^{-1}; $n^{25}D$ 1.5327 [lit.[40] $n^{25}D$ 1.5347, bp 112–114° (0.20 mm)]; yield, 47.1 g (41.4%).

3-Methyl-4-pentenophenone. Rearrangement of crotyl benzoylacetate was accomplished by heating the 47-g portion at 250–260° for 3 hr. Vacuum distillation at 1.0–1.2 mm yielded a fraction boiling at 84–92°. This material (30 g) was analyzed by vpc and was found to be an 85:15 mixture of two components. It was divided into two 15-g portions, one of which was deuterated (below). The second portion of the mixture was resolved by preparative scale vpc utilizing an 11 ft × 3/8 in. 20% cyanosilicone XF-1150 column. The major component was identified as 3-methyl-4-pentenophenone on the basis of the parent peaks in its mass spectrum of *m/e* 174, its infrared spectrum (characteristic absorptions at 1700, 1650, 1600, 1450, 1010, 910, 757, and 693 cm^{-1}), and the following nmr spectrum (values in δ units): multiplet at 7.9 (2 H), multiplet at 5.9 (1 H), triplet at 5.0 (2 H), two multiplets centered at ~2.9 (3 H), and a doublet at 1.1 (3 H). Its semicarbazone was prepared, mp 178–180° (lit.[40] mp 176–177.5°).

Similarly, a less pure sample of the minor component of the mixture (contaminated up to 25% by 3-methyl-4-pentenophenone) was obtained and identified as 4-hexenophenone on the basis of its molecular weight (mass spectrum parent peak, *m/e* 174), its infrared spectrum (characteristic absorptions of 1700, 1650, 1600, 1450, 970, 743, and 692 cm^{-1}), and the following nmr spectrum (in δ): multiplet at 7.9 (2 H), multiplet at 7.4 (3 H), multiplet at 5.4 (2 H), triplet at 2.9 (2 H), multiplet at 2.3 (2 H), and doublet at 1.6 (3 H). Its semicarbazone was prepared, mp 134–135° (lit.[40] mp 129–130°).

3-Methyl-4-pentenophenone-2-d_2. The isomer mixture of 3-methyl-4-pentenophenone and 4-hexenophenone (15 g) was heated under reflux for 24 hr with a mixture of freshly distilled triethylamine (30 ml), *p*-dioxane (30 ml), and deuterium oxide (10 g, 98% deuterated). The water–amine azeotrope was removed by distillation, and the amine and deuterium oxide were replenished. The heating under reflux was repeated, and the azeotrope was again removed. This treatment was repeated a third time, and the deuterated isomers were recovered by vacuum distillation.

Separation of the deuterated isomers was achieved as with the nondeuterated mixture. Mass spectrometry indicated that the deuterated 3-methyl-4-pentenophenone contained 1.72 deuterons per molecule, whereas electronic integration showed a decrease of 1.67 in the proton integral at 2.9 in the nmr spectrum (see foot note *b*, Table III).

4-Methyl-4-pentenophenone-2-d_2. β-Methylallyl Benzoylacetate. Sodium (0.5 g) was dissolved in β-methylallyl alcohol (300 g, 4.15 moles), and ethyl benzoylacetate (144 g, 0.75 mole) was added. The mixture was distilled slowly (reflux ratio 99:1) over a period of 18 hr, and 45 ml of material boiling below 85° was obtained. The residue was diluted with 500 ml of ether and washed several times with 100-ml portions of 5% hydrochloric acid and brine. After drying over sodium sulfate, most of the ether and residual β-methylallyl alcohol were stripped off in a rotary evaporator. Distillation at 2 mm provided 85 g (52%) of material boiling at 121–123°, $n^{25}D$ 1.5299. Prominent absorptions in the infrared spectrum were: 2920, 1740, 1690, 1640, 1455, 1415, 1330, 1270, 1215, 1190, 1150, 990, 910, 758, and 690 cm^{-1}. This material showed a tendency to solidify at room temperature.

4-Methyl-4-pentenophenone. β-Methylallyl benzoylacetate (80 g, 0.49 mole) was heated at 250° with a Wood's metal bath for 6 hr. At the end of this period, gas evolution had practically ceased. The reaction mixture was distilled at 1.5 mm, and 47 g (74%) of material boiling at 77–79° was shown to be 99% pure by vpc analysis; $n^{25}D$ 1.5265. The infrared spectrum showed strong absorption at 890 cm^{-1} and medium absorption at 990 cm^{-1}. An nmr spectrum (in δ) was completely consistent with the structure of 4-methyl-4-pentophenone: multiplet at 7.9 (2 H), multiplet at 7.4 (3 H), singlet at 4.7 (2 H), triplet at 3.0 (2 H), triplet at 2.4 (2 H), and singlet at 1.7 (3 H). The semicarbazone was prepared, mp 125.5–126.5°.

Anal. Calcd for $C_{13}H_{17}N_3O$ (semicarbazone): C, 67.49; H, 7.42. Found: C, 67.78; H, 7.62.

4-Methyl-4-pentenophenone-2-d_2. 4-Methyl-4-pentenophenone (40 g, 0.23 mole) was refluxed over 40-, 24-, and 36-hr periods with fresh mixtures of triethylamine (46.5 g, 0.46 mole), deuterium oxide (98% 15 g, 0.75 mole), and *p*-dioxane (50 ml). At the end of each reflux period, the amine, water, and *p*-dioxane were distilled out until the distillate was clear and boiled at 90°. The residue from the last distillation was vacuum distilled at 83–87° (1.5 mm). The distillate was shown to be 98–99% pure by vpc. The nmr absorption observed for the α-CH_2 in the undeuterated compound (at δ 3.0) was reduced to 0.07 H, and the δ 2.4 triplet collapsed into a singlet.

III. Thermal Rearrangements. In all of the experiments reported below, unless stated otherwise, samples were sealed in Pyrex tubes at reduced pressures equal to or less than 0.1 mm. Before final sealing, samples were degassed by freezing and melting at 0.1 mm until bubbles no longer were evolved. Tubes containing materials with melting points below Dry Ice–acetone temperature (the cyclopropane derivatives) were cooled and shaken vigorously before sealing. Unless otherwise stated, samples were heated in thermostated laboratory ovens.

Thermolysis of 1-Acetyl-2,2-dimethylcyclopropane. A preliminary experiment, in which the sample was heated at 140–170° under nitrogen at atmospheric pressure, yielded 89.4% of a rearrangement product after 24 hr, according to vpc analysis. Preparative vpc separation (20 ft × 3/8 in., 30% Carbowax 20M column) provided pure samples of this product, 5-methyl-5-hexen-2-one. The band at 890 cm^{-1}, characteristic of a disubstituted double bond,[30] was quite strong in the infrared spectrum, and the following nmr spectrum (in δ units) was obtained: singlet at 4.7 (2 H), overlapping multiplets at 2.7–2.8 (4 H), singlet at 2.1 (3 H), and singlet at 1.7 (3 H). The semicarbazone was prepared, mp 137.5–138.5° (lit.[40] mp 136.5–137.5°).

Kinetic studies utilized the sealed tube technique. Samples were completely immersed in a stirred oil bath in which the temperature was held constant within ±1.5°, and reactions were quenched by plunging the tubes into ice water. Analyses of reaction mixtures were made by vpc. Slopes for first-order plots were obtained by applying the method of least squares to data from five reaction mixtures at each of two temperatures. These data are given in the following order, temperature—reaction time (in hours), percentage of unchanged starting material in reaction mixture: 152 ± 1.5°—1.25, 84.6; 3.00, 70.0; 3.75, 59.1; 7.00, 37.2; 10.00,

(41) A. C. Cope, K. E. Hoyle, and D. Heyl, *J. Am. Chem. Soc.*, **63**, 1843 (1941).

(42) R. N. Greene, Ph.D. Dissertation, The University of Texas, 1965, p 92.

24.8; 163 ± 1.5°—1.90, 58.7; 3.00, 43.7; 4.50, 27.3; 6.00, 13.8; 7.00, 10.3.

Thermolysis of *trans*-1-Acetyl-2-methylcyclopropane (Attempt). After 12 hr at 160°, a sample of *trans*-1-acetyl-2-methylcyclopropane was unchanged. A sample heated to 179–180° for 24 hr did discolor, but neither vpc nor infrared analysis detected any rearrangement.

Thermolysis of *cis*-1-Acetyl-2-methylcyclopropane. A tube containing *cis*-1-acetyl-2-methylcyclopropane was subjected to 160° temperature concurrently with the *trans* isomer above for 12 hr. Almost total conversion to allylacetone was achieved, as evidenced by vpc analysis and an infrared spectrum which was almost identical with that of authentic material (Borden Chemical Co.).

Thermolysis of 4-Pentenophenone-2-d_2. Thermal rearrangements were performed using 0.3–0.5-g samples which were heated at 202 ± 2°. Progress of reactions was monitored by nmr. The doublet absorption noted at δ 2.4 collapsed to a complex multiplet as deuterium was exchanged for hydrogen. The amounts of deuterium per position after the various reaction periods are listed in Table I. Absorption peak areas were derived from the average values obtained from three electronic integrations per sample. Mass spectral analysis of the sample heated 72 hr revealed the following distribution of deuterium-labeled species: 5.6% d_4 molecules, 18.0% d_3 molecules, 37.4% d_2 molecules, 18.4% d_1 molecules, and 20.6% d_0 molecules.

Thermolysis of 3-Methyl-4-pentenophenone-2-d_2. The nmr data obtained after heating 0.5–0.6-g samples at 202 ± 2° are summarized in Table II. The starting material contained 1.72 deuterons per molecule; after 120 hr of heating, the value was 1.61 per molecule (see footnote *b*, Table II).

Thermolysis of 1:1 Mixture of 4-Pentenophenone-2-d_2 and 3-Methyl-4-pentenophenone. The 0.6-g sample was heated for 17 hr at 202 ± 2°. The higher molecular weight compound picked up 1.5 deuterons per molecule on the average; the specific composition was as follows: 9.5% d_4 molecules, 11.3% d_3 molecules, 23.5% d_2 molecules, 30.8% d_1 molecules, and 24.8% d_0 molecules. The 4-pentenophenone retained 0.3 deuterium per molecule on the average; the specific composition was: 29.9% d_1 molecules and 70.1% d_0 molecules.

Thermolysis of 4-Methyl-4-pentenophenone-2-d_2. Samples of the deuterated material (0.3–0.5 g) were subjected to thermal rearrangement at 202 ± 2°. Reaction times longer than 90 hr gave rise to considerable decomposition and polymerization which interfered with electronic integration of the nmr spectrum. Use of diphenyl ether in one experiment as a solvent did not slow the interfering processes. Usable data were obtained from samples distilled from a "kugelrohr" at less than 100° (1.3–2.3 mm). As deuterium from the α carbon exchanged for protons on the δ methylene, the nmr absorption at δ 2.4 broadened into a doublet with shoulders. The absorption at β-CH_2 was taken as an internal standard for two protons, and deuterium distributions after various heating periods were as listed in Table III. Absorption peak areas were derived from the average values obtained from three electronic integrations per sample.

Reactions of Active Nitrogen with Organic Substrates. V. Resynthesis and Rearrangement in the Reaction of Propylene. The Molecular Mechanism[1]

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Abstract: Propylene was recovered after contact of each of the three ^{14}C-labeled isomers with excess active nitrogen in a fast flow apparatus at 3 torr. With (N)/(C_3H_6) equal to 6, the mean changes in total molar activity of recovered propylene and their standard deviations were from C_3H_6-1-^{14}C, −7.7 ± 1.3%; from C_3H_6-2-^{14}C, +5.9 ± 0.85%; from C_3H_6-3-^{14}C, −3.8 ± 1.2%. Mean changes in atomic activity at C-1 which occurred under the same conditions were from C_3H_6-1-^{14}C, −15.3 ± 1.8%; from C_3H_6-2-^{14}C, + 7.0 ± 3.0%; from C_3H_6-3-^{14}C, +12.5 ± 1.6%. Similar data were obtained with (N)/(C_3H_6) equal to 12. The changes in total molar activity establish that part of the recovered propylene is reconstituted from fragments of two or more molecules of reactant propylene. The changes in atomic activity at C-1 indicate that interconversion of C-1 and C-3 is superimposed on the resynthesis process. Resynthesis is best interpreted as involving recombination of a two-carbon fragment which is composed of one original C-2 atom plus either a C-3 or a C-1 atom with a one-carbon fragment which may be derived from any of the original carbon atoms. The latter always becomes C-1 of the reconstituted molecule. Several plausible mechanisms capable of rationalizing the interconverson of C-1 and C-3 are described. One of these involves reversible addition of N(^{4}S) to the double bond followed by reversible rearrangement of the excited adduct to an excited azacyclobutyl radical, $(CH_2)_3N^*$. Consideration of the decomposition modes of the two intermediates and of the attack of one of the decomposition products, methylcarbene, or N(^{4}S) on the intermediates provides a mechanistic scheme which correlates not only the resynthesis data but also previously reported data on the molecular origins of CH_3CN, C_2H_6, C_2H_4, C_2H_2, and C_3H_8 which are formed in this reaction.

A previous paper in this series[3] reported an investigation of the molecular origins of a number of the products of the reaction of active nitrogen with propylene variously labeled with ^{14}C. Within the limits of accuracy of that work, the recovered propylenes appeared to have molar activities identical with those of the original substrates. Application of a more accurate static counting procedure has, however, established that when excess active nitrogen is employed, original and recovered propylenes differ significantly in specific activity. These data have been supplemented by selectively removing the methylene carbon (C-1)

(1) This work was supported in part by the U. S. Atomic Energy Commission Contract AT(30-1)2383 and in part by U. S. Army Research Office Grant DA-ARO(D)-31-124-G171.

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