of **5** by benzophenone and acetone is attributed to eq 13, energy transfer to B to regenerate A. Since eq 13 simply increases the steady-state concentration of A and eq 8 and 12 have been included, operation of eq 13 can enhance the yield of **4** as well as that of **5**.

The observed results can be explained by assuming that A and B are tetramethylcyclobutadienes differing in multiplicity, one a singlet state and the other a triplet. Conversion of A to B, eq 10, could easily be assisted by long-lived radical species ($O_2 \cdot CCl_3$, and other intermediates) or by heavy atoms in the solute. This could also explain the sensitivity of G_5 to impurities present in the additives and those building up during the course of the irradiation. It is tempting to suggest that A is a triplet cyclobutadiene and B is a lower energy singlet. Theoretical calculations[52] suggest that for free cyclobutadiene a "rectangular" singlet should lie 14–21 kcal/mol below a "square" triplet. Recent experimental evidence appears to indicate a rectangular singlet is the ground state of cyclobutadiene.[53] Such an energy difference would explain a lack of quenching of A (and hence **5**) by azulene ($E_T \approx 31$–39 kcal/mol)[54] and other additives with higher triplet energies. Presumably lack of observed increases in G_5 could be due to short lifetimes for triplets of 1,3-cyclohexadiene and azulene.[55] It is reasonable that singlet tetramethylcyclobutadiene should react rapidly with 2-butyne in an allowed, concerted reaction; it is also conceivable that the triplet might react slowly with 2-butyne, but very rapidly either with another triplet or with the singlet in a Diels–Alder reaction.

Examination of data in Table I reveals that formation of the initial tetramethylcyclobutadiene is very difficult to quench. While an extremely short-lived excited state or ion from **1** (different from the precursor of the radical products) cannot be excluded as the precursor, an attractive alternative possibility is that the tetramethylcyclobutadiene is formed within the region where energy is initially deposited by a process not involving one discrete activated molecule. The fact that radiolysis of liquid alkynes offers a direct route to uncomplexed cyclobutadienes offers interesting possibilities for future investigation.

Acknowledgment. We are grateful for support of this work by the University of North Carolina Materials Research Center in conjunction with the Advanced Projects Research Agency (Contract No. SD-100). We thank Professor M. S. Brookhart for helpful discussion and valuable assistance in product identification.

(52) M. J. S. Dewar and G. J. Gleicher, *J. Amer. Chem. Soc.*, **87**, 3255 (1965).

(53) P. Reeves, T. Henery, and R. Pettit, *ibid.*, **91**, 5888 (1969); P. Reeves, T. Devon, and R. Pettit, *ibid.*, **91**, 5890 (1969).

(54) A. A. Lamola, W. G. Herkstroeter, and G. S. Hammond, *J. Chem. Phys.*, **42**, 1715 (1965).

(55) Quenching by 1,3-cyclohexadiene might produce an excited singlet. The cyclohexadiene singlet intersystem crosses with very low efficiency.[56,57]

(56) G. F. Vesley, Ph.D. Thesis, Caltech, 1968; D. Valentine, N. J. Turro, Jr., and G. S. Hammond, *J. Amer. Chem. Soc.*, **86**, 5202 (1964).

(57) D. I. Schuster, F. H. Lee, A. Padwa, and P. G. Gassman, *J. Org. Chem.*, **30**, 2262 (1965).

Homo-Favorskii Rearrangement

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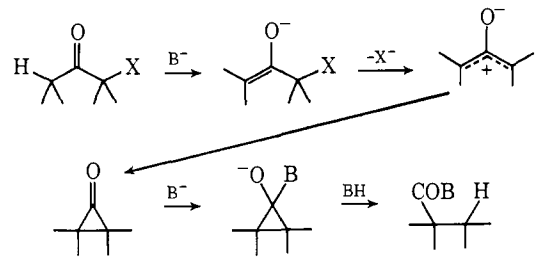
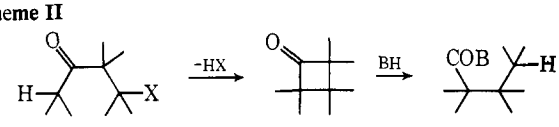
Abstract: The structures of the acidic products of the reaction between 3,6-dimethyl-6-dichloromethyl-2-cyclohexenone and aqueous base have been revised. Full mechanistic and stereochemical analyses of the homo-Favorskii rearrangement (base-induced dehydrochlorination of β-haloketones, followed by scission of the resultant cyclobutanones in analogy with reactions of the Haller–Bauer type) of 6-dichloromethyl-6-methyl-2-cyclohexenone and of the hydrolyses of 2-dichloromethyl-2-methylcyclohexanone, 2-keto-1-methylcyclohexylcarbinyl *p*-toluenesulfonate, and the enol ether of the latter are presented.

In analogy with the Favorskii rearrangement,[1] the base-induced dehydrohalogenative conversion of α-haloketones into carboxylic acids or their derivatives (*cf.* Scheme I), a homo-Favorskii rearrangement can be envisaged to involve a similar transformation of β-haloketones (*cf.* Scheme II). However, two facts mitigate against a frequent occurrence of the latter reaction. Firstly, exposure of β-haloketones to base normally leads to α,β-unsaturated ketones. Hence, the production of cyclobutanone intermediates (Scheme II) can be

Scheme I



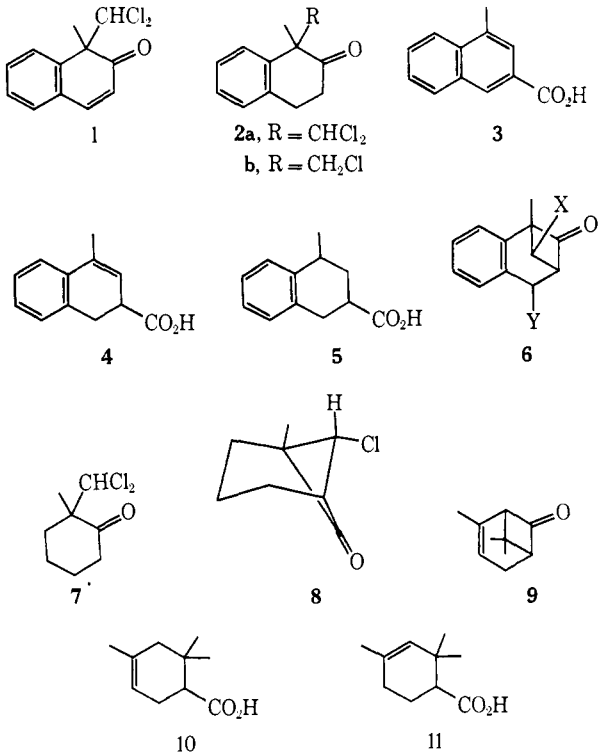
Scheme II



(1) A. Favorskii, *J. Russ. Phys.-Chem. Soc.*, **26**, 559 (1894); *J. Prakt. Chem.*, [2] **51**, 533 (1895); A. Kende, *Org. React.*, **11**, 261 (1960); N. J. Turro, *Accounts Chem. Res.*, **2**, 25 (1969); F. G. Bordwell and M. W. Carlson, *J. Amer. Chem. Soc.*, **92**, 3370, 3377 (1970), and references cited therein; F. G. Bordwell, *Accounts Chem. Res.*, **3**, 281 (1970).

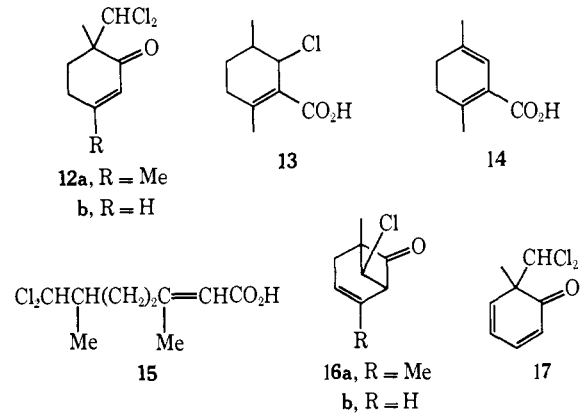
anticipated only in cases of starting ketones containing one or more α' hydrogens but no α hydrogen or possessing the type of steric environment which prohibits the introduction of double bonds at the α,β-carbon sites. Secondly, in contrast to the base lability of cyclopropanones, the Favorskii reaction intermediates (Scheme I), cyclobutanones are normally stable, although their fragmentation in the sense of the Haller–Bauer reaction[2] has been observed.[3,4]

Dichloromethylcyclohexadienones, products of Reimer–Tiemann reactions, and their reduction products are most susceptible to homo-Favorskii rearrangements. For example, alkali treatment of the naphthalenone **1** and the β-tetralones **2a** and **2b** has been shown to lead *inter alia* to acids **3**, **4**, and **5**, respectively.[5] The postulated cyclobutanone intermediates



6 could not be isolated and their lability was attributed to the presence of the neighboring benzene ring. This assumption was strengthened by the ready conversion of the saturated haloketone **7** into a stable cyclobutanone **8** (and an acyclic ester) on alkoxide treatment[5,6] as well as by the known, facile, base-induced ring opening of β,γ-unsaturated cyclobutanones,[4c] *e.g.*, chrysanthenone **9** → cyclogeranic acids **10** and **11**.

In the face of the above self-consistent picture, an early report[7] of the transformation of 3,6-dimethyl-6-dichloromethyl-2-cyclohexenone (**12a**) into the acids **13** and **14** on alkali treatment appeared puzzling. While the acid **15** had been formulated as an intermediate, present-day theory requires cyclobutanone **16a** to be the intermediate and to cleave at the site of the bond dissected by the dotted line in formula **16a**. This would result in the production of acids of different structures than **13** and **14**. Even though the configuration of these substances had been established on the basis of the thermal conversion of the chloro acid **13** into the dienoic acid **14**, the acid-catalyzed formation of 1,4-dimethyl-1,3-cyclohexadiene from the latter, and the transformation of **14** into 2,5-dimethylbenzoic acid by bromination and subsequent base treatment, the structures of the products of apparently the earliest homo-Favorskii rearrangement needed reappraisal.



Repetition of the base treatment of **12a**, prepared by the interaction of methylmagnesium iodide with 6-dichloromethyl-6-methyl-2,4-cyclohexadienone (**17**) and subsequent acid-catalyzed isomerization of the resultant ketone mixture **18a**,[8] led to a chloroolefinic acid and dienoic acid whose melting characteristics were identical with those of the compounds reported 60 years ago.[7] However, proton magnetic resonance spectral analysis showed the substances to possess structures **19a** and **20a**, respectively. The chloro acid was characterized as a dihalolactone by treatment with iodine and base. While the reported[7,9] acid-induced decarboxylation of the dienoic acid with formation of 1,4-dimethyl-1,3-cyclohexadiene was reproducible, aromatization of the acid by bromination and base treatment[7] yielded no xylenoic acid but only intractable material. Those facts are in accord with the assignment of formula **20a** for the dienoic acid.[10]

(2) K. E. Hamlin and A. W. Weston, *Org. React.*, **9**, 1 (1957); P. G. Gassman, J. T. Lumb, and F. V. Zalar, *J. Amer. Chem. Soc.*, **89**, 946 (1967).

(3) J. R. Lewis, G. R. Ramage, J. L. Simonsen, and W. G. Wainwright, *J. Chem. Soc.*, 1837 (1937); E. H. Farmer and M. O. Farooq, *ibid.*, 1925 (1938); L. I. Smith, C. L. Agre, R. M. Leekley, and W. W. Prichard, *J. Amer. Chem. Soc.*, **61**, 7 (1939); C. D. Hurd and R. D. Kimbrough, Jr., *ibid.*, **82**, 1373 (1960); R. N. McDonald and A. C. Kovelesky, *J. Org. Chem.*, **28**, 1433 (1963); T. J. Katz and R. Dessau, *J. Amer. Chem. Soc.*, **85**, 2172 (1963); H. C. Stevens, D. A. Reich, D. R. Brandt, K. R. Fountain, and E. J. Gaughan, *ibid.*, **87**, 5257 (1965); L. Ghosez, R. Montaigne, and P. Mollet, *Tetrahedron Lett.*, 135 (1966); T. R. Potts and R. E. Harmon, *J. Org. Chem.*, **34**, 2792 (1969); F. Nerdel, D. Frank, W. Metasch, K. Gerner, and H. Marschall, *Tetrahedron*, **26**, 1589 (1970), and references therein; T. Asao, T. Machigushi, T. Kitamura, and Y. Kitahara, *Chem. Commun.*, 89 (1970).

(4) (a) F. Nerdel, D. Frank, and H. Marschall, *Chem. Ber.*, **100**, 720 (1967); (b) G. Brieger, D. L. Hachey, and D. Ciaramitaro, *J. Org. Chem.*, **34**, 220 (1969); (c) W. Erman, E. Wenkert, and P. W. Jeffs, *ibid.*, **34**, 2196 (1969), and references therein.

(5) R. M. Dodson, J. R. Lewis, W. P. Webb, E. Wenkert, and R. D. Youssefyeh, *J. Amer. Chem. Soc.*, **83**, 938 (1961).

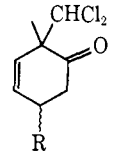
(6) E. Wenkert, P. Bakuzis, R. J. Baumgarten, D. Doddrell, P. W. Jeffs, C. L. Leicht, R. A. Mueller, and A. Yoshikoshi, *ibid.*, **92**, 1617 (1970).

(7) K. Auwers and M. Hessenland, *Ber.*, **41**, 1816 (1908).

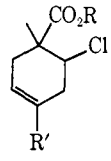
(8) K. Auwers, *ibid.*, **39**, 3748 (1906); K. Auwers and M. Hessenland, *ibid.*, **41**, 1790 (1908).

(9) K. von Auwers and R. Hinterseber, *ibid.*, **48**, 1357 (1915).

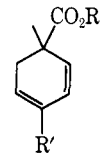
(10) The isolation of a small quantity of 2,5-dimethylbenzoic acid by Auwers on aromatization of the dienoic acid[7] is explained best on the basis of an impurity having been carried through two reactions. If it be assumed that the acid-catalyzed isomerization of the γ,δ-unsaturated ketone **18a** into the conjugated enone **12a** had been incomplete, base treatment of the former should have yielded some dienoic acid iii (by way of intermediate i) in accompaniment with the normal acid **20a**. In contrast to the behavior of **20a** the acid iii can be expected to undergo



18a, R = Me
b, R = H



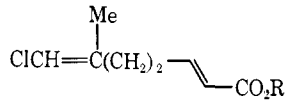
19



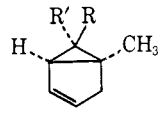
20

a, R = H; R′ = Me
b, R = R′ = H
c, R = Me; R′ = H

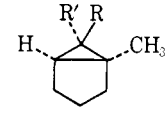
Revision of the configurations **13** and **14** into the structures **19a** and **20a**, respectively, places the reaction of ketone **12a** with base into the normal framework of the homo-Favorskii rearrangement (Scheme II). In order to gain more insight into the intimate details of the rearrangement an exhaustive study of the reactions of structurally simpler ketones **12b** and **7** with aqueous base was undertaken. Treatment of 6-dichloromethyl-6-methyl-2-cyclohexenone (**12b**) with potassium hydroxide in aqueous dioxane yielded an array of acids from which the homo-Favorskii products **19b** and **20b** could be isolated readily because of their ease of crystallization. Esterification of the mixture of acids with diazomethane allowed isolation of five methyl esters—**19c**, **20c**, **21a**, **22a**, and **22b**—whose structures were determined in the following manner.[11]



21a, R = Me
b, R = H



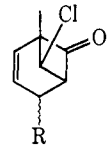
22



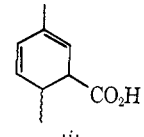
23

a, R = H; R′ = CO_2Me
b, R = CO_2Me; R′ = H
c, R = H; R′ = CO_2H
d, R = CO_2H; R′ = H

ready aromatization. The study of the behavior of ketone **18b** toward base[11] supports these assumptions.



i, R = Me
ii, R = H

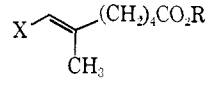


iii

(11) A qualitative study of the reaction between **18b** and potassium hydroxide in aqueous dioxane has revealed the products to be acids and *exo*-7-chloro-1-methyl-2-bicyclo[3.1.1]hepten-6-one (ii) [ir (neat) C=O 5.61 (s), C=C 6.17 μ (w); pmr δ 1.26 (s, 3, Me), 2.9–3.2 (m, 2, methylene), 3.31 (t, 1, J = 3.0 Hz, methine), 4.18 (s, 1, chloromethine), 5.5–5.9 (m, 2, olefinic H's)] whose hydrogenation yielded the known chlorocyclobutanone **8**. Diazomethane treatment of the mixture of acids led predominantly to methyl 1,6-dihydro-3-methylbenzoate [ir (neat) C=O 5.77 (s), C=C 6.26 μ (w); pmr δ 1.75 (t, 3, J = 3.0 Hz, Me), 2.2–2.6 (m, 2, methylene), 3.0–3.6 (m, 1, methine), 3.68 (s, 3, OMe), 5.4–5.9 (m, 3, olefinic H's)] as well as to methyl 3,6-dihydro-3-methylbenzoate [ir (neat) C=O 5.82 (s), C=C 6.09 μ (m); pmr δ 1.14 (d, 3, J = 7.0 Hz, Me), 2.8–3.0 (m, 3, methylene and methine), 3.76 (s, 3, OMe), 5.4–5.9 (m, 2, H-4 and H-5), 6.8–6.9 (m, 1, H-2)], 5-carbomethoxy-4-chloro-3-methylcyclohexene [ir (neat) C=O 5.76 μ (s); pmr δ 1.11 (d, 3, J = 7.0 Hz, Me), 2.2–3.1 (m, 4, methylene and methines), 3.73 (s, 3, OMe), 4.41 (m, 1, chloromethine), 5.63 (m, 2, olefinic H's)], methyl 7-chloro-6-methyl-4,6-heptadienoate [ir (neat) C=O 5.76 (s), C=C 6.18 μ (w); pmr δ 1.71 (d, 3, J = 2.0 Hz, Me), 2.2–2.7 (m, 4, methylenes), 3.68 (s, 3, OMe), 5.3–5.8 (m, 2, H-4 and H-5), 5.9–6.1 (m, 1, H-7)] and a 6-epimer mixture of methyl 1-methyl-2-bicyclo[3.1.0]hexen-6-carboxylate [ir (neat) C=O 5.79 (s), C=C 6.24 μ (w); pmr δ 1.12 (d, 1, J = 3.5 Hz, endo H-6 of major isomer), 2.0–2.3, 2.4–2.7 (m, 3, methylene and methine of major isomer), 1.5–2.1, 2.8–3.1 (m, 4, methylenes and methines of minor isomer), 3.58 (s, 3, OMe of minor isomer), 3.68 (s, 3, OMe of major isomer), 5.4–5.7 (m, 2, olefinic H's of minor isomer), 5.4–6.0 (m, 2, olfinic H's of major isomer)].

The dienoic ester **20c** is a known substance.[12] The structures of the two chloroolefinic esters, **19c** and **21a**, were determined by proton magnetic resonance spectral analysis (see Experimental Section), while the cyclopropanecarboxylic ester epimers, **22a** and **22b**, were analyzed by spectral means (see Experimental Section) and by comparison of their dihydro products **23a** and **23b** with the products of a copper-catalyzed reaction between methyl diazoacetate and 1-methylcyclopentene.[13]

Treatment of 2-dichloromethyl-2-methylcyclohexanone (7) with potassium hydroxide in aqueous dioxane in a manner identical with the base treatment of ketone **12b** yielded the cyclobutanone **8** and a mixture of acids whose methyl esters (from treatment of the acids with diazomethane) were identified as **23a**, **23b**, and **24a**.[14]



24a, R = Me; X = Cl
b, R = H; X = Cl

Three distinct paths of the base-induced reactions of α-dichloromethylketones can be discerned from the above results: (a) one involving 1,3 eliminations leading to acyclic products—**12b** → **21b** and **7** → **24b**—the mechanistic details of which have been discussed already;[5,6,15] (b) another incorporating the homo-Favorskii rearrangement—**12b** → **19b** + **20b**—interrupted in the case of a saturated ketone at the cyclobutanone stage—**7** → **8**; and (c) a third path embodying another rearrangement—**12b** → **22c** + **22d** and **7** → **23c** + **23d**—to be described below. The homo-Favorskii reaction, best exemplified by the production of chloroolefinic acid **19b** and dienoic acid **20b** from cyclohexenone **12b**, required further analysis. Assumption of the dienoic acid being merely a product of a side reaction emanating from the primary product, the chloroolefinic acid, after the initial rearrangement, was invalidated by the discovery of the exposure of **19b** to the conditions of the homo-Favorskii reaction indeed yielding **20b** but also leading to recovery of an appreciable quantity of starting chloro compound. Thus, at least in part, the two acids had been formed from their common precursor, the cyclobutanone **16b**, by independent routes. The separate formation of the dienoic acid lends itself to two interpretations. (a) The immediate progenitor **16b** consists of a mixture of stereoisomers **25** or wholly of **25b** and the latter, possessing a nearly trans diaxial geometry of the vicinal C(1)–C(6) and C(7)–C(1) bonds requisite for facile reaction, undergoes 1,3 elimination reminiscent of the reactions leading to the acyclic acids

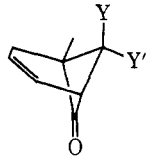
(12) J. Wolinsky, R. Novak, and R. Vasileff, *J. Org. Chem.*, **29**, 3596 (1964).

(13) This reaction was modeled after the reaction of ethyl diazoacetate with cyclopentene [J. Meinwald, S. S. Labana, and M. S. Chadha, *J. Amer. Chem. Soc.*, **85**, 582 (1963)] and with cyclopentadiene [J. Warkentin, E. Singleton, and J. F. Edgar, *Can. J. Chem.*, **43**, 3456 (1965)] and similarly gave predominantly the exo isomer. This fact and comparison of the spectral characteristics of compounds **22** and **23** with those of the cyclopentadiene and cyclopentene adducts, respectively, as well as with those of other cyclopropane systems [W. G. Dauben and W. T. Wipke, *J. Org. Chem.*, **32**, 2976 (1967)] aided in the assignment of the stereochemistry of **22a** and **22b**.

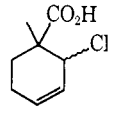
(14) The stereochemistry of **24a** is based on that of the *tert*-butyl ester analog whose stereochemistry has been determined.[6]

(15) M. G. Reinecke, *J. Org. Chem.*, **29**, 299 (1964).

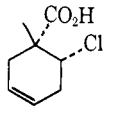
21b and **24b**. (b) Irrespective of the stereochemistry of the cyclobutanone, its ring opening leads to two chloroolefinic acids **19b** and **26**, in analogy with the base cleavage of a variety of β,γ-unsaturated, bicyclic cyclobutanones[4c] and, being an allylic chloride, **26** undergoes rapid elimination of hydrogen chloride. While neither route was verified directly by experiment, path b was shown indirectly to be operative, but not necessarily exclusive.



25a, Y = H; Y′ = Cl
b, Y = Cl; Y′ = H



26

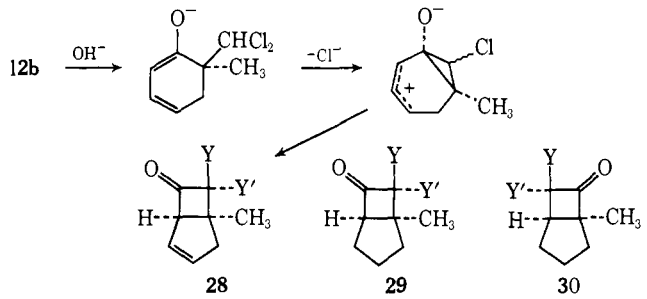


27

One method of distinguishing path a from path b depended on determination of the stereochemistry of the cyclobutanone intermediate. Were the reaction of **12b** → **16b** as stereospecific as the conversion of **7** into cyclobutanone **8** had been shown to be,[6] **25a** would be the intermediate, a fact which would militate against path a. Unfortunately the stability of **8** in aqueous base (see Experimental Section) had not been matched by the behavior of **16b** preventing a study of the stereochemistry of the latter produced in the medium of the homo-Favorskii reaction.[16] However, the ketone could be prepared by a reaction between **12b** and sodium hydride in dimethylformamide.[17] The product proved to be **25a** in view of its transformation into **8** on hydrogenation. Exposure of the cyclobutanone **25a** to the conditions of the homo-Favorskii rearrangement yielded acids **19b** and **20b**. These facts can be interpreted best in terms of route b.[18] Furthermore, the exclusive formation of **19b** and **20b** in the ring opening reaction confirms their being the only homo-Favorskii products among the five acids obtained from the base treatment of ketone **12b** (*vide supra*). Finally, acid **19b** being derived from a cyclobutanone of now known stereochemistry permits assignment of stereostructure **27** to this acid.[19]

The least expected products of the reactions of ketones **12b** and **7** with aqueous base were the cyclopropanecarboxylic acids. If it be assumed that the first phase of their production involves a rearrangement (*vide infra*), first observed in the base treatment of 2-methyl-2-tosyloxymethylcyclohexanone,[4a,20] and the formation of α-chlorocyclobutanones of type **28** and **29**, the cyclopropanes can be envisaged to be products of semibenzilic acid rearrangements of these cyclobutanone intermediates.[21]

While no data substantiated the first of the postulated consecutive dehydrochlorinations, the second could be verified by experiment. Ketone **28a**, previously prepared by acid-catalyzed rearrangement of **25a**,[22] was transformed into a mixture of **22c** and **22d** on exposure to the reaction conditions which led to these acids from ketone **12b**. Ketone **29a**[22] was converted into **23c** and **23d** in a similar manner.



28 **29** **30**

On the assumption of the semibenzilic acid rearrangement being a stereospecific pathway,[23] the stereochemistry of the cyclopropane derivatives reflects the stereochemistry of the chlorocyclobutanones **28** and **29** formed in the initial rearrangement and their ease of isomerization in the alkaline medium. Isolation of more than one cyclopropanecarboxylic acid from the rearrangement of **28a** as well as of **29a** indicated that isomerization of these ketones had occurred. But in the absence of a study of the behavior of their epimers, **28b** and **29b**, respectively, toward base, it is impossible to ascertain how far the isomerization had progressed toward equilibrium prior to the semibenzilic acid rearrangement. Base treatment of a related set of epimeric ketones,[22] **30a** and **30b**, yielded acids **23c** and **23d** in the same exo–endo ratio of 0.8 indicating that full preequilibrium of ketones prior to rearrangement had been attained in these cases.

The experimental data accumulated thus far indicated that the first phase of the homo-Favorskii rearrangement, the cyclobutanone formation, can take place along two paths, *e.g.*, bicycloheptanones of both the [3.1.1] and [3.2.0] types had been intermediates in the base-induced reaction of ketone **12b**. In order to gain more insight into the details of this part of the rearrangement, a study of the reactions of keto tosylate **31a** and its enol ether **32b** with aqueous base under the conditions of the reactions of **12b** and **7** was undertaken. While initially **31a** had been reported to be converted into bicycloheptanone **33**,[24] it later was shown to yield both **33** and **34**.[4a,20] Now, however, solvolysis of **31a** in alkaline dioxane–water led to bicycloheptanones **33** and **34** as well as 2-methylcyclohexanone (**31b**). Solvolysis of the enol ether **32b** gave only the ketones **33** and **34**. The bicyclo[3.2.0]heptanone **34** was the preponderant

(16) In contrast to the behavior of **16b**, base-induced ring cleavage of its double bond isomer ii is slow enough to permit isolation of the latter at the end of a homo-Favorskii reaction.[11]

(17) It is noteworthy that despite the similarity between the sodium dienolate intermediate in this reaction and the magnesium dienolate intermediate in the conversion of **17** into **18a**, the former had undergone intramolecular chloride displacement, while the latter had remained inert. This contrast may have been due to the insolubility of the magnesium dienolate in ether as well as the much lower polarity of ether than that of dimethylformamide. Indeed, when the intermediate magnesium salt from the Grignard addition of **17** was transferred from its ether suspension into a dimethylformamide solution a cyclobutanone epimer mixture resulted.

(18) Solvolysis of the chloride, assisted by the homoallylic double bond, in **25a** or, preferably, its ketone hydrate, followed by ring cleavage, may not be overlooked as an alternate route for the transformation of **25a** into **20b**.

(19) Base cleavage of ii yielded predominantly 1,6-dihydro-3-methylbenzoic acid.[11]

(20) (a) K. B. Wiberg and G. W. Klein, *Tetrahedron Lett.*, 1043 (1963); (b) K. B. Wiberg, *Advan. Alicyclic Chem.*, 2, 185 (1968); (c) J. Julia and C. Gueremy [*Bull. Soc. Chim. Fr.*, 2994 (1963)] carried out the reaction with 2-methyl-2-bromomethylcyclohexanone.

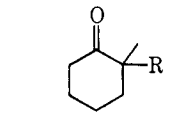
(21) J. Salaun and J. M. Conia, *ibid.*, 3735 (1968), and references therein; P. R. Brook, J. M. Harrison, and A. J. Duke, *Chem. Commun.*, 589 (1970); V. R. Fletcher and A. Hassner, *Tetrahedron Lett.*, 1071 (1970).

(22) W. F. Erman, R. S. Treptow, E. Wenkert, and P. Bakuzis, *J. Amer. Chem. Soc.*, **93**, 657 (1971).

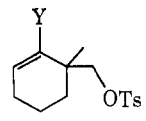
(23) P. R. Brook, *Chem. Commun.*, 565 (1968); P. R. Brook and A. J. Duke, *ibid.*, 652 (1970).

(24) E. Wenkert and D. P. Strike, *J. Org. Chem.*, 27, 1833 (1962).

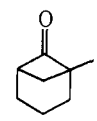
product of both reactions, the [3.2.0]:[3.1.1] ratio of the reaction of **31a**[25] being 1.3 and that of **32b** 4.3. Comparison of qualitative rates of reaction showed an order of **31a** ≫ **32a**[26] ≫ **32b**. This observation and the fact that no reaction occurred on attempted solvolysis of **31a** at pH 7 showed that neither **31a** nor its enol **32c**, but its enolate **32d** was the reacting species in the solvolysis of the keto tosylate.



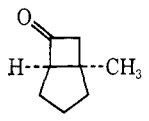
31a, R = CH_2OTs
b, R = H
c, R = CH_2OH



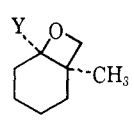
32a, Y = H
b, Y = OMe
c, Y = OH
d, Y = O^-



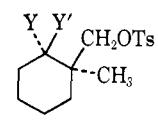
33



34



35a, Y = OH
b, Y = H

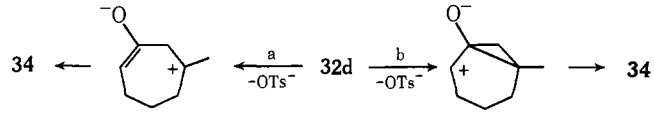


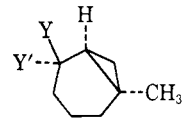
36a, Y = OH; Y′ = H
b, Y = H; Y′ = OH

Formation of 2-methylcyclohexanone (**31b**), the minor product of the solvolysis of the tosylate **31a**, is explained best by assuming the intermediacy of ketol **31c** and its retroaldol reaction. Formation of the ketol, in turn, is unlikely to occur by direct hydroxide displacement at the neopentyl carbon site of the keto tosylate **31a** or even its enolate **32d** in view of lack of such reaction in the solvolysis of the enol ether **32b**. Instead, hydration of the keto group of **31a**[27] followed by intramolecular tosylate displacement can be envisaged to yield the hemiketal **35a** whose unravelling leads to the ketol **31c**.[28] Although no direct evidence for this mechanism was obtained, the likelihood of its reality was strengthened by the observation of the hydrolysis of a mixture of hydroxy tosylates **36**, prepared by reduction of **31a** with sodium borohydride, in alkaline dioxane–water yielding oxetane **35b**.

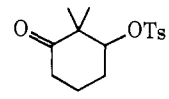
Two possible paths emerge for the unusual rearrangement of enolate **32d** into ketone **34** (*vide infra*): (a) alkenyl migration followed by zwitterion collapse;[20a] (b) homoallyl → cyclopropylcarbinyl → cyclobutyl cation rearrangements.[29] Path a is least likely, since 1,2 migration of the methyl group involving a homoallyl-to-allyl cation change would be preferred greatly over migration of the alkenyl moiety and the intermediate cycloheptyl zwitterion is of too low a ring size for efficient π-bond p-orbital overlap needed for construction of the bicyclo[3.2.0] system. Path b presents one dilemma—carbon–carbon bond formation at the least electron-rich site of an enolate. However, if this unprecedented behavior of an enolate as a homoallyl system is accepted, the subsequent cyclopropylcarbinyl-to-cyclobutyl rearrangement finds precedent in the acid-induced transformation of alcohols **37** into ketone **34**.[30]

The conversion of enol ether **32b** into ketone **34** can be visualized to follow path b also, but requires hydration of the final methoxycarbonium ion and loss of methanol of the product. The slowness of the solvolysis of the enol ether in comparison to that of the olefin **32a**[26] is ascribable to the unfavorable inductive effect of the methoxy group, while the contrasting rapidity of the solvolysis of the enolate may be due to the proximity of the oxy anion to the incipient carbonium ion site.





37a, Y = OH; Y′ = H
b, Y = H; Y′ = OH



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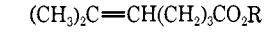


39a, R = H
b, R = Me

Experimental Section

Melting points were determined on a Reichert micro-hot stage and are uncorrected. Infrared spectra were obtained on Perkin-Elmer Model 137 and 137B spectrophotometers. Proton magnetic resonance spectra of deuteriochloroform solutions (unless otherwise noted) containing tetramethylsilane (δ = 0 ppm) as internal standard were taken on Varian Associates Model A-60 and HA-100 spectrometers.

1,4-Dimethyl-4-carboxy-5-chloro-1-cyclohexene (19a) and 2,5-Dimethyl-5-carboxy-1,3-cyclohexadiene (20a). Repetition of the Auwers reaction between dienone **17** and methylmagnesium iodide[8] gave an 80% yield of a *ca.* 4:3 epimer mixture of 2,5-dimethyl-2-dichloromethyl-3-cyclohexenone (**18a**): bp 68–70° (0.25 Torr); ir (neat) C=O 5.81 μ (s); pmr δ 1.14 (d, 3, J = 7.0 Hz, C(5)–Me), 1.31 (s, 3, C(2)–Me of minor component), 1.32 (s, 3, C(2)–Me of major component), 2.1–2.9 (m, 3, CH_2 and CH), 5.8–6.1 (m, 2, olefinic H's), 6.08 (s, 1, $CHCl_2$ of minor component), 6.13 (s, 1, $CHCl_2$ of major component).

Repetition of the Auwers isomerization of **18a**[8] produced a 77% yield of 3,6-dimethyl-6-dichloromethyl-2-cyclohexenone (**12a**): mp 39–41°; bp 81° (0.30 Torr); ir (neat) C=O 6.00 (s), C=C 6.12 μ (m); pmr δ 1.22 (s, 3, Me), 1.97 (d, 3, apparent J = 2.0 Hz, olefinic Me), 1.9–2.5 (m, 4, methylenes), 5.79 (m, 1, olefinic H), 6.28 (s, 1, $CHCl_2$).

Repetition of the Auwers reaction betwen ketone **12a** and ethanolic potassium hydroxide[7] yielded two crystalline acids. One was **19a**: mp 142–144° (lit.[7] mp 141.5°); pmr δ 1.28 (s, 3, Me), 1.69 (m, 3, olefinic Me), 1.7–3.1 (m, 4, methylenes), 4.43 (t, 1, apparent J = 3.0 Hz, chloromethine), 5.40 (m, 1, olefinic H). The second acid was **20a**: mp 40–42° (lit.[7] mp 40–42°); ir (melt) OH 2.8–3.4 (s), 3.75 (m), C=O 5.86 (s), C=C 6.26 μ (w); pmr δ 1.28 (s, 3, Me), 1.71 (q, 3, apparent J = 2 Hz, olefinic Me), pair of doublets of multiplets 2.21 (m, 1, J = 17.5 Hz, H-6 cis to Me), 2.70 (m, 1, J = 17.5 Hz, H-6 trans to Me), 5.44 (m, 1, H-1), 5.81 (d, 2, J = 2.0 Hz, H-3 and H-4).

Anal. Calcd for $C_9H_{12}O_2$: C, 71.03; H, 7.95. Found: C, 70.92; H, 7.96.

Iodolactonization of 110 mg of acid **19a** according to the procedure of Rondestvedt and Ver Nooy[31] yielded 122 mg of crude

(25) Change of the solvent from dioxane–water to *tert*-butyl alcohol suppressed drastically the production of **34** (P. Bakuzis, unpublished observation; *cf.* also ref 6).

(26) E. Albers, M. S. Dissertation, Indiana University, 1969.

(27) The hydrate is also the reacting species in the 1,3 elimination (*cf.* 7 → **24b**) leading to acid product which in the case of the hydrolysis of **31a** was not investigated. In an attempt to prepare the highly strained bicyclo[2.2.0]hexanone or bicyclo[2.1.1]hexanone systems the keto tosylate **38** was exposed to alkaline hydrolysis (see Experimental Section), but only the 1,3 elimination product **39a** was produced.

(28) Similarly, one of the products of methoxide interaction with an α-arenesulfonoxymethyl-α-methylbutyraldehyde has been shown to be 2-methoxy-3,3-diethyloxetane [J. Jančuler, F. Nerdel, D. Frank, and G. Barth, *Chem. Ber.*, **100**, 715 (1967)].

(29) P. C. Mukharji, P. K. Sen Gupta, and G. S. Sambamurti, *Tetrahedron*, **25**, 5287 (1969).

(30) E. Wenkert, R. A. Mueller, E. J. Reardon, Jr., S. S. Sathe, D. J. Scharf, and G. Tosi, *J. Amer. Chem. Soc.*, **92**, 7428 (1970).

(31) C. R. Rondestvedt and C. D. Ver Nooy, *ibid.*, 77, 4878 (1955).

product. Crystallization from hexane–carbon tetrachloride gave crystalline chloroiodolactone: mp 103–105°; ir (Nujol) C=C 5.62 μ (s).

Anal. Calcd for $C_9H_{12}O_2ClI$: C, 34.37; H, 3.88. Found: C, 34.38; H, 3.87.

Repetition of the Auwers reaction between acid **20a** and oxalic acid[7,9] yielded 1,4-dimethyl-1,3-cyclohexadiene: pmr (CCl_4) δ 1.73 (broad s, 6, methyls), 2.06 (m, 4, methylenes), 5.46 (m, 2, olefinic H's). A solution of the latter (from 180 mg of **20a**) and 80 mg of maleic anhydride in a mixture of carbon tetrachloride and benzene was refluxed for 8 hr. Evaporation of the solvents left 168 mg of a solid whose crystallization from ether–hexane yielded a Diels–Alder adduct: mp 57–59° (lit.[32] mp 58°); ir (CCl_4) C=O 5.32 (w), 5.42 (w), 5.60 μ (s); pmr δ 1.43 (m, 4, methylenes), 1.52 (s, 6, methyls), 2.85 (s, 2, methines), 5.97 (s, 2, olefinic H's).

Treatment of 6-Dichloromethyl-6-methyl-2-cyclohexenone (12b) with Alkali. A solution of 4.8 g of potassium hydroxide in 15 ml of water was added over a 5-min period to a stirring solution of 6.3 g of **12b** in 30 ml of purified dioxane and 10 ml of water under nitrogen at 75°. After 1.5 hr, water was added and the solution was extracted with ether. The extract was washed with water, dried over sodium sulfate, and evaporated. The neutral residue, 0.90 g, was not investigated further. The basic, aqueous solution from the extraction was acidified and extracted with ether. Evaporation of the extract yielded 4.3 g of crude acids whose chromatography on silica gel and elution with 20:1 hexane–ether gave 1.4 g of dienoic acid. Crystallization of the latter from hexane produced 1-methyl-2,4-cyclohexadienecarboxylic acid (**20b**): mp 61–63°; ir (Nujol) OH 2.9–3.3 (m), 3.75 (w), C=O 5.90 (s), C=C 6.32 μ (w); pmr δ 1.30 (s, 3, Me), pair of doublets of multiplets 2.28 (m, 1, J = 18.0 Hz, H-6 cis to Me), 2.75 (m, 1, J = 18.0 Hz, H-6 trans to Me), 5.88 (m, 4, olefinic H's).

Anal. Calcd for $C_8H_{10}O_2$: C, 69.54; H, 7.30. Found: C, 69.09; H, 7.26.

Elution with 20:1 to 10:1 hexane–ether gave 0.59 g of chloro acid whose crystallization from hexane afforded 6-chloro-1-methyl-3-cyclohexanecarboxylic acid (**19b**): mp 122–124°; OH 3.0–3.3 (m), 3.75 (w), 5.89 μ (s); pmr δ 1.30 (s, 3, Me), 1.7–3.1 (m, 4, methylenes), 4.44 (t, 1, J = 3.0 Hz, chloromethine), 5.65 (m, 2, olefinic H's); double resonance, irradiation at 1.82 ppm simplified the olefinic signal but left the chloromethine signal unaffected; irradiation at 5.65 ppm left the chloromethine signal unaffected.

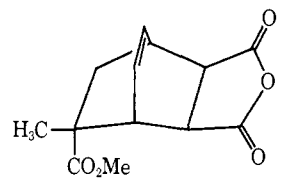
Anal. Calcd for $C_8H_{11}O_2Cl$: C, 55.05; H, 6.36. Found: C, 55.05; H, 6.47.

A mixture of 85 mg of acid **20b** and 10 mg of 10% palladium/charcoal in 2 ml of ethanol was hydrogenated at room temperature and atmospheric pressure. The mixture was filtered and the filtrate evaporated. The residue, 83 mg, was 1-methylcyclohexanecarboxylic acid: mp 36–38°; spectra identical with those of an authentic sample.[33]

A solution of 0.70 g of acid **20b** in 10 ml of ether was poured into an ethereal solution of excess diazomethane and evaporated after 1 hr. A solution of the residual ester **20c** [ir (neat) C=O 5.77 (s), C=C 6.32 μ (w); pmr δ 1.25 (s, 3, Me), pair of doublets of multiplets 2.25 (m, 1, J = 18.0 Hz, H-6 cis to Me), 2.72 (m, 1, J = 18 Hz, H-6 trans to Me), 3.69 (s, 3, OMe), 5.85 (m, 4, olefinic H's)], 0.50 g, and 0.30 g of maleic anhydride in 5 ml of benzene was refluxed for 36 hr and then evaporated. Chromatography of the residue on silica gel and elution with 1:1 benzene–ether gave 0.70 g of a solid whose crystallization from benzene yielded the Diels–Alder adduct **38**: mp 113–114° (lit.[22] mp 113.5–115°); ir (Nujol) C=O 5.41 (m), 5.62 (s), 5.81 μ (s); pmr δ 1.16 (q, 1, J = 13.0, 2.6 Hz, methylene H cis to Me), 1.18 (s, 3, Me), 2.50 (q, 1, J = 13.0, 2.3 Hz, methylene H trans to Me), 3.18 (d, 2, apparent J = 1.5 Hz, α-ketomethines), 3.25 (m, 2, bridgehead methines), 3.75 (s, 3, OMe), 6.31 (q, 2, J = 4.0, 2.5 Hz, olefinic H's).

Anal. Calcd for $C_{13}H_{14}O_5$: C, 62.39; H, 5.64. Found: C, 62.66; H, 5.56.

A mixture of 450 mg of **38** and 50 mg of 10% palladium/charcoal in 5 ml of ethyl acetate was hydrogenated at room temperature and atmospheric pressure. The usual work-up gave 451 mg of solid whose chromatography on Florosil, sublimation at 85° (0.1 Torr), and crystallization from ether–chloroform yielded *endo*-5-carbomethoxy-*exo*-5-methylbicyclo[2.2.2]octan-*exo*-2,3-dicarboxylic anhydride: mp 116.5–117°; ir (Nujol) C=O 5.40 (m), 5.62 (s), 5.81 μ (s); pmr δ 1.1–1.7 (m, 6, methylenes), 1.39 (s, 3, Me), 2.2–2.5 (m, 2, methines), 3.10 (m, 2, α-ketomethines).



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Anal. Calcd for $C_{13}H_{16}O_5$: C, 61.89; H, 6.39. Found: C, 62.17; H, 6.40.

A solution of 80 mg of acid **19b** in 10 ml of ether was poured into an ethereal solution of excess diazomethane and evaporated after 1 hr. Distillation of the residue, 78 mg, gave liquid methyl 6-chloro-1-methyl-3-cyclohexenecarboxylate (**19c**): ir (neat) C=O 5.75 (s), C=C 6.03 μ (w); pmr δ 1.22 (s, 3, Me), 1.7–3.1 (m, 4, methylenes), 3.72 (s, 3, OMe), 4.43 (t, 1, J = 3.0 Hz, chloromethine), 5.62 (m, 2, olefinic H's).

Anal. Calcd for $C_9H_{13}O_2Cl$: C, 57.30; H, 6.95. Found: C, 57.14; H, 6.86.

A mixture of 50 mg of **19c** and 6 mg of platinum oxide in 5 ml of methanol was hydrogenated at room temperature and atmospheric pressure. The usual work-up and distillation of the product, 48 mg, yielded oily methyl 2-chloro-1-methylcyclohexanecarboxylate: ir (neat) C=O 5.77 μ (s); pmr δ 1.31 (s, 3, Me), 1.2–2.3 (m, 8, methylenes), 4.23 (m, 1, chloromethine).

Anal. Calcd for $C_9H_{13}O_2Cl$: C, 56.84; H, 7.90. Found: C, 57.05; H, 7.95.

A solution of 5.00 g of ketone **12b** in 10 ml of dioxane was added over a 4-hr period to a stirring solution of 5.0 g of potassium hydroxide in 45 ml of water and 35 ml of dioxane under nitrogen at 85°. After an additional hour, the solution was worked up as above. A solution of the acidic products, 3.97 g, in 25 ml of ether was poured into a solution of excess diazomethane in 100 ml of ether and the excess reagent was decomposed by the addition of 10% hydrochloric acid 0.5 hr later. The ether solution was washed with 5% potassium hydroxide solution and water, dried over magnesium sulfate, and evaporated. Distillation of the highly volatile residue through an 8-in. vacuum-jacketed column gave a fraction [bp 60–62° (4.0 Torr)], 2.15 g, whose pmr analysis at 100 MHz revealed three components [*ca.* 75% **20c**, 19% **22a**, and 6% **22b**] unseparable by gas-phase chromatography, and a fraction [bp 71–73° (0.5 Torr)], 1.00 g, whose gpc analysis revealed five more components. The low-boiling fraction was treated with maleic anhydride as above and the product mixture chromatographed on silica gel. While elution with 1:1 benzene–ether yielded 2.15 g of **38**, earlier 9:1 hexane–ether eluates led to 0.32 g of a mixture of **22a** and **22b** which was separated by preparative gpc on a 20 ft × 3/8 in. 30% SE-30 column at 130° with 140 ml/min helium flow. The material with 42-min retention time was liquid methyl *exo*-5-methyl-2-bicyclo[3.1.0]hexen-6-carboxylate (**22a**): ir ($CDCl_3$) cyclopropyl H, 1.678 (w), (neat) C=O 5.78 (s), C=C 6.23 μ (w); pmr δ 1.10 (d, 1, J = 3.0 Hz, α-ketomethine), 1.43 (s, 3, Me), 2.28 (m, 1, methine or a H of methylene), 2.52 (m, 2, methylene or methine and H of methylene), 3.68 (s, 3, OMe), 5.5 and 5.9 (m, 2, olefinic H's).

Anal. Calcd for $C_9H_{12}O_2$: C, 71.03; H, 7.95. Found: C, 70.83; H, 8.10.

The material with 36-min retention time was liquid methyl *endo*-5-methyl-2-bicyclo[3.1.0]hexen-6-carboxylate (**22b**): ir ($CDCl_3$) cyclopropyl H 1.6 (w), (neat) C=O 5.79 (s), C=C 6.24 μ (w); pmr δ 1.33 (s, 3, Me), 1.72 (d, 1, J = 8.0 Hz, α-ketomethine), 2.13 (q, 1, J = 8.0, 3.0 Hz, methine), 2.31 (d, 1, J = 18.0 Hz, methylene endo H), 2.87 (q, 1, J = 18.0, 3.0 Hz, methylene exo H), 3.58 (s, 3, OMe), 5.62 (m, 2, olefinic H's). (J values obtained from double resonance by irradiation at 5.62 ppm.) Chromatography of 0.90 g of the high-boiling fraction of esters on silica gel and elution with 30:1 hexane–ether gave two sets of mixtures whose pmr analysis revealed the earlier eluate, 0.63 g, to be predominantly **19c** and to contain some **21a** and the later mixture, 75 mg, to be mostly **21a**. Purification of the former was accomplished by way of preparative gpc on a 10 ft × 3/8 in. 30% XF-1150 column at 185° with 200 ml/min helium flow, collection of material, 0.35 g, with retention time of 24–33 min, two chromatographies on silica gel and distillation of the proper eluates, 0.24 g, at bath temperature 70° (0.7 Torr); spectra of **19c** were identical with

(32) K. Alder and H. van Brachel, *Justus Liebigs Ann. Chem.*, **608**, 215 (1957).

(33) E. Wenkert, P. Bakuzis, and F. Haviv, *J. Org. Chem.*, **35**, 2092 (1970).

those of the specimen above. Purification of all fractions containing **21a** was executed by chromatography on silica gel and elution with 65:1 hexane–ether. Distillation of the eluates, 58 mg, yielded liquid methyl 7-chloro-6-methyl-2,6-heptadienote (**21a**): ir (neat) C=O 5.81 (s), C=C 6.03 μ (m); pmr δ 1.78 (d, 3, J = 1.5 Hz, Me), 2.1–2.5 (m, 4, methylenes), 3.73 (s, 3, OMe), 5.83 (d of m, 1, J = 16.0 Hz, H-2), 5.85 (m, 1, H-7), 6.89 (d of t, 1, J = 16.0, 6.0 Hz, H-3); double resonance, irradiation at 2.32 ppm made 5.85 and 6.89 signals doublets; irradiation at 5.77 ppm made the 6.94 signal a broad triplet.

Anal. Calcd for $C_9H_{13}O_2Cl$: C, 57.30; H, 6.95. Found: C, 57.22; H, 7.17.

Methyl 1-Methylbicyclo[3.1.0]hexane-6-carboxylates (23a and 23b). Methyl diazoacetate, 3.1 g, was added slowly over a period of 2 hr to a refluxing mixture of 0.10 g of copper powder in 2.5 g of 1-methylcyclopentene under nitrogen and the heating continued for another 1.5 hr. Filtration of the cooled mixture through activity II alumina and elution with 1:1 hexane–ether gave 0.90 g of a sweet-smelling oil. Separation of the mixture by preparative gpc on a 20 ft × $^3/_8$ in. 30% SE-30 column at 125° with 140 ml/min helium flow yielded 98 mg of an ester with retention time of 86 min and 230 mg of an isomer with retention time of 115 min. The latter compound was the liquid exo isomer (**23a**): ir (neat) cyclopropyl H 3.27 (w), C=O 5.78 μ (s); pmr δ 1.31 (s, 3, Me), 1.4–2.0 (m, 8, methylenes and methines), 3.63 (s, 3, OMe).

Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.29; H, 9.27.

The first substance was the liquid endo isomer **23b**: ir (neat) cyclopropyl H 3.28 (w), C=O 5.78 μ (s); pmr δ 1.27 (s, 3, Me), 1.3–2.1 (m, 8, methylenes and methines), 3.63 (s, 3, OMe).

Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H,9.15. Found: C, 70.09; H, 9.20.

A mixture of 40 mg of **22a** and 4 mg of platinum oxide in 3 ml of methanol was hydrogenated at atmospheric pressure and room temperature. After cessation of hydrogen uptake, the mixture was filtered, the filtrate evaporated, and the resultant residual oil, 38 mg, recognized as **23a** by the identity of its infrared and pmr spectra with those of an above sample of **23a**. A similar hydrogenation of 35 mg of **22b** yielded 33 mg of **23b**.

Treatment of 2-Dichloromethyl-2-methylcyclohexanone (7) with Alkali. A solution of 10.0 g of **7** in 20 ml of dioxane was added over a 4-hr period to a solution of 10.0 g of potassium hydroxide in 70 ml of dioxane and 90 ml of water at 85° under nitrogen. After another 2 hr, the solution was cooled, diluted with 250 ml of water, and extracted exhaustively with pentane. The extract was washed with saturated brine solution, dried, and concentrated at atmospheric pressure through an 8-in. vacuum-jacketed column. Distillation of the residue gave 3.67 g of *exo*-7-chloro-1-methylbicyclo-[3.1.1]heptan-6-one (**8**): bp 60° (0.7 Torr); spectra identical with those of an authentic sample.[6]

The aqueous fraction from the extraction was concentrated under reduced pressure to a *ca.* 50-ml volume, 10% hydrochloric acid was added until pH 5, and the mixture was extracted with ether. The extract was washed with saturated brine solution, dried, and evaporated. A solution of the acid residue, 4.62 g, in 10 ml of ether, was added to an ethereal solution of excess diazomethane. The excess reagent was destroyed by cautious addition of dilute hydrochloric acid and the ether solution was washed with water, dried, and concentrated at atmospheric pressure through an 8-in. vacuum-jacketed column. Distillation of the residue yielded two fractions: bp 75–77° (3.8 Torr), 519 mg; bp 75° (0.4 Torr), 3.19 g. Analysis of the low-boiling fraction by gpc on a 10 ft × $^3/_8$ in. 30% QF-1 column at 160° with 140 ml/min helium flow showed it to contain 80% of a substance of 11.3-min retention time and 20% of another of 9.6-min retention time. Isolation by preparative gpc on a 10 ft × $^3/_8$ in. 30% FFAP column at 120° and identification by infrared, pmr, and gpc comparison with authentic specimens revealed the major product to be **23a** and the minor component to be **23b**. Analysis of the high-boiling fraction by gpc (QF-1 column at 171°) showed it to consist of 92% of a compound of 25-min retention time, 3% of an unidentified substance (23-min retention time), 4% **23a**, and 1% **23b**. Purification of the major component by preparative gpc on a QF-1 column and distillation yielded liquid methyl 7-chloro-6-methyl-6-heptenoate (**24a**): infrared (neat) C=O, 5.75 (s), C=C 6.08 μ (m); pmr δ 1.4–1.7 (m, 4, methylenes), 1.77 (d, 3, J = 2.0 Hz, Me), 1.9–2.5 (m, 4, α-keto and allyl H's), 3.65 (s, 3, OMe), 5.79 (q, 1, J = 2.0 Hz, olefinic H).

Anal. Calcd for $C_9H_{13}O_2Cl$: C, 56.69; H, 7.93. Found: C, 56.74; H, 7.91.

A mixture of 560 mg of **24a** and 100 mg of 10% palladium-charcoal in 2 ml of ethyl acetate was hydrogenated at room temperature and atmospheric pressure. After cessation of hydrogen uptake, the mixture was filtered and the filtrate diluted with ether and washed with water. The organic solution was dried and evaporated. Purification of the residue, 440 mg, by preparative gpc on a 10 ft × $^3/_8$ in. 30% FFAP column at 110° with 160 ml/min helium flow (retention time 32 min) and distillation gave methyl isoenanthate: ir (neat) C=O 5.75 μ (s); pmr δ 0.87 (d, 6, J = 6.0 Hz, methyls), 1.0–1.8 (m, 7, methylenes and methine), 2.30 (m, 2, α-ketomethylene), 3.63 (s, 3, OMe).

Anal. Calcd for $C_9H_{18}O_2$: C, 68.31; H, 11.47. Found: C, 68.00; H, 11.35.

7-*exo*-Chloro-5-methyl-2-bicyclo[3.1.1]hepten-6-one (16b). A solution of 5.00 g of ketone **12b** in 10 ml of thoroughly dried dimethylformamide was added over a 3-hr period to a stirring suspension of 1.4 g of sodium hydride (50% oil dispersion) in 50 ml of dimethylformamide at room temperature under nitrogen. After another hour, the mixture was poured into 125 ml of water and extracted with ether. The aqueous solution was acidified with 10% hydrochloric acid and extracted with ether. The extract was dried and evaporated. Pmr analysis of the residue, 0.80 g, showed it to consist mostly of dimethylformamide and acid **20b**. The ether extract of neutral products was washed with water, dried, and concentrated by solvent removal through an 8-in. vacuum-jacketed column. Distillation of the residue yielded 1.68 g of ketone **16b**: bp 70° (0.75 Torr); ir (neat) C=O 5.59 (s), C=C 6.13 μ (w); pmr δ 1.21 (s, 3, Me), 2.93 (q, 2, J = 3.0, 2.0 Hz, methylene), 3.31 (d, 1, J = 7.5 Hz, methine), 4.20 (s, 1, chloromethine), 5.73 (d of t, 1, J = 8.0, 3.0 Hz, H-3), 6.05 (d of d of t, 1, J = 8.0, 7.5, 2.0 Hz, H-2).

Anal. Calcd for C_8H_9OCl: C, 61.35; H, 5.79. Found: C, 61.43; H, 5.86.

A mixture of 88 mg of **16b** and 10 mg of 10% palladium/charcoal in 10 ml of ethanol was hydrogenated at room temperature and atmospheric pressure. The usual work-up led to 88 mg of ketone **8**, spectrally identical with an authentic sample.[5,6]

A solution of 138 mg of **16b** and 64 mg of potassium hydroxide in 3 ml of 1:1 water–dioxane was stirred at 85° under nitrogen for 1 hr. A solution of 10% sodium hydroxide saturated with salt was added until pH 10 was reached and the mixture extracted with ether. The usual work-up of this extract yielded 52 mg of starting ketone. Acidification of the aqueous, basic solution to pH 4 with 10% hydrochloric acid, extraction with 1:1 methylene chloride–ether, washing of the extract with saturated brine solution, drying, and evaporation gave 78 mg of a mixture of acids identified by pmr spectroscopy as 35% **19b** and 65% **20b**. A similar run with 325 mg of **16b** and 300 mg of potassium hydroxide in 6 ml of 1:1 dioxane–water at 85° under nitrogen for 1.5 hr and similar work-up led to no starting ketone, but only 260 mg of acidic products. Their esterification with diazomethane and gpc analysis of the resultant esters on a 30% XF-1150 column indicated the product composition to be 37% **19c** and 63% **20c**.

A solution of 50 mg of **19b** and 50 mg of potassium hydroxide in 1 ml of 1:1 dioxane–water was stirred at 85° under nitrogen for 3 hr. Work-up as above gave 44 mg of acid product shown by pmr to be a 1:1 mixture of **19b** and **20b**. Resubmittal of this mixture to a second base treatment under identical conditions produced 40 mg of a 2:1 mixture of **20b** and **19b**, respectively.

A solution of 1.00 g of ketone **8** and 1.0 g of potassium hydroxide in 18 ml of 1:1 dioxane–water was stirred at 85° under nitrogen for 3 days. Work-up as above yielded 0.74 g of starting ketone and 0.21 g of unidentified acidic material.

Treatment of 6-*exo*-Chloro-5-methyl-2-bicyclo[3.2.0]hepten-7-one (28a) with Alkali. A solution of 345 mg of ketone **28a**[22] and 320 mg of potassium hydroxide in 7 ml of 1:1 dioxane–water was stirred at 85° under nitrogen for 3 hr. Work-up as above gave 302 mg of a mixture of acids whose pmr analysis showed it to contain **22c** and **22d** in a ratio of 3. (This ratio unfortunately varied over several runs.) Chromatography on silica gel (50–200 mesh) and elution with 20:1 pentane–ether yielded 170 mg of a solid whose crystallization from hexane gave acid **22c**: mp 60–61°; ir (Nujol) OH 2.8–3.3 (m), C=O 5.91 μ (s); pmr δ 1.10 (d, 1, J = 3.0 Hz, α-ketomethine), 1.48 (s, 3, Me), 2.2–2.7 (m, 3, methylene and methine), 5.4–5.6, 5.8–6.1 (m, 2, olefinic H's).

Anal. Calcd for $C_8H_{10}O_2$: C, 69.55; H, 7.30. Found: C, 69.62; H, 7.37.

Diazomethane treatment of **22c** as above yielded **22a** spectrally identical with a sample described above. Further elution with 6:1 pentane–ether afforded 86 mg of a solid whose crystallization

from hexane led to acid **22d**: mp 54–55°; ir (Nujol) OH 2.8–3.3 (m), C=O 5.89 μ (s); pmr δ 1.32 (s, 3, Me), 1.71 (d, 1, J = 8.0 Hz, α-ketomethine), 2.1–3.1 (m, 3, methylene and methine), 5.5–5.8 (m, 2, olefinic H's).

Anal. Calcd for $C_8H_{10}O_2$: C, 69.55; H, 7.30. Found: C, 69.45; H, 7.50.

Diazomethane treatment of **22d** as above yielded **22b** spectrally identical with ester **22b** described above. A solution of 28 mg of exo acid **22c** and 29 mg of potassium hydroxide in 0.7 ml of 1:1 dioxane–water was stirred at 85° under nitrogen for 3 hr. Work-up as above gave 26 mg of starting material shown by pmr analysis to contain no epimeric acid.

Treatment of Ketones 29a, 30a, and 30b with Alkali. A solution of 78 mg of ketone **29a** and 71 mg of potassium hydroxide in 1.4 ml of 1:1 dioxane–water was stirred at 85° under nitrogen for 3 hr. Work-up as above yielded 66 mg of crystalline acids whose esterification with diazomethane as above afforded 70 mg of a mixture of esters **23a** and **23b** shown by gpc analysis (QF-1 column) to constitute an exo–endo ratio of 7. A solution of 60 mg of ketone **30a** and 55 mg of potassium hydroxide in 1.1 ml of 1:1 dioxane–water was stirred at 85° under nitrogen for 3 hr. Work-up as above gave 49 mg of acids whose treatment with diazomethane as above led to 42 mg of a mixture of esters **23a** and **23b** shown by gpc analysis (QF-1 column) to be present in an exo–endo ratio of 0.8. The analysis also revealed 5% of a substance of unknown constitution. A solution of 110 mg of ketone **30b** and 100 mg of potassium hydroxide in 2 ml of 1:1 dioxane–water was stirred at 85° under nitrogen for 3 hr. Work-up as above gave 92 mg of acids identified by pmr analysis to be a 1:1 mixture of **23c** and **23d**. Gpc analysis of their esters (diazomethane treatment) showed **23a** and **23b** to be present in a ratio of 0.8.

1-Methyl-2-ketocyclohexylcarbinyl (31a) and 1-Methyl-2-methoxy-2-cyclohexenylcarbinyl (32b) *p*-Toluenesulfonates. A solution of 5.5 g of methyl 1-methyl-2-ketocyclohexanecarboxylate, 8 ml of methyl orthoformate, and 12 drops of concentrated sulfuric acid in 30 ml of dry methanol was left standing at room temperature for 2 days. It then was diluted with 100 ml of ether and washed with sodium bicarbonate solution. The washings were extracted with ether and the combined ether solutions dried and evaporated. Distillation of the residue, 5.9 g, yielded 4.9 g of pale yellow, liquid methyl 1-methyl-2-methoxy-2-cyclohexenecarboxylate: bp 60–62° (0.75 Torr); ir (neat) C=O 5.75 (s), C=C 6.01 μ (s); pmr δ 1.32 (s, 3, Me), 1.4–2.4 (m, 6, methylenes), 3.48 (s, 3, OMe), 4.71 (q, 1, J = 4.0, 3.0 Hz, olefinic H). A mixture of 5.0 g of this ester and 0.96 g of lithium aluminum hydride in 100 ml of dry ether was stirred at room temperature under nitrogen for 4 hr. Moist sodium sulfate was added and the mixture was filtered. The filtrate was washed with sodium bicarbonate solution, dried, and evaporated. The oily residue, 3.9 g, decomposed on distillation and hydrolyzed on attempted chromatography on silica gel. Hence the product, 1-methyl-2-methoxy-2-cyclohexenylcarbinol [ir (neat) OH 2.93 (s), C=C 6.01 μ (s); pmr δ 1.05 (s, 3, Me), 1.2–2.2 (m, 6, methylenes), 3.42 (q, 2, oxymethylene), 3.44 (s, 3, OMe), 4.62 (t, 1, J = 3.5 Hz, olefinic H)], was used for the next two reactions without purification. A solution of 5.00 g of the alcohol and 5 ml of 2 N hydrochloric acid in 45 ml of tetrahydrofuran was stirred at room temperature under nitrogen for 8 hr. Saturated sodium bicarbonate solution, 40 ml, was added and the mixture concentrated under vacuum. Upon removal of most of the tetrahydrofuran the mixture was extracted with ether. The extract was dried and evaporated leaving 4.3 g of liquid 2-hydroxymethyl-2-methylcyclohexanone (**31c**)[34]: ir (neat) OH 2.90 (s), C=O 5.83 μ (s); pmr δ 1.18 (s, 3, Me), 1.2–2.5 (m, 8, methylenes), 3.52 (s, 2, oxymethylene). *p*-Toluenesulfonyl chloride, 6.0 g, was added in portions to a solution of 5.0 g of the enol ether carbinol in 12 ml of pyridine kept at 5–10° and the mixture was then stirred for 3 hr at room temperature. It was poured into ether and the mixture was washed with sodium bicarbonate. The ether solution was dried and evaporated. Chromatography of the residue on Florosil and elution with hexane yielded 6.1 g of a clear oil whose crystallization from pentane–ether gave **32b**: mp 48–49°; ir (Nujol) C=C 6.01 (s), 6.24 μ (s); pmr δ 1.02 (s, 3, Me), 1.1–2.1 (m, 6, methylenes), 2.42 (s, 3, aromatic Me), 3.31 (s, 3, OMe), 3.92 (q, 2, oxymethylene), 4.61 (t, 1, J = 3.0 Hz, olefinic H), AB pair 7.31, 7.77 (d, 2 each, J = 8.0 Hz, aromatic H's); *m/e* 310.12387 (calcd 310.12387). It was exceedingly unstable toward atmospheric moisture.

A solution of 4.5 g of the sulfonate **32b** and 5 ml of 2 N hydrochloric acid in 40 ml of tetrahydrofuran was stirred at room temperature under nitrogen for 4 hr. Upon addition of 40 ml of saturated sodium bicarbonate solution, the tetrahydrofuran was removed under vacuum and the concentrated mixture extracted with ether. The extract was dried and evaporated. Crystallization of the residue, 4.0 g, from pentane–ether gave **31a**: mp 60–62° (lit.[24] 57–59°); ir (neat liquid) C=O 5.81 (s), C=C 6.24 μ (s); pmr δ 1.11 (s, 3, Me), 1.2–2.5 (m, 8, methylenes), 2.42 (s, 3, aromatic Me), 4.02 (s, 2, oxymethylene), AB pair 7.35, 7.78 (d, 2 each, J = 8.0 Hz, aromatic H's). *p*-Toluenesulfonyl chloride, 5.0 g, was added in portions to a solution of 3.4 g of ketol **31c** in 8 ml of pyridine kept at less than 10° and the mixture was then stirred at room temperature for 4 hr. Hydrochloric acid, 50 ml of 2 N, and crushed ice were added and the mixture was extracted with benzene. The extract was washed with 2 N hydrochloric acid, sodium bicarbonate, and saturated brine solutions, dried, and evaporated. Chromatography of the residue, 6.9 g, on Florosil and elution with 1:1 pentane–ether gave 6.5 g of solid whose crystallization from pentane–ether afforded **31a**: mp 60–62°; spectrally identical with that of an authentic sample.[24]

Ketones 33 and 34. A solution of 200 mg of **31a** and 53 mg of sodium hydroxide in 10 ml of dioxane and 5 ml of water was kept at 90° under nitrogen in a sealed ampoule for 3 hr. Thereupon it was extracted with 40 ml of pentane. The extract was washed with saturated sodium bicarbonate solution and dried over sodium sulfate. It then was analyzed by gpc on a FFAP column at 73° with the use of an internal standard. The total ketone yield was 86% and the mixture consisted of 9% **31b**, 40% **33**, and 51% **34**. Eight runs indicated that the ketone distribution was invariant with time. Preparative gpc on a LAC column at 90° permitted isolation of **31b**. Acidic products from the sodium bicarbonate solution were not investigated.

The same procedure of reaction of **31a** and sodium hydroxide was carried out at room temperature for 68 hr. The same work-up and product analysis led to the recovery of 36% starting keto ester **31a** and a 67% total yield of ketones composed of 13% **31b**, 37% **33**, and 49% **34**.

A solution of 200 mg of **32b** and 52 mg of sodium hydroxide in 10 ml of dioxane and 5 ml of water was kept at 90° under nitrogen in a sealed ampoule for 72 hr. Work-up and analysis as above afforded a total ketone yield of 98% composed of 27% **33** and 73% **34**. Five runs indicated the ketone distribution to be invariant with time and the half-life of the reaction to be *ca.* 13 hr. Separation of the ketones was carried out by preparative gpc on a FFAP column at 90°. Ketone **33** always was accompanied by an extraneous ketone **39**,[35] which could be shown to originate by rearrangement of **33**, but not of **34**, on the gpc column or at the gpc injection port (165°).[22]

1-Methyl-7-oxabicyclo[4.2.0]octane (35b). A solution of 68 mg of sodium borohydride in 5 ml of ethanol was added dropwise to a solution of 1.00 g of tosylate **31a** in 10 ml of ethanol at 0° and the mixture was stirred at room temperature for 15 hr. Hydrochloric acid, 5 ml of 2 N, was added and ethanol removed under vacuum. Water, 5 ml, was added and the mixture extracted with ether. The extract was dried and evaporated leaving 1.0 g of a colorless liquid residue whose pmr analysis revealed it to be a 7:3 mixture of **36a** and **36b**, respectively: ir (neat) OH 2.80 (m), 2.90 (m), C=C 6.26 μ (m); pmr δ 0.84 (s, 3, Me of **36a**), 0.99 (s, 3, Me of **36b**), 3.78 (q, 2, J = 7.5 Hz, oxymethylene of **36b**), 3.86 (q, 2, J = 9.5 Hz, oxymethylene of **36a**); pmr (pyridine) δ 1.01 (s, 3, Me of **36a**), 1.10 (s, 3, Me of **36b**), 3.72 (m, 2, oxymethylene of **36b**), 4.25 (m, 2, oxymethylene of **36a**). A solution of this oily mixture and 0.28 g of sodium hydroxide in 20 ml of dioxane and 10 ml of water was stirred at room temperature under nitrogen for 4 days. It then was extracted with pentane and the extract washed with water, dried, and evaporated at 20 Torr and room temperature. Chromatography on alumina (activity 1V) and elution with 4:1 pentane–ether yielded 0.11 g of oxetane **35b**: pmr δ 1.13 (s, 3, Me), 1.3–1.9 (m, 8, methylenes), AB pair 4.15 (d, 1, J = 5.0 Hz, oxymethylene H), 4.31 (d, 1, J = 5.0 Hz, oxymethylene H), 4.58 (m, 1, oxymethine); *m/e* 126.10408 (calcd 126.10446).

Further elution yielded 0.58 g of viscous oil whose crystallization from pentane gave tosylate **36a**: mp 73–75°; ir (Nujol) OH 6.01

(34) E. Buchta and G. Wolfrum, *Justus Liebigs Ann. Chem.*, **580**, 132 (1953).

(35) E. Wenkert, B. L. Mylari, and L. L. Davis, *J. Amer. Chem. Soc.*, **90**, 3870 (1968).

(m), C=C 6.26 μ (m); pmr δ 0.84 (s, 3, Me), 1.0–1.9 (m, 8, methylenes), 3.4–3.7 (m, 1, oxymethine), 3.86 (q, 2, J = 9.5 Hz, oxymethylene), AB pair 7.32, 7.77 (d, 2 each, J = 8.0 Hz, aromatic H's).

Anal. Calcd for $C_{15}H_{22}O_4S$: C, 60.39; H, 7.43. Found: C, 60.56; H, 7.27.

2,2-Dimethyl-3-ketocyclohexyl *p*-Toluenesulfonate. A mixture of 2.0 g of 2,2-dimethyl-1,3-cyclohexanedione[36] and 0.54 g of lithium aluminum hydride in 45 ml of ether was stirred at room temperature for 4 hr. Moist sodium sulfate was added, the mixture was filtered, and the filtrate was evaporated.[37] A solution of 2.7 g of *p*-toluenesulfonyl chloride in 25 ml of methylene chloride was added over a 2-hr period to a solution of the residue (2.1 g of viscous oily 2,2-dimethyl-1,3-cyclohexanediol epimer mixture) in 25 ml of pyridine at 0° and the mixture was then stirred at room temperature for 20 hr. It was poured onto 25 ml of concentrated hydrochloric acid and crushed ice and extracted with methylene chloride. The extract was washed with saturated brine solution, dried, and evaporated, leaving 2.7 g of viscous oily 2,2-dimethyl-3-hydroxycyclohexyl tosylate.[37] A solution of 0.86 g of chromium trioxide in 6 ml of 1:1 water–acetic acid was added dropwise to a solution of 3.5 g of the hydroxy tosylate in 25 ml of acetic acid at room temperature. The mixture was stirred at 65° for 2 hr, poured into ice water, and extracted with methylene chloride. The extract was washed with 2 *N* ammonium hydroxide and with saturated sodium chloride solutions, dried, and evaporated. Crystallization of the colorless residual oil, 2.9 g, from pentane–ether yielded **38**: mp 78–80°; ir (Nujol) C=O 5.81 (s), C=C 6.22 μ (w); pmr δ 1.01 (s, 3, Me), 1.07 (s, 3, Me), 1.5–2.2 (m, 4, methylenes), 2.3–2.5 (m, 2, α-ketomethylene), 2.42 (s, 3, aromatic Me), 4.57 (q, 1, J = 4.0, 6.0 Hz, oxymethine), AB pair 7.30, 7.73 (q, 4, J = 8.0 Hz, aromatic H's).

Anal. Calcd for $C_{15}H_{20}O_4S$: C, 60.80; H, 6.80. Found: C, 60.81; H, 6.72.

6-Methyl-5-heptenoic Acid (39a). A solution of 200 mg of **38** and 54 mg of sodium hydroxide in 5 ml of water and 10 ml of dioxane was stirred at room temperature for 24 hr. Work-up as in the above solvolyses yielded 3 mg of unidentified neutral material and 90 mg of colorless, viscous, oily **39a**.[38] Esterification of the latter with diazomethane (*vide supra*) gave colorless, liquid ester **39b**: one gpc peak (FFAP column at 90°); ir (neat) C=O 5.74 μ (s); pmr δ 1.60 (broad s, 3, Me), 1.70 (broad s, 3, Me), 1.5–2.5 (m, 6, methylenes), 3.67 (s, 3, OMe), 5.10 (t of m, 1, J = 7.0 Hz, olefinic H). Hydrogenation of this ester as above yielded methyl isoenanthate identical in infrared and pmr spectra and gpc retention time with the sample from the hydrogenation of **24a** (*vide supra*).

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(36) S. Eskola, A. Auvinen, A. Hirvimies, T. Rinne, and R. Waris, *Suom. Kemistilehti B*, 27, 88 (1954); S. Swaminathan, S. Ramachandran, and S. K. Sankarappa, *Tetrahedron*, 20, 1119 (1964).

(37) *Cf.* E. Wenkert and Y. Gaoni, *J. Org. Chem.*, **31**, 3809 (1966).

(38) M. F. Ansell and S. S. Brown, *J. Chem. Soc.*, 1788 (1957).

Configurational Stabilities of Strained α-Sulfonyl Carbanions. Kinetics of Base-Catalyzed Racemization and Deuterium Exchange of Representative Thiete and Thietane Dioxides[1]

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Abstract: Rate constants and activation parameters for racemization and hydrogen–deuterium exchange have been measured for optically active (*R*)-(+)-2-methyl-3,8-diphenyl-2*H*-naphtho[2,3-*b*]thiete 1,1-dioxide (**10**), a representative thiete dioxide, and (*R*)-(−)-2-methylthietane 1,1-dioxide (**11**), a typical saturated four-membered cyclic sulfone. Because these two molecules represent the smallest sulfone systems yet examined, knowledge of the stereochemical fate of the derived α-sulfonyl carbanions was of considerable interest. In the case of **10**, k_e/k_α values were essentially unity in *tert*-butyl alcohol-d_1–benzene (70:30), denoting complete racemization. In methanol-d_1–benzene (70:30), the rate constants for racemization were consistently somewhat larger than those for exchange ($k_e/k_\alpha \approx 0.90$). The isotopic exchange and racemization rates for **11** in methanol-d_1 were too slow to measure. In *tert*-butyl alcohol-d_1 (neat or admixed with benzene), **11** was seen to react approximately 10^5 times more slowly than **10** in both processes. Also, the k_e/k_α ratios were notably smaller (0.60–0.67). These results are discussed in terms of configurational and conformational considerations and proton transfer phenomena, and a comparison with open-chain α-sulfonyl carbanions is made.

Unconstrained α-sulfonyl carbanions enjoy a unique position among reactive organic intermediates by virtue of their intrinsic ability to maintain configurational stability. The innate structure of such species and the causative factor(s) behind the relatively high activation energy for their racemization continue to be a subject of controversy. In the first alternative, these carbanions are denoted as having an effectively planar (sp^2) geometry at carbon with electrostatic inhibition to rotation about the C_α–S bond. Because of their capability to support asymmetry, the model is required to be of structure **1** rather than **2** (plane of symmetry) with proton transfer to **1** (and its microscopic reverse) occurring almost totally from a single direction.[4] In an elegant experiment supporting this concept, Corey and Lowry[4b] have established that, in the case of the α-

(1) Unsaturated Heterocyclic Systems. LXXXI. The previous paper in this series is L. A. Paquette, J. P. Freeman, and S. Maiorana, *Tetrahedron*, in press.

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(4) (a) E. J. Corey, H. König, and T. H. Lowry, *Tetrahedron Lett.*, 515 (1962); (b) E. J. Corey and T. H. Lowry, *ibid.*, 793 (1965); (c) E. J. Corey and T. H. Lowry, *ibid.*, 803 (1965).