allyl ethyl ether or 1,1-dimethylallyl chloride under conditions identical with those employed for vinylsilane additions.

The following compounds were prepared for comparison purposes and/or for use as starting materials for vinyl additions: 3-methylbutyltrimethylsilane, 3-methylbutylethoxydimethylsilane, diphenylvinylsilane, 3-methylbutyldiphenylsilane. Syntheses were accomplished by the reaction of Grignard reagents and/or lithium aluminum hydride with the appropriate silanes. Standard methods were used in all instances and no unusual procedures were required for purification.

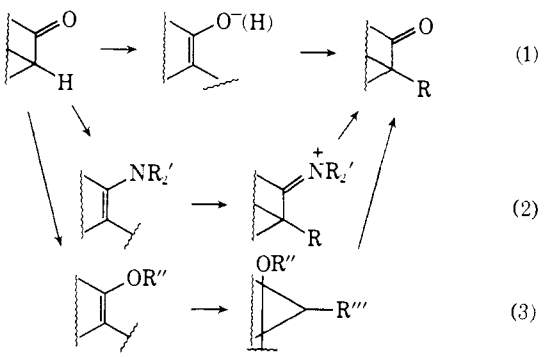
Cyclopropanol Derivatives as Intermediates for Organochemical Synthesis

Ernest Wenkert,* Richard A. Mueller, Edward J. Reardon, Jr.,[1] S. S. Sathe, D. J. Scharf,[1] and Giorgio Tosi

Contribution from the Department of Chemistry, Indiana University, Bloomington, Indiana 47401. *Received April 15, 1970*

Abstract: A design of terpene synthesis based on the acid-induced transformations of cyclopropyl ethers and β-methoxycyclopropylcarbinols into quaternary α-methyl and α-vinyl carbonyl compounds, respectively, is described. Similar reactions with *gem*-dimethoxycyclopropanes are portrayed. A cyclopropylamine is shown to be inert. β-Methoxycyclopropanecarboxylic esters are converted into γ-ketocarboxylic acid derivatives. A similar ring unravelling of a β-acetoxycyclopropyl ketone is used for the synthesis of dihydrojasmone. An α-methoxycyclopropylcarbinol is transformed into a cyclobutanone on acid treatment and a mechanistically related cyclobutanone interconversion process is utilized for the construction of a bicyclic intermediate on route to the bourbonene sesquiterpenes.

The α-substitution of carbonyl compounds (*cf.* eq 1) has constituted the backbone of organochemical synthesis for many years. Despite the wide use of this carbon–carbon bond-forming process its limitations are being encountered with growing frequency as the complexity of structure of the substances in need of synthesis increases. Some of the resultant demand for alternate methods of synthesis have been met, *inter alia*, by the use of enamines (*cf.* eq 2),[2] but further flexibility in this area is desirable. The present communication describes a new procedure for α-alkylation of aldehydes and ketones *via* cyclopropyl ether and ester intermediates (*cf.* eq 3).



(1)

(2)

(3)

Broad advances in the chemistry of carbenes and carbenoid substances in the last two decades[3] have made cyclopropanation of olefins a facile process and cyclopropanes readily available materials. The fairly high reactivity of cyclopropanes, especially in ring cleavage reactions, has favored their use as intermediates in organochemical synthesis.[4] Our attention was drawn to the possible exploitation of cyclopropanols and their O-alkyl or O-acyl derivatives in synthesis by the exhaustive study of their chemistry by DePuy[5] and by our postulation of the intermediacy of cyclopropanediols in the Clemmensen reduction of β-diketones[6] and isolation of methoxycyclopropanes from a Clemmensen reduction of a vinylogous β-diketone.[7] As a consequence a study of the synthesis of alkoxy- and acyloxycyclopropanes and their protolysis was undertaken.

Methoxycyclopropanes. As first objective the construction of quaternary α-methylcarbonyl systems by way of unsymmetrically alkylated cyclopropyl ethers was investigated. Two model cyclopropanes, **4a** and **8a**, were chosen for this study. The former was prepared by consecutive transformations of 2,6-dimethylcyclohexanone (**1a**) into ketal **2**, acid-induced demethanolation,[8] and cyclopropanation of the resultant enol ether (**3a**) by the Simmons–Smith pro-

* To whom correspondence should be addressed.

(1) Public Health Service postdoctoral fellow, 1969–1970.

(2) G. Stork, R. Terrell, and J. Szmuszkovicz, *J. Amer. Chem. Soc.*, **76**, 2029 (1954), and subsequent papers; J. Szmuszkovicz, *Advan. Org. Chem.*, 4, 1 (1963).

(3) W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964.

(4) The following represent applications of four distinct methods of unravelling of cyclopropanes: (a) metal–ammonia reduction of acylcyclopropanes [T. Norin, *Acta Chem. Scand.*, **19**, 1289 (1965); W. G. Dauben and E. J. Deving, *J. Org. Chem.*, **31**, 3794 (1966)]; (b) hydrogenolysis of cyclopropanes [J. Jacobus, Z. Majerski, K. Mislow, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **91**, 1998 (1969)]; (c) base treatment of cyclopropylcarbinyl ketones [J. J. Bonet, H. Wehrli, and K. Schaffner, *Helv. Chim. Acta*, **45**, 2615 (1962); R. Ginsig and A. D. Cross, *J. Amer. Chem. Soc.*, **87**, 4629 (1965); J. J. Sims and V. K. Honwad, *J. Org. Chem.*, **34**, 496 (1969)]; (d) pyrolysis of cyclopropylacetic acids [T. Hanafusa, L. Birladeanu, and S. Winstein, *J. Amer. Chem. Soc.*, **87**, 3510 (1965); J. J. Sims, *ibid.*, **87**, 3511 (1965); J. J. Sims and L. H. Selman, *Tetrahedron Lett.*, 561 (1969)].

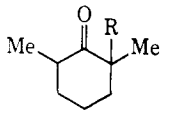
(5) C. H. DePuy, *Accounts Chem. Res.*, **1**, 33 (1968).

(6) E. Wenkert and E. Kariv, *Chem. Commun.*, 570 (1965).

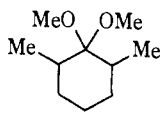
(7) E. Wenkert and J. Zylber, unpublished data cited in E. Kariv, Ph.D. Dissertation, The Weizmann Institute of Science, Rehovoth, Israel, 1967, and in J. G. St. C. Buchanan and P. D. Woodgate, *Quart. Rev., Chem. Soc.*, **23**, 522 (1969).

(8) J. H.-H. Chan and B. Rickborn, *J. Amer. Chem. Soc.*, **90**, 6406 (1968).

cedure.[9] The spiro octyl ether **8a** was prepared by two methods: (a) interaction of cyclohexylmagnesium bromide with trimethyl orthoformate,[10] demethanolation[8] of acetal **6**,[11] and Simmons–Smith reaction on enol ether **7a**; (b) treatment of methylenecyclohexane (**7b**) with chloromethyl ether and *tert*-butyllithium.[12] Acid hydrolysis of cyclopropanes **4a** and **8a** yielded 2,2,6-trimethylcyclohexanone (**1b**) and α-methylhexahydrobenzaldehyde (**5b**), respectively. These conversions are formally equivalent to α-methylations of ketone **1a** and aldehyde **5a** and constitute a good omen for application of the new method of alkylation to the construction of quaternary carbon centers, *e.g.*, C(4) and C(13) in the pimaric acids (**9**), in terpenic natural products.



1a, R = H
b, R = Me
c, R = vinyl



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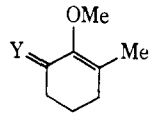
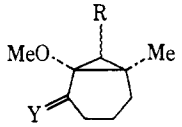
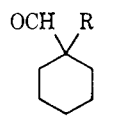


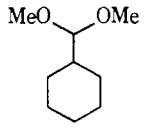
3a, Y = H, Me
b, Y = O
c, Y = H, OH



4a, R = H; Y = H, Me
b, R = H; Y = α-H, β-OH
c, R = H; Y = O
d, R = H; Y = α-OH, β-H
e, R = CO_2Et; Y = H, Me
f, R = CH_2OH; Y = H, Me



5a, R = H
b, R = Me
c, R = vinyl



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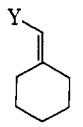
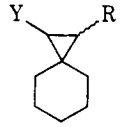
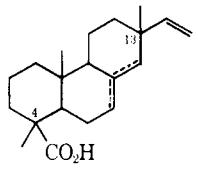


7a, Y = OMe
b, Y = H
c, Y = $N(CH_2)_4$

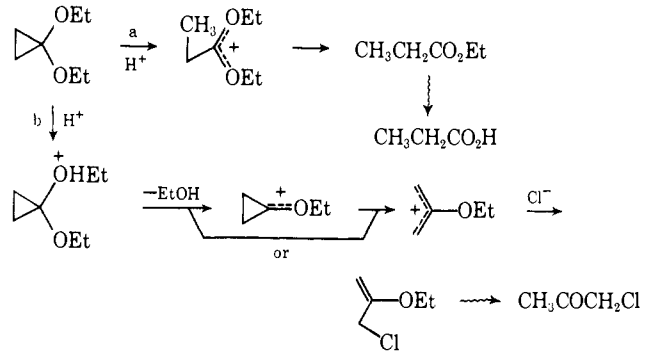


8a, R = H; Y = OMe
b, R = H; Y = $N(CH_2)_4$
c, R = CO_2Et; Y = OMe
d, R = CH_2OH; Y = OMe
e, R = CO_2Et; Y = $N(CH_2)_4$

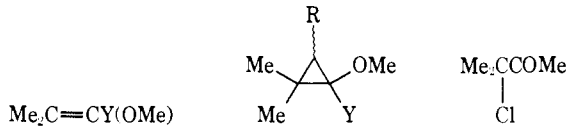


9

The formation of aldehyde **5b** from methoxycyclopropane **8a** suggested that α-quaternized carboxylic acids or esters might be obtained from *gem*-dialkoxycyclopropanes. The lone, related example—hydrolysis of 1,1-diethoxycyclopropane with hydrochloric acid[13]—had revealed that this scheme of synthesis was feasible but competitive with an undesired mode of cyclopropane scission reminiscent of some of the chemistry of cyclopropanone.[14] Propionic acid and ethyl propionate, products of reaction path a, were accompanied by chloroacetone, a consequence of path b.



Treatment of 1,1-dimethoxy-2,2-dimethylcyclopropane (**11a**), prepared by a Simmons–Smith reaction[9] on dimethylketene dimethyl acetal (**10a**),[15] with hydrochloric acid yielded 3-chloro-3-methyl-2-butanone (**12**).[16] While thus unfortunately the O-protonation route of ring opening (path b) had outweighed completely the sterically less favorable C-protonation route (path a), the desired cleavage could be accomplished in an oxidation–reduction manner. Bromination[13] of **11a** gave the bromo ester **13a**, whose reduction with tri-*n*-butyltin hydride led to methyl pivalate (**13b**).[17]



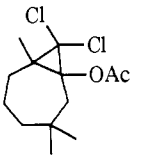
10a, Y = OMe
b, Y = H

11a, R = H; Y = OMe
b, R = CO_2Et; Y = H
c, R = CH_2OH; Y = H
d, R = CO_2Et; Y = OMe
e, R = CH_2OH; Y = OMe

12

13a, R = CH_2Br; Y = OMe
b, R = Me; Y = OMe
c, R = vinyl; Y = H
d, R = vinyl; Y = OMe
e, R = vinyl; Y = OH
f, R = CH_2CO_2Et; Y = OMe

14



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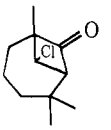


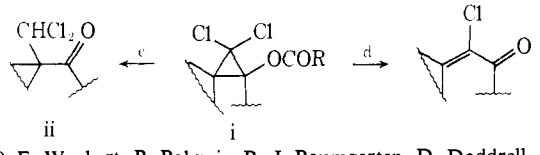
16

(9) H. E. Simmons and R. D. Smith, *J. Amer. Chem. Soc.*, **81**, 4256 (1959).
(10) *Cf.* C. E. Wood and M. A. Comley, *J. Soc. Chem. Ind.* (*London*), **42**, 428T (1923).
(11) P. L. Barrick and A. A. Pavlic, U. S. Patent 2,491,915 (Dec 20, 1949); *Chem. Abstr.*, **44**, 3008 (1950).
(12) U. Schöllkopf, A. Lerch, and J. Paust, *Chem. Ber.*, **96**, 2266 (1963).
(13) S. M. McElvain and P. L. Weyna, *J. Amer. Chem. Soc.*, **81**, 2579 (1959).
(14) N. J. Turro, *Accounts Chem. Res.*, **2**, 25 (1969).
(15) S. M. McElvain and C. L. Aldridge, *J. Amer. Chem. Soc.*, **75**, 3987 (1953).
(16) D. P. Wyman and P. R. Kaufman, *J. Org. Chem.*, **29**, 1956 (1964).
(17) Halo substituents exert a strong effect on the nature of the cleavage of cyclopropyl ethers or esters. The cyclopropyl acetate **15** was prepared from the enol acetate (**14**) of tetrahydroeucarvone (see Experimental Section) in the hope of its hydrolysis following path c (*vide infra*) and the resultant α-dichloromethyl ketone ii being induced by base to undergo cyclization into the cyclobutanone derivative **16** in analogy with the behavior of α-dichloromethylcyclohexanones.[18] However, this project of possible synthesis of the sesquiterpene α-longipinene was interrupted upon the appearance of reports of the

Aminocyclopropane. The alkoxycyclopropane route of α-alkylation of carbonyl compounds should function in principle also with N- or S-attached[19] cyclopropanes. One test with an aminocyclopropane was undertaken. Acid hydrolysis of **8b**, prepared by treatment of hexahydrobenzaldehyde pyrrolidine enamine (**7c**) with diazomethane and cuprous chloride,[20] failed under any of a variety of conditions. The inertness of the cyclopropylamine may be ascribed not only to preference of N over C protonation but also to an apparent deactivation of the cyclopropane ring in the presence of a neighboring ammonium salt group.[21,22]

α-Oxycyclopropylcarbinols. A cationoid center attached to the cyclopropane ring modifies drastically the chemical behavior of the latter. While the ready interconversion of cyclopropylcarbinyl, cyclobutyl, and homoallyl systems[23] causes product control of reactions proceeding by a cyclopropylcarbonium ion path to be frequently difficult, reactions involving oxycyclopropylcarbonium ion intermediates can be expected to be unidirectional. On the assumption of oxycarbonium ions representing the penultimate stage of the reaction sequence (path e below) the products of rearrangement of α-oxycyclopropylcarbinyl systems should be cyclobutanones. This view is supported by the few such rearrangements encountered heretofore[24] and was strengthened by the following study.

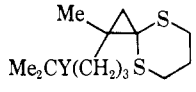
hydrolysis or hydride reduction of *gem*-dichlorocyclopropyl esters (i) proceeding by way of path d [R. C. Selms, *Tetrahedron Lett.*, 1965 (1966); G. Stork, M. Nussim, and B. August, *Tetrahedron Suppl.*, **8**, 105 (1966)] in analogy with the solvolytic behavior of *gem*-dichlorocyclopropyl ethers [A. J. Birch, J. M. H. Graves, and J. B. Siddall, *J. Chem. Soc.*, 4234 (1963); W. E. Parham, R. W. Soeder, J. R. Throckmorton, K. Kuncl, and R. M. Dodson, *J. Amer. Chem. Soc.*, **87**, 321 (1965); L. Skattebøl, *J. Org. Chem.*, **31**, 1554 (1966)].



ii i

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

(19) The ease of cleavage of a thiocyclopropane has been inspected. Reduction of chloride iii [J. P. O'Brien, A. I. Rachlin, and S. Teitel, *J. Med. Chem.*, **12**, 1112 (1969)], kindly donated by Dr. Rachlin, with tri-*n*-butyltin hydride yielded the cyclopropanone thioketal iv (see Experimental Section) which proved inert toward acid under a variety of conditions.



iii, Y = Cl
iv, Y = H

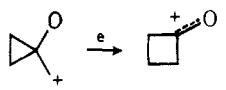
(20) D. L. Muck and E. R. Wilson, *J. Org. Chem.*, **33**, 419 (1968).

(21) Several primary cyclopropylamines and one *tert-gem*-dichlorocyclopropylamine have been shown to be inert toward acid: (a) J. Weinstock, *J. Org. Chem.*, **26**, 3511 (1961); (b) C. Kaiser, B. M. Lester, C. L. Zirkle, A. Burger, C. S. Davis, T. J. Delia, and L. Zirngibl, *J. Med. Chem.*, **5**, 1243 (1962); (c) J. E. Hodgkins and R. J. Flores, *J. Org. Chem.*, **28**, 3356 (1963); (d) J. Wolinsky, D. Chan, and R. Novack, *Chem. Ind. (London)*, 720 (1965)].

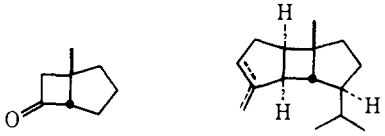
(22) In view of the availability of other cyclopropane scission reactions[4,5] a modified cyclopropylamine route of synthesis is still worthy of further investigation.

(23) M. Hanack and H.-J. Schneider, *Fortschr. Chem. Forsch.*, **8**, 554 (1967).

(24) An acid-induced rearrangement of phorbol [L. Crombie, M. L. Games, and D. J. Pointer, *J. Chem. Soc. C*, 1347 (1968); H. W. Thielmann and H. Hecker, *Justus Liebigs Ann. Chem.*, **728**, 158 (1969)] and some reactions of cyclopropanone [N. J. Turro and R. B. Gagosian, *J. Amer. Chem. Soc.*, **92**, 2036 (1970); H. H. Wasserman, R. E. Cochoy, and M. S. Baird, *ibid.*, **91**, 2376 (1969)].

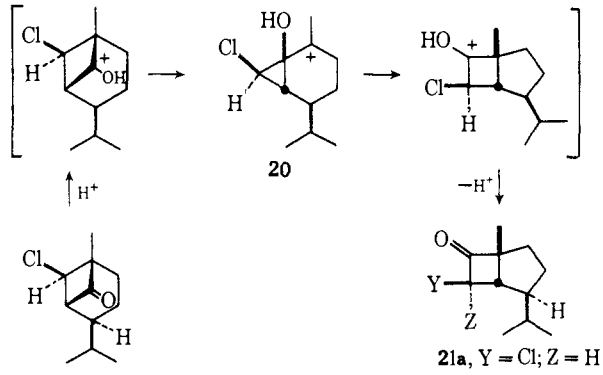


Acid treatment of either carbinol **4b**, prepared by the lithium aluminum hydride reduction of ketone **3b**[25] followed by Simmons–Smith reaction[9,26] on alcohol **3c**, or **4d**, produced by a Fétizon oxidation[27] of **4b** followed by lithium aluminum hydride reduction of **4c**, led to the bicyclic ketone **17**.[18,28] These transformations could serve as model reactions for the synthesis of the sesquiterpenes bourbonenes (**18**).[29] Furthermore, they shed some light on the mechanism of the homo-Favorskii rearrangement.[28]



17 18

A reaction in which α-oxycyclopropylcarbinyl systems play an important role is the acid-catalyzed rearrangement of cyclobutanones.[30] One manifestation thereof is the following transformation of a cyclobutanone intermediate on route to the sesquiterpene family of the copaenes and ylangenes into one on route to the bourbonenes (**18**). Treatment of bicyclic chloro ketone **19**[18] with formic acid yielded isomer **21a**. This change proceeded most likely by way of the α-hydroxycyclopropylcarbonium ion **20** (*vide infra*). Extended acid treatment led also to the epimer **21b** as part of a *ca.* 3:10:7 mixture of **19**, **21a**, and **21b**, respectively. This appeared to be an equilibrium mixture as evinced from similar results of independent treatments of **21a** and **21b** with formic acid. Palladium-induced hydrogenolysis of the last two substances yielded cyclobutanone **21c** and hence direct entry into the bourbonene field.



19 20 21a, Y = Cl; Z = H
b, Y = H; Z = Cl
c, Y = Z = H

(25) E. Wenkert, D. Berges, K. Kavkova, and S. S. Sathe, manuscript in preparation.

(26) W. G. Dauben and G. H. Berezin, *ibid.*, **85**, 468 (1963).

(27) M. Fétizon and M. Golfier, *C. R. Acad. Sci., Paris, Ser. C*, **267**, 900 (1968); M. J. Brienne, C. Ouannes, and J. Jacques, *Bull. Soc. Chim. Fr.*, 1036 (1968); M. Fétizon, M. Golfier, and J. M. Louis, *Chem. Commun.*, 1102, 1118 (1969).

(28) E. Wenkert, P. Bakuzis, R. J. Baumgarten, C. L. Leicht, and H. P. Schenk, submitted for publication.

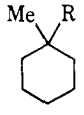
(29) J. Krěpinský, Z. Samek, F. Šorm, D. Lamparsky, P. Ochsner, and Y. R. Naves, *Tetrahedron Suppl.*, **8**, 53 (1966), and preceding papers; J. D. White and D. N. Gupta, *J. Amer. Chem. Soc.*, **90**, 6171 (1968); M. Brown, *J. Org. Chem.*, **33**, 162 (1968).

(30) W. F. Erman, R. S. Treptow, E. Wenkert, and P. Bakuzis, *J. Amer. Chem. Soc.*, in press.

β-Oxycyclopropylcarbinols and Related Substances. Creation of a cationoid center in a 1,2-relationship to an oxy substituent on a cyclopropane ring would be expected to unravel the latter according to path f (*vide infra*) and produce a β,γ-unsaturated carbonyl compound.[31] Since such reaction may lead to quaternary α-vinylcarbonyl systems, its exploitation for terpene synthesis was of importance.

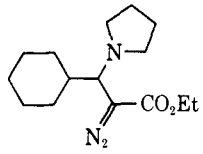
Decomposition of ethyl diazoacetate[32] under the influence of copper–bronze[21c] in the presence of enol ethers **10b**,[33,34] **3a** and **7a** yielded stereoisomer mixtures of esters **11b**, **4e**, and **8c**, respectively, whose reduction with lithium aluminum hydride gave carbinols **11c**, **4f**, and **8d**, respectively. Treatment of each of these β-methoxycyclopropylcarbinols with acid afforded the keto compounds **13c**,[31] **1c**, and **5c**, respectively. In anticipation of possible future needs for unravelling of β-oxycyclopropylcarbinyl systems containing acid-labile groups one of the carbinols was cleaved in basic medium. Treatment of the spiro compound **8d** with *p*-toluenesulfonyl chloride in aqueous sodium hydroxide also converted it into the aldehyde **5c**.

2,6-Dimethyl-2-vinylcyclohexanone (**1c**) and 1-vinylcyclohexanecarboxaldehyde (**5c**) can be considered as models of the C(13) environment of the pimaric acids (**9**). An even closer representation of the substitution pattern at C(13) of **9** was obtained by the transformation of the aldehyde **5c** into 1-methyl-1-vinylcyclohexane (**22a**)[35] by lithium aluminum hydride reduction of **5c** *p*-toluenesulfonylhydrazone.[36] An authentic sample of the hydrocarbon was prepared by pyrolysis of the stearate of alcohol **22b**,[37] but could not be obtained efficiently by the reported copyrolysis of **22b** and boric acid.[35a] Instead, in conformity with the known misbehavior of alkyl borates on pyrolysis[38] rearrangement products, among which isopropylidenecyclohexane[39] and 1-isopropylcyclohexene could be identified, accompanied **22a**.

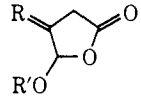


22a, R = vinyl
b, R = $(CH_2)_2OH$

The above results encouraged a study of β,β-dioxycyclopropylcarbinyl and β-aminocyclopropylcarbinyl systems. Copper–bronze-induced decomposition of ethyl diazoacetate in the presence of the highly nucleophilic olefin **10a** yielded ester **11d**[40] whose reduction with lithium aluminum hydride produced carbinol **11e**. Treatment of the latter with acid gave the olefinic ester **13d** whose alkaline hydrolysis afforded the known acid **13e**.[41] Preparation of a β-aminocyclopropylcarbinol failed in the initial ring-forming step. A reaction between the enamine **7c** and ethyl diazoacetate catalyzed by cuprous chloride led to the diazo compound **23** instead of the expected cyclopropane **8e**.[42]



23



24a, R = $(CH_2)_5$; R′ = Me
b, R = Me_2; R′ = H
c, R = Me_2; R′ = Me

In principle the cationoid center responsible for initiation of the ring cleavage of the β-oxycyclopropylcarbinyl moiety need not be at the oxidation level of an alcohol. The following cases show the potential for ring scission among carboxylic esters.[43] Treatment of **8c**, **11b**, and **11d** with acid produced **24a**, **24b**, and **13f**, respectively. Base hydrolysis of the diester **13f** yielded α,α-dimethylsuccinic acid (**13g**).[44] Finally, the following synthesis of dihydrojasmone (**28**) illustrates the utilization of an acyloxycyclopropane whose cationoid center is at the oxidation level of a ketone.[45] An interaction between 1-diazo-2-octanone (**25**), isopropenyl acetate (**26**), and copper–bronze yielded a mixture of stereoisomeric cyclopropanes (**27**) whose treatment with base gave dihydrojasmone (**28**).[46]

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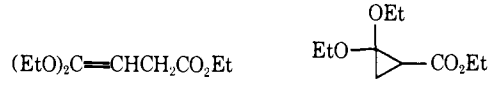
(40) Contrastingly, a reaction of ethyl diazoacetate, 1,1-diethoxyethylene, and cuprous bromide or copper powder has been reported to yield the acyclic ester v [M. F. Dull and P. G. Abend, *J. Amer. Chem. Soc.*, **81**, 2588 (1959)]. Proof of the structure of the product rested solely on its conversion to succinic acid on acid treatment and subsequent basic hydrolysis, an analysis of its infrared spectrum, and detection of unsaturation by bromination and oxidation tests. However, these data are compatible also with the product having been a mixture of the desired cyclopropane derivative vi and diethyl maleate and/or fumarate, normal side products of the decomposition of ethyl diazoacetate.



v vi

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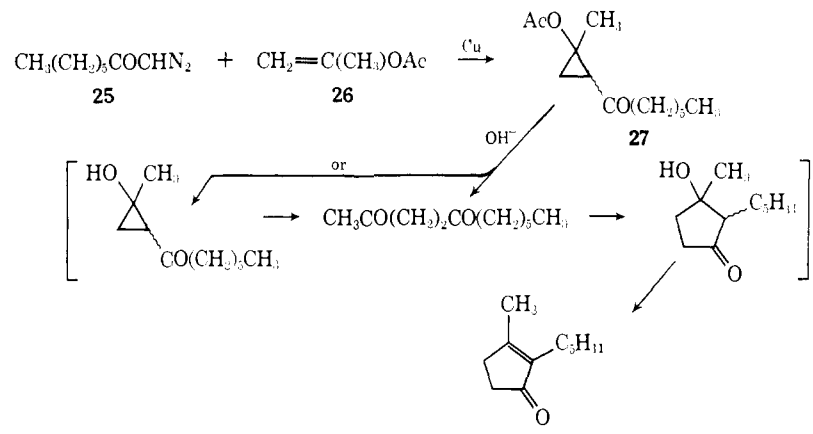

Experimental Section

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

2,2,6-Trimethylcyclohexanone (1b). A solution of 20.0 g of 2,6-dimethylcyclohexanone (**1a**), 23.5 g of methyl orthoformate, and 18 drops of concentrated sulfuric acid in 160 ml of anhydrous methanol was stirred at room temperature for 3 days. Enough methanolic sodium methoxide was added to dissipate the color of the orange solution and the latter concentrated under vacuum. Aqueous (5%) sodium bicarbonate was added and the mixture extracted with ether. The extract was washed with 5% sodium bicarbonate, dried over magnesium sulfate, and evaporated. Distillation of the residue yielded 25.0 g of a stereoisomer mixture of 1,3-dimethyl-2,2-dimethoxycyclohexane (**2**): bp 94–96° (10 Torr); pmr spectrum δ 0.99 (d, 6, J = 7.0 Hz, methyls), 1.3–2.2 (m, 8, methylenes and methines), 3.13 (s, 3, OMe of *cis*-ketal), 3.20 (s, 3, OMe of *cis*-ketal), 3.24 (s, 6, methoxyls of *trans*-ketal).

Anal. Calcd for $C_{10}H_{20}O_2$: C, 69.72; H, 11.70. Found: C, 69.99; H, 11.83.

By use of the procedure for the preparation of enol ether **7a** (*vide infra*) ketal **2** was converted in over 95% yield into 1,3-dimethyl-2-methoxycyclohexene (**3a**): bp 68–70° (6 Torr); infrared (neat) C=C 5.93 (m) μ; pmr δ 1.02 (d, 3, Me), 1.60 (m, 3, olefinic Me), 1.2–2.5 (m, 7, methylenes and methine), 3.45 (s, 3, OMe). A solution of 6.0 g of the latter in 40 ml of ether was added dropwise over a period of 30 min to a mixture of 22 g of freshly prepared zinc–copper couple,[47] 69.2 g of methylene iodide, and 150 mg of iodine in 80 ml of sodium-dried ether which had been refluxed gently for 1.3 hr. The mixture was refluxed for 72 hr, cooled, and decomposed with 100 ml of saturated aqueous ammonium chloride. The aqueous layer was extracted with ether and the combined organic solutions were washed with saturated sodium bicarbonate solution and with water, dried, and evaporated. Distillation of the residue gave 5.9 g of a stereoisomer mixture of 1-methoxy-2,6-dimethylbicyclo[4.1.0]heptane (**4a**): bp 87–90° (60 Torr); pmr spectrum δ 0.38, 0.40 (s, 2, cyclopropyl CH_2), 1.00, 1.12 (d, 3, J = 7.0 Hz, Me), 1.22 (s, 3, cyclopropyl Me), 3.22, 3.28 (s, 3, OMe).

Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.61; H, 11.66.

A solution of 3.0 g of **4a** and 10 ml of concentrated hydrochloric acid in 10 ml of methanol was refluxed for 2 hr, then cooled and diluted with 100 ml of water. The mixture was extracted with ether and the extract washed with saturated sodium bicarbonate and brine solutions, dried, and evaporated. Distillation of the residue yielded 1.9 g of 2,2,6-trimethylcyclohexanone (**1b**): bp 68° (10 Torr) (lit.[48] bp 66° (11 Torr)); infrared (neat) C=O 5.86 (s) μ; pmr δ 0.99 (d, 3, J = 7.0 Hz, secondary Me), 1.04 (s, 3, Me), 1.18 (s, 3, Me); semicarbazone mp 193–195° (lit.[49] mp 194–196°).

1-Formyl-1-methylcyclohexane (5b). A mixture of 15 g of magnesium turnings, 5.0 g of cyclohexyl bromide, and a crystal of iodine in 30 ml of sodium-dried ether was stirred. Upon initiaton of reaction 150 ml of ether was added and thereafter a solution of 95.0 g of cyclohexyl bromide in 100 ml of ether was trickled into the mixture over a period of 2 hr. After the mixture had been refluxed for an additional period of 30 min, 57.2 g of methyl orthoformate was added over a period of 20 min and the mixture refluxed for 6 hr. Sodium bicarbonate solution (200 ml of 5%) was added, the aqueous solution was extracted with ether and the combined organic solutions were washed with 5% sodium bicarbonate, dried, and evaporated. Distillation of the residue yielded 93.0 g of dimethoxymethylcyclohexane (**6**), bp 90–93° (10 Torr) (lit.[11] bp 65–68° (12 Torr)); pmr spectrum δ 3.30 (s, 6, methoxyls), 3.98 (d, 1, J = 7.0 Hz, oxymethine).

Anal. Calcd for $C_9H_{18}O_2$: C, 68.31; H, 11.47. Found: C, 68.53; H, 11.53.

Methanol was produced and removed from a mixture of 30.0 g of **6** and 3 drops of concentrated sulfuric acid by distillation at 40° (110 Torr) for 2 hr. Distillation of the residue yielded 23.5 g of methoxymethylenecyclohexane (**7a**): bp 89–90° (60 Torr) (lit.[50] bp 85–89° (60 Torr)); infrared (neat) C=C 5.93 (m) μ; pmr δ 3.50 (s, 3, OMe), 5.72 (m, 1, olefinic H). A solution of 4.0 g of the latter in 20 ml of ether was added dropwise over a period of 30 min to a mixture of 8.1 g of freshly prepared zinc–copper couple,[47] 24.4 g of methylene iodide, and 50 mg of iodine in 40 ml of anhydrous ether which had been refluxed gently for 1.3 hr. The mixture was refluxed for 20 hr and the reaction worked up as for **4a**. Distillation of the product yielded 4.1 g of 1-methoxyspiro[2.5]octane (**8a**): bp 68–70° (40 Torr); pmr spectrum δ 0.2–0.4 (m, 2, cyclopropyl CH_2), 1.1–1.6 (m, 10, methylenes), 2.8–3.0 (four-line, 1, cyclopropyl methine), 3.33 (s, 3, OMe).

Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 77.21; H, 11.77.

A solution of *t*-butyllithium in pentane (25.8 ml of 1.94 *M*) was added dropwise to a stirring solution of 4.0 g of chloromethyl ether in 50 ml of methylenecyclohexane (**7b**) under nitrogen at −20° in a drybox over a period of 1.5 hr. The mixture was warmed to room temperature and treated with wet ether and then with water. The aqueous solution was extracted with ether and the combined organic solutions were washed with water, dried, and evaporated. Distillation of the residue yielded 4.8 g of **8a**, bp 68–70° (40 Torr); spectra identical with those of the preparation above.

A solution of 300 mg of **8a** and 5 ml of concentrated hydrochloric acid in 5 ml of methanol was refluxed for 2.5 hr. It was diluted with 75 ml of water and extracted with ether. The extract was washed with saturated sodium bicarbonate and brine solutions, dried, and evaporated. The residue, 300 mg, consisted of 1-formyl-1-methylcyclohexane (**5b**), infrared spectrum (neat) aldehyde H 3.64 (w), C=O 5.77 (s) μ; 2,4-dinitrophenylhydrazone, mp 153–154.5° (lit.[35a] mp 154–155°).

3-Chloro-3-methyl-2-butanone (12). A stirring mixture of 20 g of zinc–copper couple,[47] 50 g of methylene iodide, and 50 mg of iodine in 100 ml of ether was refluxed gently for 90 min. A solution of 3.5 g of dimethylketene dimethyl acetal (**10a**) [pmr δ 1.56 (s, 6, methyls), 3.51 (s, 6, methoxyls)] in 20 ml of ether was added over a

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period of 30 min and the mixture refluxed for 48 hr. Work-up as for **4a** and distillation of the product gave a fraction of bp 85° (50 Torr) and 2.0 g of 1,1-dimethyl-2,2-dimethoxycyclopropane (**11a**): bp 42–45° (50 Torr); pmr spectrum δ 0.52 (s, 2, CH_2), 1.17 (s, 6, methyls), 3.33 (s, 6, methoxyls).

Anal. Calcd for $C_7H_{14}O_2$: C, 64.58; H, 10.84. Found: C, 64.76; H, 10.92.

A solution of 1.0 g of **11a** in 20 ml of concentrated hydrochloric acid was heated at 50° for 1 hr. Water was added and the mixture extracted with ether. The extract was washed with water, dried, and evaporated. Distillation of the residue yielded 820 mg of 3-chloro-3-methyl-2-butanone (**12**): bp 142–144° (lit.[16] bp 143–145°); infrared (neat) C=O 5.80 (s) μ; pmr δ 1.69 (s, 6, gem-Me_2), 2.39 (s, 3, Me).

Methyl Pivalate (13b). A solution of 0.1 ml of bromine in 1 ml of carbon tetrachloride was added dropwise to a solution of 130 mg of **11a** in 1.5 ml of carbon tetrachloride over a period of 5 min. After an additional 10 min the solution was evaporated. Distillation of the residue gave 190 mg of methyl α,α-dimethyl-β-bromopropionate (**13a**): bp 75–78° (21 Torr); infrared (neat) C=O 5.74 (s) μ; pmr δ 1.30 (s, 6, methyls), 3.45 (s, 2, CH_2), 3.70 (s, 3, OMe).

Anal. Calcd for $C_6H_{11}O_2Br$: C, 36.95; H, 5.69. Found: C, 36.76; H, 5.66.

A mixture of 185 mg of **13a** and 575 mg of tri-*n*-butyltin hydride was stirred at 70° for 2.5 hr. Distillation yielded 41 mg of methyl pivalate (**13b**) identical in all respects with an authentic sample.

1-Acetoxy-3,3,7-trimethyl-8,8-dichlorobicyclo[5.1.0]octane (15). A solution of 10.0 g of tetrahydroeucarvone and 10 ml of acetyl chloride in 10 ml of acetic anhydride was refluxed for 2 weeks. More acetyl chloride, 10 ml, was added every *ca.* 36 hr. Distillation then yielded 8.6 g of 1-acetoxy-2,6,6-trimethylcycloheptene (**14**): infrared (neat) C=O 5.71 (s), C=C 5.90 (w) μ; pmr δ 0.92 (s, 6, methyls), 1.0–1.6 (m, 4, methylenes), 2.02 (s, 3, olefinic Me), 2.0–2.3 (m, 4, allylic methylenes). A solution of 2.0 g of the latter and 4 g of phenyltrichloromethylmercury[51] in 40 ml of benzene was refluxed under nitrogen for 40 hr. The mixture was filtered, the filtrate evaporated under reduced pressure at 25°, and the residue taken up in hot hexane. The mixture was filtered and evaporated. Crystallization of the residue, 2.2 g, from methanol yielded a solid, mp 68–70°, whose sublimation gave **15**: mp 69.5–70.5°; infrared ($CHCl_3$) C=O 5.72 (s) μ; pmr δ 0.92 (s, 3, Me), 0.97 (s, 3, Me), 1.30 (s, 3, Me), 2.02 (s, 3, Ac).

Anal. Calcd for $C_{11}H_{20}O_2Cl_2$: C, 55.92; H, 7.23; Cl, 25.40. Found: C, 56.12; H, 7.31; Cl, 25.15.

1,1-Trimethylenedithio-2-isohexyl-2-methylcyclopropane (iv). A solution of 1.0 g of thioketal iii[19] and 1.5 g of tri-*n*-butyltin hydride in 10 ml of diglyme was refluxed for 3 hr. Water was added and the mixture extracted with ether. The extract was washed with water, dried, and evaporated. Chromatography of the residue on alumina (activity 1) and elution with petroleum ether yielded 850 mg of iv as a colorless, viscous oil: pmr spectrum δ 0.88 (d, 6, J = 6.0 Hz, *i*-Pro methyls), 0.92 (s, 2, cyclopropyl CH_2), 1.37 (s, 3, Me), 2.89 (t, 4, J = 5.0 Hz, thiomethylenes).

Anal. Calcd for $C_{13}H_{24}S_2$: C, 63.91; H, 9.90. Found: C, 64.16; H, 9.91

1-(*N*-Pyrrolydinyl)spiro[5.2]octane (8b). A mixture of 22.4 g of hexahydrobenzaldehyde (**5a**), 16 g of pyrrolidine, and 80 g of molecular sieves (4A by Matheson Coleman and Bell Co.) in 20 ml of benzene was refluxed for 3 hr. Evaporation of the filtered solution and distillation of the residue yielded 30.0 g of *N*-cyclohexylidenemethylpyrrolidine (**7c**): bp 113–114° (6 Torr) (lit.[52] bp 124° (16 Torr)); infrared (neat) C=C 6.00 (m) μ; pmr δ 1.3–1.9 (m, 10, methylenes), 1.9–2.4 (m, 4, allylic Hs), 2.7–3.1 (m, 4, aminomethylenes), 5.55 (m, 1, olefinic H). A solution of 10 g of diazomethane in 80 ml of ether was added slowly over a period of 1 hr to a stirring mixture of 8.3 g of **7c** and 1 g of cuprous chloride in 30 ml of ether. After an additional 2 hr the mixture was filtered and the filtrate washed with 10% sodium bicarbonate solution, dried, and evaporated. Distillation of the residue yielded 6.3 g of the cyclopropylamine **8b**: bp 120–122° (6 Torr); infrared (neat) cyclopropyl Hs 3.20 (w) μ; pmr δ 0.2–0.5 (m, 2, cyclopropyl CH_2), 1.2–1.9 (m, 15, methylenes and aminomethine), 2.5–2.8 (m, 4, aminomethylenes).

Anal. Calcd for $C_{12}H_{21}N$: C, 80.38; H, 11.81; N, 7.81. Found: C, 80.57; H, 11.84; N, 8.03.

Bicyclo[4.1.0]heptanols. A solution of 1.4 g of 2-methoxy-3-methyl-2-cyclohexenone (**3b**)[25] in 15 ml of ether was added dropwise over a period of 30 min to a stirring suspension of 0.3 g of lithium aluminum hydride in 25 ml of ether at room temperature. Thereafter the mixture was refluxed gently for 1 hr. A moist sodium sulfate slurry was added, the solution decanted, the residue extracted with ether, and the combined organic solutions were evaporated. Distillation of the residual oil yielded 1.3 g of colorless, oily 2-methoxy-3-methyl-2-cyclohexenol (**3c**): bp 49–50° (0.3 Torr); infrared (neat) OH 2.93 (m), C=C 5.94 (m) μ; pmr δ 1.60 (broad s, 3, Me), 1.5–2.0 (m, 6, methylenes), 3.57 (s, 3, OMe), 4.15 (m, 1, oxymethine).

Anal. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 67.50; H, 9.89.

A mixture of 10.8 g of methylene iodide, three crystals of iodine, and 3.6 g of zinc–copper couple[47] in 40 ml of ether was refluxed gently for 30 min. A solution of 2.0 g of **3c** in 10 ml of ether was added dropwise over a period of 15 min and the mixture refluxed for 5 hr. It then was treated with a moist ammonium chloride slurry, filtered, and the residue extracted with ether. The combined organic solutions were washed with 5% sodium hydroxide solution and with water, dried, and evaporated. Distillation of the residue yielded 1.6 g of colorless, oily *endo*-1-methoxy-6-methylbicyclo-[4.1.0]heptan-2-ol (**4b**): bp 48–49° (0.25 Torr); infrared (neat) OH 2.95 (m), cyclopropyl Hs 3.28 (w) μ; pmr δ 0.34 (q, 1, J = 2.0, 5.5 Hz, cyclopropyl exo H), 0.70 (d, 1, J = 5.5 Hz, cyclopropyl endo H), 1.19 (s, 3, Me), 1.1–1.7 (m, 6, methylenes), 3.31 (s, 3, OMe), 4.23 (m, 1, oxymethine).

Anal. Calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.32. Found: C, 69.31; H, 10.26.

A mixture of 800 mg of **4b** and 14 g of silver carbonate–Celite reagent[27] in 100 ml of benzene was refluxed for 44 hr. The grey, suspended solid was filtered and washed with benzene and the combined organic solutions were evaporated. Distillation of the residual oil yielded 720 mg of colorless, oily 1-methoxy-6-methylbicyclo[4.1.0]heptan-2-one (**4c**): bp 65° (1.0 Torr); infrared (neat) cyclopropyl Hs 3.25 (w), C=O 5.92 (s) μ; pmr δ 0.85 (d, 1, J = 6.0 Hz, cyclopropyl exo H), 1.30 (s, 3, Me), 1.52 (d, 1, J = 6.0 Hz, cyclopropyl endo H), 1.5–2.3 (m, 6, methylenes), 3.34 (s, 3, OMe); semicarbazone, mp 177–178°.

Anal. Calcd for $C_{10}H_{17}O_2N_3$: C, 56.85; H, 8.11; N, 19.89. Found: C, 57.05; H, 8.05; N, 19.63.

A solution of 170 mg of ketone **4c** in 5 ml of ether was added dropwise over a period of 15 min to a stirring suspension of 50 mg of lithium aluminum hydride in 5 ml of ether at room temperature and the mixture stirred for 3 hr. A moist sodium sulfate slurry was added, the mixture filtered, the residue extracted with ether, and the combined organic solutions were evaporated. Distillation of the residue gave 140 mg of colorless, oily *exo*-1-methoxy-6-methylbicyclo[4.1.0]heptan-2-ol (**4d**) (containing less than 10% **4b** according to pmr analysis): bp 48–49° (0.3 Torr); infrared (neat) OH 2.91 (m), cyclopropyl Hs 3.28 (w) μ; pmr δ 0.31 (d, 1, J = 6.0 Hz, cyclopropyl H), 1.13 (s, 3, Me), 0.9–2.0 (m, 6, methylenes), 3.30 (s, 3, OMe), 4.25 (t, 1, J = 2.5 Hz, oxymethine).

Anal. Calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.32. Found: C, 69.34; H, 10.27.

1-Methylbicyclo[3.2.0]heptan-6-one (17). A mixture of 250 mg of alcohol **4b** and 5 ml of 1 *N* hydrochloric acid was stirred at room temperature for 1 hr and then extracted with petroleum ether. The extract was washed with 5% sodium bicarbonate solution and with water, dried, and evaporated. The residual, colorless oil, 180 mg, was shown by infrared, pmr, and gpc analyses to be identical with an authentic sample of ketone **17**.[18] Identical treatment of 140 mg of alcohol **4d** yielded 88 mg of **17**.

***exo*-4-Isopropyl-1-methylbicyclo[3.2.0]heptan-7-one (21c).** A solution of 5.0 g of ketone **19** in 40 ml of 98–100% formic acid was refluxed for 16 hr. The cooled solution was diluted with 100 ml of water and extracted exhaustively with petroleum ether (bp 30–60°). The extract was washed with cold, saturated brine solution, dried, and evaporated. Pmr analysis of the colorless, residual oil, 4.9 g, proved it to be one-third starting material and two-thirds ketone **21a**: infrared (neat) C=O 5.65 (s) μ; pmr δ 0.8–1.1 (m, 7, *i*-Pro and CH), 1.35 (s, 3, Me), 1.3–2.4 (m, 6, methylenes and methines), 4.45 (d, 1, J = 5.0 Hz, C(6)-H).

Similar treatment of 3.0 g of ketone **19** with formic acid for 36 hr or even for 6 days yielded 2.7 g of starting material, ketone **21a** and its epimer **21b** [infrared (neat) C=O 5.65 (s) μ; pmr δ 0.8–1.1 (m, 7, *i*-Pro and CH), 1.35 (s, 3, Me), 1.3–2.4 (m, 5, methylenes and

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CH), 2.68 (d of d, 1, J = 2.0, 10.0 Hz, C(4)-H), 5.16 (d, 1, J = 10.0 Hz, C(6)-H)] in a 3:10:7 ratio, respectively. Chromatography of the mixture on silica gel and elution with 13:1 petroleum ether (bp 30–60°)–benzene gave a mixture of only ketones **21a** and **12b**. Formic acid treatments of this mixture or others, chromatographically enriched in either of the two ketones, for 16 hr led to the same ratio of **19**, **21a**, and **21b**.

An equilibrium mixture of 1.04 g of the trio of ketones, 2.0 g of sodium carbonate, and 200 mg of 10% palladium–charcoal in 20 ml of 95% ethanol was hydrogenated at atmospheric pressure and room temperature. Upon cessation of hydrogen uptake the mixture was filtered through Celite and the filtrate diluted with 40 ml of water. The solution was extracted exhaustively with pentane and the extract washed with saturated sodium carbonate and brine solutions, dried, and evaporated. Distillation of the oily residue yielded 705 mg of colorless, liquid ketone **21c**: infrared (neat) C=O 5.64 (s) μ; pmr δ 0.91 (d, 3, J = 6.0 Hz, *i*-Pro Me), 0.98 (d, 3, J = 6.0 Hz, *i*-Pro Me), 1.22 (s, 3, Me), 1.1–2.6 (m, 7, methylenes and methines), 3.03, 3.12, 3.20, 3.29 (four-line AB part of ABX pattern, 2, C(6)-H_2); *p*-toluenesulfonylhydrazone, mp 156–157°.

Anal. Calcd for $C_{18}H_{26}O_2N_2S$: C, 64.63; H, 7.86; N, 8.37. Found: C, 64.54; H, 7.64; N, 8.60.

β-Methoxycyclopropanecarboxylic Esters. A solution of 20.0 g of isobutyraldehyde, 29.6 g of methyl orthoformate, and 3 drops of concentrated sulfuric acid in 5.7 ml of methanol was refluxed for 28 hr. The mixture was distilled rapidly at atmospheric pressure, the last trace of product being recovered at 160 Torr. Redistillation yielded 32.3 g of 1,1-dimethoxy-2-methylpropane:[33,34] bp 99–102°; pmr δ 0.90 (d, 6, J = 7.0 Hz, methyls), 1.83 (seven-line m, 1, J = 7.0 Hz, *i*-Pro methine), 3.30 (s, 6, methoxyls), 3.92 (d, 1, J = 7.0 Hz, oxymethine). Dropwise addition of 4.0 g of a pure sample of the latter to a stirring mixture of 40 mg of dry *p*-toluenesulfonic acid in 1.6 ml of quinoline[53] heated at 200° in a distilling apparatus and simultaneous distillation of the low-boiling products led according to pmr analysis to over 95% conversion. Contamination of the starting acetal with methyl orthoformate or the use of more than 4 g of the acetal rendered the acid catalyst ineffective. Under these circumstances or by too rapid addition of starting material acetal was recovered. The distillation head was maintained at 50–60° and the ether product separated from codistilled methanol by dilution of the liquid products with an equal volume of methylcyclohexane, slow addition of the resulting solution to a stirring slurry of lithium aluminum hydride in methylcyclohexane and distillation of the mixture. Fractionation of the distillate gave 2.5 g of 1-methoxy-2-methylpropene (**10b**):[33,34] bp 70–74°; pmr spectrum δ 1.52 (broad s, 3, Me), 1.58 (broad s, 3, Me), 3.49 (s, 3, OMe), 5.71 (m, 1, oxymethine).

Ethyl diazoacetate, 5.1 g, was added dropwise over a period of 3 hr to a refluxing mixture of 1.9 g of **10b**, 1.0 g of copper–bronze[21c] in 7 ml of methylcyclohexane and the mixture refluxed for 1 additional hr. Filtration and distillation of the filtrate gave 1.9 g of cyclopropane products in a fraction of bp 99–110° (41 Torr) and a mixture of diethyl fumarate, diethyl maleate, and 13% (by pmr analysis) cyclopropanes in a subsequent fraction. Chromatography on neutral alumina, activity III, and elution with hexane yielded a liquid mixture of stereoisomers (70% trans) of ethyl 2,2-dimethyl-3-methoxycyclopropanecarboxylate (**11b**): infrared (neat) C=O cis 5.77 (s), trans 5.79 (s) μ; pmr cis isomer δ 1.08 (s, 3, trans Me), 1.22 (t, 3, J = 7.5 Hz, ethyl Me), 1.35 (s, 3, cis Me), 1.36 (d, 1, J = 7.0 Hz, ketomethine), 3.21 (d, 1, J = 7.0 Hz, oxymethine), 3.30 (s, 3, OMe), 4.09 (q, 2, J = 7.5 Hz, CH_2); trans isomer δ 1.18 (s, 3, Me), 1.23 (t, 3, J = 7.5 Hz, ethyl Me), 1.23 (s, 3, Me), 1.47 (d, 1, J = 3.0 Hz, ketomethine), 3.35 (s, 3, OMe), 3.46 (d, 1, J = 3.0 Hz, oxymethine), 4.12 (q, 2, J = 7.5 Hz, CH_2).

Anal. Calcd for $C_9H_{16}O_3$: C, 62.77; H, 9.36. Found: C, 62.52; H, 9.42.

Ethyl diazoacetate, 10.3 g, was added over a period of 90 min to a refluxing mixture of 7.0 g of 1,3-dimethyl-2-methoxycyclohexene (**3a**) and 1.0 g of copper–bronze[21c] in 15 ml of methylcyclohexane and the mixture refluxed for an additional 30 min and stirred at room temperature for 5 hr. Filtration, evaporation of the filtrate, and distillation of the residual oil gave 2.5 g of starting enol ether, 2.0 g of a mixture of diethyl fumarate and diethyl maleate, and 6.0 g of a *ca.* 70:30 mixture of stereoisomers of ethyl 2,6-dimethyl-1-methoxybicyclo[4.1.0]heptane-7-carboxylate (**4e**): bp 138–140° (6 Torr); infrared (neat) C=O 5.75 (s) μ; pmr δ 1.0–1.7 (m, 17, methyls, methylenes, methines), 3.25 (s, 3, OMe of minor isomer), 3.34 (s, 3, OMe of major isomer), 4.12 (q, 2, J = 7.5 Hz, ethyl CH_2 of minor component), 4.13 (q, 2, J = 7.5 Hz, ethyl CH_2 of major component).

Anal. Calcd for $C_{13}H_{22}O_3$: C, 68.99; H, 9.80. Found: C, 68.82; H, 9.60.

Ethyl diazoacetate, 14.2 g, was added over a 90-min period to a refluxing mixture of 10.0 g of methoxymethylenecyclohexane (**7a**) and 1.0 g of copper–bronze[21c] in 15 ml of methylcyclohexane and the mixture refluxed for an additional 30 min and stirred at room temperature for 12 hr. Filtration, evaporation of the filtrate, and distillation of the residual oil gave a 125–135° (16 Torr) fraction of 3.5 g of impure **8c** and a 135–140° (16 Torr) fraction of 10.0 g of an isomer mixture (*ca.* 70% trans) of ethyl 2-methoxyspiro[2.5]octane-1-carboxylate (**8c**): infrared (neat) C=O 5.79 (s) μ; pmr cis isomer δ 1.22 (t, 3, J = 7.5 Hz, Me), 1.49 (d, 1, J = 7.0 Hz, ketomethine), 3.21 (d, 1, J = 7.0 Hz, oxymethine), 3.32 (s, 3, OMe), 4.10 (q, 2, J = 7.5 Hz, ethyl CH_2); trans isomer δ 1.22 (t, 3, J = 7.5 Hz, Me), 1.51 (d, 1, J = 3.0 Hz, ketomethine), 3.33 (s, 3, OMe), 3.51 (d, 1, J = 3.0 Hz, oxymethine), 4.10 (q, 2, J = 7.5 Hz, ethyl CH_2).

Anal. Calcd for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50. Found: C, 67.72; H, 9.69.

Ethyl diazoacetate, 22.0 g, was added dropwise over a period of 6 hr to a refluxing mixture of 1,1-dimethoxy-2-methylpropene (**10a**)[15] and 4.0 g of copper–bronze[21c] in 25 ml of methylcyclohexane and the mixture refluxed for an additional 2 hr. Filtration and distillation of the filtrate gave 13.9 g of cyclopropane product, containing a small amount of diester by-products, in the 109–130° (32 Torr) fraction. Chromatography of the distillate on neutral alumina, activity III, and elution with 100:1 hexane–benzene yielded liquid ethyl 2,2-dimethoxy-3,3-dimethylcyclopropanecarboxylate (**11d**): bp 110–114° (27 Torr); infrared (neat) C=O 5.74 (s) μ; pmr δ 1.26 (t, 3, J = 7.5 Hz, ethyl Me), 1.26 (s, 3, Me), 1.38 (s, 3, Me), 1.61 (s, 1, ketomethine), 3.37 (s, 3, OMe), 4.12 (q, 2, J = 7.5 Hz, CH_2).

Anal. Calcd for $C_{10}H_{18}O_4$: C, 59.39; H, 8.97. Found: C, 59.18; H, 8.95.

β-Methoxycyclopropylcarbinols. A mixture of 1.9 g of cis and trans esters **11b** and 0.4 g of lithium aluminum hydride in 250 ml of dry ether was stirred at room temperature for 12 hr. Moist sodium sulfate was added, the slurry filtered, and the filtrate evaporated. Distillation of the residual oil, 1.2 g, gave a stereoisomer mixture of 2,2-dimethyl-3-methoxycyclopropyl carbinols (**11c**): bp 99–100° (27 Torr); pmr δ both isomers 0.7–1.0 (m, 1, CH), 3.4–3.7 (m, 2, CH_2); cis isomer 1.02 (s, 3, Me), 1.09 (s, 3, Me), 2.92 (d, 1, J = 7.0 Hz, oxymethine), 3.38 (s, 3, OMe); trans isomer 1.07 (s, 3, Me), 1.19 (s, 3, Me), 2.80 (d, 1, J = 3.0 Hz, oxymethine), 3.35 (s, 3, OMe).

Anal. Calcd for $C_7H_{14}O_2$: C, 64.58; H, 10.84. Found: C, 64.44; H, 10.86.

A mixture of 3.0 g of cis and trans esters **4e** and 1.9 g of lithium aluminum hydride in 25 ml of ether was stirred at room temperature for 12 hr. Work-up as above and distillation of the product yielded 2.1 g of a stereoisomer mixture of 2,6-dimethyl-7-hydroxymethyl-1-methoxybicyclo[4.1.0]heptane (**4f**): bp 142–144° (6 Torr); pmr δ 0.8–1.7 (m, 14, methylenes, methines), 3.28 (s, 3, OMe), 3.5–3.9 (m, 2, oxymethylene).

Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.70; H, 10.94. Found: C, 71.41; H, 11.00.

A mixture of 5.0 g of cis and trans esters **8c** and 3.8 g of lithium aluminum hydride in 50 ml of ether was stirred at room temperature for 4 hr. Work-up as above and distillation of the product gave 4.2 g of stereoisomers of 1-hydroxymethyl-2-methoxyspiro[2.5]-octane (**8d**): bp 139–140° (20 Torr); pmr δ both isomers 0.7–1.1 (m, 1, CH), 1.3–1.6 (m, 10, methylenes), 3.4–3.8 (m, 2, oxymethylene); cis isomer 2.92 (d, 1, J = 8.0 Hz, oxymethine), 3.38 (s, 3, OMe); trans isomer 2.83 (d, 1, J = 3.0 Hz, oxymethine), 3.35 (s, 3, OMe).

Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.28; H, 10.71.

A mixture of 6.0 g of ester **11d** and 1.2 g of lithium aluminum hydride in 200 ml of ether was stirred at room temperature for 12 hr. Work-up as above and distillation of the product yielded 3.9 g of 2,2-dimethyl-3,3-dimethoxycyclopropylcarbinol (**11e**): bp 110–113° (27 Torr); pmr δ 1.00 (t, 1, J = 7.5 Hz, CH), 1.12 (s, 3, Me), 1.17 (s, 3, Me), 3.32 (s, 3, OMe), 3.63 (d, 2, J = 7.5 Hz, CH_2).

Anal. Calcd for $C_8H_{16}O_3$: C, 59.98; H, 10.07. Found: C, 59.85; H, 10.05.

α-Vinylcarbonyl Compounds. A solution of 310 mg of *cis*- and *trans*-carbinols **11c** and 1.5 ml of 1 *N* hydrochloric acid in 1.5 ml of methanol was refluxed 15 min, then diluted with water and ex-

(53) *Cf.* B. M. Mikhailov and L. S. Povarov, *Zh. Obshch. Khim.*, **29**, 2048 (1959) [*Chem. Abstr.*, **54**, 10851 (1960)]; A. F. Thomas, *J. Amer. Chem. Soc.*, **91**, 3281 (1969).

tracted with ether. Evaporation of the extract yielded 300 mg of *ca.* 2:1 **13c** dimethyl acetal and **13c** (by pmr analysis). Hydrolysis of this mixture in 1 ml of refluxing concentrated hydrochloric acid for 2 hr led to 2,2-dimethyl-3-butenal (**13c**): semicarbazone mp 157–159° (lit.[31] mp 158–159°,[54] 158.5–160°).

A solution of 3.0 g of carbinols **4f** and 12 ml of 20% hydrochloric acid in 20 ml of methanol was heated to 50° for 45 min, then diluted with water, and extracted with ether. The extract was washed with water, dried, and evaporated. Distillation of the residual oil yielded 2.6 g of a stereoisomeric mixture of 2,6-dimethyl-2-vinylcyclohexanone (**1c**): bp 65–68° (20 Torr); infrared (neat) C=O 5.83 (s), C=C 6.20 (m) μ; pmr δ 1.00 (d, 3, J = 7.0 Hz, secondary Me), 1.12 (s, 3, Me), 1.0–2.8 (m, 7, CH and methylenes), 4.7–5.3, 5.7–6.3 (ABC m, 3, olefinic Hs).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.81; H, 10.52.

A solution of 0.90 g of *cis*- and *trans*-carbinols **8d** and 10 ml of 5% hydrochloric acid in 10 ml of methanol was heated to 50° for 30 min, then diluted with water and extracted with ether. The extract was washed with saturated sodium bicarbonate and brine solutions, dried, and evaporated. Distillation of the residual oil gave 0.65 g of liquid 1-vinylcyclohexanecarboxaldehyde (**5c**): bp 190–192° (lit.[55] bp 190–195°); infrared (neat) aldehyde CH 3.63 (w), C=O 5.77 (s) μ; 2,4-dinitrophenylhydrazone, mp 148–149°.

Anal. Calcd for $C_{15}H_{18}O_4N_4$: C, 56.60; H, 5.70; N, 17.60. Found: C, 56.71; H, 5.73; N, 17.52.

A solution of 0.50 g of *cis*- and *trans*-carbinols **8d**, 0.80 g of *p*-toluenesulfonyl chloride, and 15 ml of 5% sodium hydroxide in 10 ml of tetrahydrofuran was refluxed for 15 hr, then diluted with water, and extracted with ether. The extract was washed with sodium bicarbonate solution and with water, dried, and evaporated. Infrared and pmr spectral analysis showed the residual oil, 0.40 g, to be exclusively aldehyde **5c**.

A solution of 200 mg of alcohol **11e** and 1.5 ml of 1 *N* hydrochloric acid in 1.5 ml of methanol was refluxed for 1.5 hr, then diluted with saturated brine solution and extracted with ether. The extract was dried and evaporated leaving 150 mg of oily ester **13d** whose spectral analysis proved it identical with the ester, bp 120–123°, prepared by diazomethane treatment of acid **13e**. A solution of 300 mg of the ester [infrared (neat) C=O 5.74 (s), C=C 6.08 (m) μ; pmr δ 1.31 (s, 6, methyls), 3.67 (s, 3, OMe), 4.9–5.0, 5.1–5.3, 5.8–6.3 (ABC m, 3, olefinic Hs] and 2 ml of 10% sodium hydroxide in 2 ml of methanol was refluxed for 8 hr, then acidified and extracted with ether. The extract was dried and evaporated leaving 240 mg of liquid 2,2-dimethyl-3-butenoic acid (**13e**) identical in infrared and pmr spectra with an authentic sample.[41]

1-Methyl-1-vinylcyclohexane (22a). A solution of 200 mg of aldehyde **5c** and 270 mg of *p*-toluenesulfonylhydrazine in 5 ml of ethanol was refluxed for 3 hr, then diluted with water and extracted with ether. Evaporation of the extract, chromatography of the residue on alumina, activity II, and elution with petroleum ether yielded 350 mg of colorless, oily **5c**-tosylhydrazone: infrared (neat) NH 3.04 (m), C=N 6.08 (w), C=C 6.22 (m) μ; pmr δ 1.0–2.0 (m, 10, methylenes), 2.39 (s, 3, Me), 4.8–5.9 (ABC m, 3, olefinic Hs), 7.08 (s, 1, iminomethine), 7.34, 7.81 (AB pair of d, 4, J = 8.0 Hz, aromatic Hs). A mixture of 500 mg of the latter and 1.14 g of lithium aluminum hydride in 20 ml of tetrahydrofuran was refluxed for 12 hr. Water was added cautiously to the cooled mixture and after complete hydride decomposition the mixture was acidified and extracted with ether. The extract was washed with water, dried, and evaporated. Distillation of the residue gave 160 mg of 1-methyl-1-vinylcyclohexane (**22a**): bp 80° (95 Torr) (lit.[35a] bp 80° (95 Torr)); infrared (neat) C=C 6.11 (w), C=CH 10.99 (m) μ; pmr δ 0.97 (s, 3, Me), 1.29 (s, 2, C(2)-H and C(6)-H), 1.43 (broad s, 8, methylenes), 4.7–4.9, 5.0–5.2, 5.6–6.1 (ABC m, 3, olefinic Hs).

Stearyl chloride, 9.7 g, was added slowly to a solution of 4.0 g of 1-methyl-1-(β-hydroxyethyl)cyclohexane (**22b**)[35a] in 70 ml of pyridine and the mixture stirred for 12 hr. It then was diluted with water and extracted with ether. The extract was washed with 1 *N* hydrochloric acid solution and with water, dried, and evaporated yielding 10.0 g of ester; infrared spectrum (neat) C=O 5.74 (s) μ. The latter, 4.5 g, was placed in a distillation apparatus heated by a Wood's metal bath. The bath temperature was raised over a 30-min period to 450° and kept there for 3 hr. The distillate was diluted with 50 ml of ether and dried. Evaporation of the solvent and distillation of the residue yielded 1.1 g of hydrocarbon **22a**, bp and spectra identical with those of the above sample.

A mixture of 3.0 g of alcohol **22b** and 2.3 g of boric acid was heated at 350° for 30 min, refluxed for another 30 min, and then distilled. Ether was added to the distillate and the solution dried and evaporated. The residual oil (57% recovery) was fractionated by preparative gas-phase chromatography (SE 30 column at 75°, flow rate 30 ml/min): fraction 1, 15%, retention time 2.6 min, hydrocarbon **22a**; fraction 2, 30%, 3.3 min, 1-isopropylcyclohexene; fraction 3, 9%, 4.2 min, a two-component mixture not further characterized; fraction 4, 3%, 4.8 min, isopropylidenecyclohexane; 43% starting alcohol recovered. The olefins were identified by direct comparison with authentic samples.

Diazo Ester 23. Ethyl diazoacetate, 2.8 g, was added dropwise over a 2-hr period to a mixture of 2.0 g of enamine **7c** and 1.0 g of cuprous chloride in 40 ml of dry ether and the mixture stirred at room temperature for an additional 2 hr. It was filtered and the filtrate washed with saturated sodium bicarbonate and with water, dried, and evaporated. Chromatography of the residue on activity II alumina and elution with petroleum ether yielded 3.5 g of ethyl β-cyclohexyl-β-(*N*-pyrrolydinyl)α-diazopropionate (**23**) (distilled at 105° ($<10^{-3}$ Torr)): infrared (neat) N_2 4.79 (s), C=O 5.89 (s) μ; pmr δ 1.28 (t, 3, J = 7.2 Hz, Me), 0.8–2.0 (m, 15, CH and methylenes), 2.4–2.7 (m, 4, aminomethylenes), 3.30 (d, 1, J = 7.5 Hz, aminomethine), 4.18 (q, 2, J = 7.2 Hz, oxymethylenes).

Anal. Calcd for $C_{15}H_{25}O_2N_3$: C, 64.49; H, 9.02; N, 15.04. Found: C, 64.30; H, 8.94; N, 15.26.

Lactones 24. A solution of 1.0 g of cis and trans esters **8c** and 4 ml of concentrated hydrochloric acid in 16 ml of methanol was refluxed for 2 hr, then diluted with water, and extracted with ether. The extract was dried and evaporated. Distillation of the residue yielded 0.80 g of β,β-pentamethylene-γ-methoxy-γ-butyrolactone (**24a**): bp 128° (20 Torr); infrared (neat) C=O 5.59 (s) μ; pmr δ 1.4–1.6 (m, 10, methylenes), 2.35 (d, 2, J = 2.0 Hz, ketomethylene), 3.49 (s, 3, OMe), 4.98 (s, 1, oxymethine).

Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 64.75; H, 8.59.

A solution of 2.5 g of *trans*-**11b** and 20 ml of 20% sulfuric acid in 20 ml of dioxane was refluxed for 6 hr. Pmr analysis of the mixture at this stage revealed it to be a 1:1 mixture of pseudo ester **24c** [δ 1.15 (s, 6, methyls), 2.35 (center of AB pair of doublets, 2, CH_2), 3.51 (s, 3, OMe), 4.95 (s, 1, oxymethine)] and pseudo acid **24b**. Hence refluxing was continued for 5.5 hr. The mixture was saturated with sodium chloride and extracted with ether. The extract was dried and evaporated. Distillation of the residue gave 1.7 g of β,β-dimethyl-γ-hydroxy-γ-butyrolactone (**24b**): bp 90–94° (0.35 Torr); infrared (CCl_4) OH 2.92 (m), C=O 5.55 (s), 5.63 (s), 5.85 (m), 5.92 (m) μ; pmr δ 1.16 (s, 6, methyls), 2.43 (d, 2, J = 6.0 Hz, CH_2) 5.47 (broad s, 1, oxymethine); yellow 2,4-dinitrophenylhydrazone, mp 188–190°.

Anal. Calcd for $C_{10}H_{14}O_6N_2$: C, 46.45; H, 4.55; N, 18.06. Found: C, 46.11; H, 4.85; N, 17.94.

A solution of 220 mg of ester **11d** and 1.5 ml of 1 *N* hydrochloric acid in 1.5 ml of methanol was refluxed for less than 1 min, then saturated with sodium chloride, and extracted with ether. The extract was dried and evaporated. Distillation of the residue, 187 mg, gave methyl ethyl α,α-dimethylsuccinate (**13f**): bp 104–106° (27 Torr); infrared (neat) C=O 5.72 (s) μ; pmr δ 1.22 (t, 3, J = 7.5 Hz, ethyl Me), 1.27 (s, 6, methyls), 2.59 (s, 2, CH_2), 3.69 (s, 3, OMe), 4.12 (q, 2, J = 7.5 Hz, oxymethylene). A solution of 900 mg of **13f** and 10 ml of 10% sodium hydroxide in 10 ml of dioxane was stirred at room temperature for 24 hr. It was diluted with ether and the two phases were separated. The aqueous solution was acidified with concentrated hydrochloric acid, benzene added, and water removed azeotropically. The mixture was filtered from precipitated sodium chloride, the precipitate extracted with benzene, and the combined organic solutions evaporated. Crystallization of the product, 510 mg, mp 137–140°, from benzene yielded α,α-dimethylsuccinic acid (**13g**): mp 138–140° (lit.[44] mp 138–139°); spectra identical with published data.

Dihydrojasmone (28). A solution of 10.1 g of *n*-enanthyl chloride in 100 ml of dry ether was added dropwise over a period of 3 hr to a solution of diazomethane (from 43.0 g of *N*-nitroso-*N*-methylurea) in 400 ml of ether at 0°. The solution was stirred for 12 hr while slowly warming to room temperature. Evaporation yielded 10.1 g of oil whose pmr analysis revealed it to contain *ca.* 10% chloro ketone. Chromatography of 2.4 g of the oil on alumina, activity I, and elution with hexane gave chloro ketone.

(54) H. Adkins and K. Folkers, *J. Amer. Chem. Soc.*, **53**, 1416 (1931).
(55) J. Stewart, J. Staib, and F. Knoth, Jr., U. S. Patent 2,810,748 (Oct 22, 1957) [*Chem. Abstr.*, **52**, 3857 (1958)].

Subsequent elution with 1:1 hexane–benzene yielded 1.7 g of desired product whose distillation afforded 1.6 g of 1-diazo-2-octanone (**25**): bp 55° (0.3 Torr); infrared (neat) N_2 4.74 (s), C=O 6.08 (s) μ; pmr δ 0.7–1.0 (m, 3, Me), 1.1–1.9 (m, 8, methylenes), 2.1–2.5 (m, 2, ketomethylene), 5.28 (s, 1, CH).

A solution of 1.4 g of **25** in 3 ml of methylcyclohexane was added over a period of 1 hr to a refluxing mixture of 0.80 g of isopropenyl acetate and 0.2 g of copper–bronze[21c] in 5 ml of methylcyclohexane and the mixture refluxed for an additional 12 hr. It was filtered, the residue washed with methylcyclohexane, and the combined organic solutions were evaporated. Chromatography of the residual oil, 1.4 g, on alumina, activity I, and elution with hexane gave 1.0 g of colorless oil whose distillation produced a stereoisomeric mixture of 1-acetoxy-1-methyl-2-enanthylcyclopropane (**27**): bp 92–94° (1 Torr); infrared (neat) C=O 5.73 (s), 5.88 (s) μ; pmr δ 1.44 (s, 3, quaternary Me in one isomer), 1.53 (s, 3, quaternary Me in other isomer), 2.00 (s, 3, Ac in one isomer), 1.92 (s, 3, Ac in other isomer), 0.7–2.8 (m, 16, other Hs).

Anal. Calcd for $C_{13}H_{22}O_3$: C, 68.99; H, 9.80. Found: C, 69.13; H, 9.90.

A solution of 800 mg of **27** and 10 ml of 5% sodium hydroxide in 10 ml of methanol was kept at room temperature for 20 hr. The alcohol was removed under vacuum and the remaining aqueous solution extracted with ether. The extract was washed with water, dried, and evaporated. The residual oil, 590 mg, was chromatographed on activity I alumina. Elution with hexane yielded 490 mg of dihydrojasmone (**28**), infrared and pmr spectrally identical with an authentic specimen; semicarbazone, mp, mmp 173–175°.

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The Crystal and Molecular Structure of 3,7-Bis(*p*-iodophenyl)-4,5,6-triphenyl-4*H*-1,2-diazepine

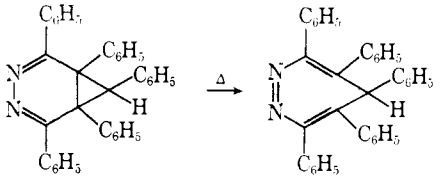
J. N. Brown, R. L. Towns, and L. M. Trefonas*

Contribution from the Department of Chemistry, Louisiana State University in New Orleans, New Orleans, Louisiana 70122. *Received May 18, 1970*

Abstract: The crystal and molecular structure of 3,7-bis(*p*-iodophenyl)-4,5,6-triphenyl-4*H*-1,2-diazepine has been determined by single-crystal X-ray diffraction methods. The compound crystallizes in space broup $P\bar{1}$ (No. 2) with unit cell constants: a = 10.463 (1), b = 13.418 (1), c = 12.082 (1) Å, α = 97.86 (1), β = 107.06 (1), and γ = 109.19 (1)°. The structure was solved by the heavy-atom method and refined by block-diagonal least-squares to a final R value of 0.072 for the 2654 independently measured, statistically significant reflections. The seven-membered ring differs in conformation and location of the double bonds from either of the previously postulated structures. A mechanism for the formulation of this thermal isomer is proposed herein.

The synthesis and characterization of heterocyclic unsaturated seven-membered ring systems is a relatively new field. The inherent synthetic difficulties with these compounds are further complicated by the ambiguities resulting in structure assignments based on routine physical techniques (ir, uv, nmr, mass spectrum fragmentation).

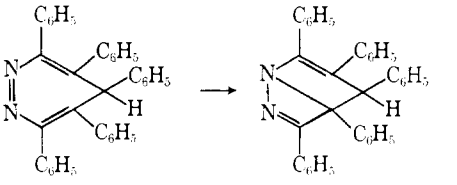
For example, the adduct of triphenylcyclopropene with diphenyl-*s*-tetrazine can be thermally isomerized at temperatures above 100° to a second stable compound. Sauer and Heinrich[1] postulated structures for the two isomeric forms on the bases of uv correlations as shown in (A). Battiste and Barton,[2] using



(A)

I II

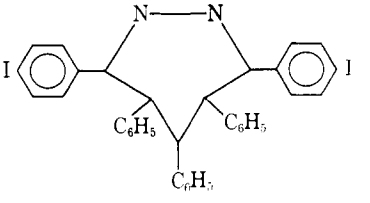
ir, uv, and nmr techniques, reasonably established that the structure of the low-temperature isomer was that previously assigned to the high-temperature form, namely II. Battiste then suggested that the high-temperature thermal isomer was a bicyclic system (both are illustrated in (B)) from which one could then easily rationalize mass spectrum fragmentation products such as benzonitrile.



(B)

II III

In order to resolve this difference and to establish definitely the structure of the high-temperature form, a single-crystal X-ray structure determination was undertaken. The compound studied, a heavy atom derivative, is shown in IV (bonding within the seven-



IV

membered ring not indicated here). The structure determination indicated that both previous authors

* To whom correspondence should be addressed.

(1) J. Sauer and E. Heinriche, *Tetrahedron Lett.*, 4979 (1966).

(2) M. A. Battiste and T. J. Barton, *ibid.*, 1227 (1967).