mmol) of 12-Br in 20 ml of 3.8 *M* sodium methoxide in absolute methanol.

The samples were treated in the manner described for the neutral methanolysis, but the recovered ethers were not recrystallized. Because the 3.8 *M* methoxide solution contained large amounts of dissolved solids, the solution was poured into water which was then extracted with dichloromethane. After the solution was dried over anhydrous magnesium sulfate, the ethers were isolated by vacuum evaporation. All products were 1:1 12-OCH_3 and 13-OCH_3 by pmr analysis. The pmr spectrum had absorbances at τ 2.8 m (12 aromatic H), 5.25 s (H-5), 5.45 s, and 5.57 s (0.5 proton each, H-1 and H-2).

Silver Ion Assisted Acetolysis of 10-Br.—Compound 10-Br (200 mg, 0.575 mmol) was added to 10 ml of glacial acetic acid which contained 111 mg (0.664 mmol) of silver acetate. The mixture was stirred and heated for 10 min. The reaction flask was cooled; silver bromide was collected by filtration and washed with several portions of ether. The combined filtrates were washed with water, 10% sodium carbonate solution, and saturated sodium chloride. The ether solution was dried ($MgSO_4$) and the ether evaporated to give 186 mg (99%) of 2-tribenzobicyclo[3.2.2]nonatrienyl acetate (10-OAc), mp 177–178°, after recrystallization from benzene–petroleum ether; pmr τ 2.8 m (12 aromatic H), 3.83 d (J = 4.5 Hz, H-2), 5.17 s (H-5) 5.44 d (H-1), and 7.93 s (3, $OCOCH_3$).

Anal. Calcd for $C_{23}H_{18}O_2$: C, 84.64; H, 5.56. Found: C, 84.83; H, 5.73.

Attempted Silver Ion Assisted Acetolysis of 5-Cl and 6-Cl.—A mixture of 202 mg (0.666 mmol) of 5-Cl and 120 mg (0.720 mmol) of silver acetate in 10 ml of glacial acetic acid was set under reflux for 50 hr. The organic solids were isolated according to the procedure outlined above. Only starting chloride was obtained. When the reaction was repeated at 210° for 48 hr, in a sealed tube, starting material was again isolated. Similar experiments with 6-Cl also led to recovery of starting material.

Treatment of Acetates with Perchloric Acid in Acetic Acid.—A solution of 100 mg of 10-OAc in 1 *M* perchloric acid in glacial acetic acid was heated at reflux for 1 hr. Work-up gave only recovered 10-OAc. When the experiment was conducted for 26 hr, the acetate was destroyed and no material could be recovered. Similar treatments of 5-OAc and 6-OAc for 2 hr gave recovery of starting materials.

Pmr Spectra of Some Triptycenes.—Some triptycene derivatives were prepared as synthetic intermediates and it seems reasonable to record their pmr spectra here. The spectrum of triptycene (3)itself has been recorded[16] and our data are consistent: τ 2.7 m (6 aromatic H), 3.1 m (6 aromatic H), and 4.62 s (2, H-9, H-10). New data include: **1-aminomethyltriptycene** (4),[5] τ 2.6 m (6 aromatic H), 3.1 (6 aromatic H), 4.64 s (H-10), and 5.69 broad s, (2, CH_2); **1-triptycenecarboxaldehyde**,[5] τ 2.5 m (6 aromatic H), 3.1 m (6 aromatic H), and 4.66 s (H-10); **1-hydroxymethyltriptycene**[5] (6-OH), τ 2.5 m (6 aromatic H), 3.1 m (6 aromatic H), 4.54 s (H-10), 4.82 d (2, J = 4 Hz, CH_2), and 5.61 t (OH); **1-acetoxymethyltriptycene** (6-OAc), mp 218–221°, prepared from 6-OH with acetic anhydride in pyridine, pmr τ 2.7 m (6 aromatic H), 3.1 m (6 aromatic H), 4.37 s (2, CH_2), 4.64 s (10-H), and 7.85 s ($OCOCH_3$) (*Anal.* Calcd for $C_{23}H_{18}O_2$: C, 84.64; H, 5.56. Found: C, 84.40; H, 5.58.); **1-ethylenedioxymethyltriptycene**,[5] τ 2.5 m (6 aromatic H), 3.0 m (6 aromatic H), 3.73 s (CH(–O)–O), 4.69 s (H-10), and 5.75 m (4, CH_2CH_2); **1-dimethoxymethyltriptycene**,[5] τ 2.6 m (6 aromatic H), 2.9 m (6 aromatic H), 4.14 s (CH(–O)–O), 4.64 s (H-10), and 5.92 s (6, OCH_3).

Registry No.—**1**, 24098-00-8; **4**, 4423-42-1; **5**-OH, 24098-02-0; **5**-OAc, 24098-03-1; **5**-Cl, 24098-04-2; **5**-OEt, 24098-05-3; **6**-Cl, 1469-58-5; **6**-H, 793-39-5; **6**-OH, 1469-57-4; **6**-OAc, 24098-09-7; **10**-Br, 24098-10-0; **10**-OCH_3, 24098-11-1; **10**-OEt, 24098-12-2; **10**-OH, 24098-13-3; **10**-OAc, 24098-14-4; **11**-Br, 24098-15-5; **11**-D, 24098-16-6; **12**-OH, 24098-17-7; **12**-Br, 24098-18-8; **12**-OCH_3, 24098-19-9; **13**-OCH_3, 24098-20-2; **15**, 24098-21-3; 2-bromo-1-chlorotribenzobicyclo[3.2.2]nonatriene, 24098-22-4; 1-triptycenecarboxaldehyde, 1469-54-1; 1-ethylenedioxymethyltriptycene, 1469-55-2; 1-dimethoxymethyltriptycene, 1469-56-3.

Acknowledgment.—The authors are indebted to the National Science Foundation for support of this work.

Transition-State Conformations in the Reductive Opening of Cyclopropyl Methyl Ketones[1]

WILLIAM G. DAUBEN AND RICHARD E. WOLF

Department of Chemistry, University of California, Berkeley, California 94720

Received December 1, 1969

The transition-state conformations in the lithium–ammonia reduction of three cyclopropyl methyl ketones, **1–3**, were determined through trapping of the enolates formed in the process. In the ketones studied, the cisoid conformer was found to predominate in the transition-state population distribution. The conformer population is more cisoid if the cyclopropane ring is unsubstituted or substituted in the 2 position than if it is substituted in the 1 position. The enolate trapping experiments show a similarity between ground-state (as calculated from nmr spectral data) and transition-state conformations in the lithium–ammonia reduction of cyclopropyl methyl ketones.

The importance of transition-state conformational preferences in photochemical excitation[2–4] or lithium–ammonia reductions[5–8] of various conjugated cyclopropyl ketones has been well documented. In the photochemical excitation or the lithium–ammonia reduction of fused-ring conjugated cyclopropyl ketones, fragmentation occurs with the cyclopropane bond that has the better orbital overlap with the adjacent carbonyl π system. The conformational geometry of these ring systems is fixed by the fusion of the two rings.

In acyclic conjugated cyclopropyl alkyl ketones the conformational restraints are removed and the ketone carbonyl is allowed to rotate freely over both bonds of the cyclopropane ring. The lithium–ammonia reduction of acyclic cyclopropyl ketones has also been shown to be a highly selective process[7,8] where the cyclopropane bond that cleaves is controlled by both steric and electronic factors. In the reductive cleavage of *cis*- and *trans*-2-methylcyclopropyl methyl ketone, rupture of the C-1–C-3 bond gives rise to a more thermody-

(1) This work was supported in part by Public Health Service Grant CY-04284, National Cancer Institute, U. S. Public Health Service.

(2) W. G. Dauben and G. W. Shaffer, *Tetrahedron Lett.*, 4415 (1967).

(3) L. D. Hess and J. N. Pitts, Jr., *J. Amer. Chem. Soc.*, **89**, 1973 (1967).

(4) W. G. Dauben, L. Schutte, R. E. Wolf, and E. J. Deviny, *J. Org. Chem.*, **34**, 2512 (1969).

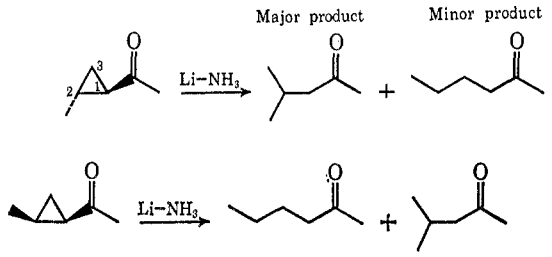
(5) T. Norin, *Acta Chem. Scand.*, **19**, 1289 (1965).

(6) W. G. Dauben and E. J. Deviny, *J. Org. Chem.*, **31**, 3794 (1966).

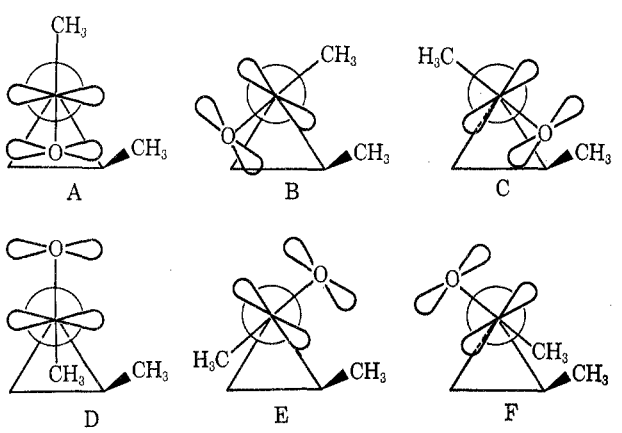
(7) R. Fraise-Jullien and C. Frejaville, *Bull. Soc. Chim. Fr.*, 4449 (1968).

(8) W. G. Dauben and R. E. Wolf, *J. Org. Chem.*, **35**, 374 (1970).

namically stable carbanion intermediate (primary carbanion) than does fragmentation of the C-1–C-2 bond (secondary carbanion). When no steric interaction occurs between the carbonyl group and the 2-methyl substituent (such as is the case with *trans*-2-methylcyclopropyl methyl ketone), ring opening occurs at the



C-1–C-3 bond in accord with relative carbanion stabilities. Reductive cleavage of *cis*-2-methylcyclopropyl methyl ketone, however, occurs with fragmentation of the C-1–C-2 bond leading to the less stable carbanion intermediate. This result suggests a conformational preference in the transition state of the reductive process where one of the cyclopropane bonds has a preferential overlap with the carbonyl π system. In the case of the *cis*-substituted cyclopropane, a steric element causes overlap control of the reaction to be in competition with electronic control. The contrasting ring-opening pattern of the isomeric cyclopropyl alkyl ketones can best be explained by the consideration of several conformers.

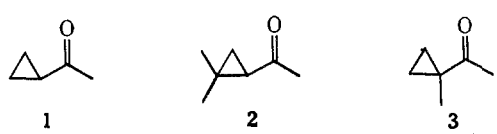


The "bisected conformers A and D represent the situation where both bonds of the cyclopropane ring have equal overlap with the carbonyl π cloud. Because of the high bond-breaking selectivity of the lithium–ammonia reduction it is felt that these conformers contribute little to the transition state at the moment of ring opening. Rather, it is more important to consider the cisoid (B and C) and transoid (E and F) *gauche* conformers. Transition states related to conformations B and E would be expected to lead to C-1–C-2 fragmentation whereas conformations C and F would be responsible for C-1–C-3 cleavage. In the absence of a steric element at C-2, either of the respective *gauche* conformers (B and C or E and F) has equal probability, and the electronic factor controls the reductive process. The rotation of the carbonyl is restricted when a *cis* substituent is present (for transition-state conformations C and F would be expected to be of higher energy). Transition state conformations B and E are preferred and the ring cleavage occurs at the C-1–C-2 bond.

As was previously reported,[8] the product ratio of the ring-opened ketones is insensitive to a variation of size in the reducing metal. This result suggested that the conformation of the transition state did not change significantly because of the increased size of the metal atom. This insensitivity could be due either to the fact that the lithium atom (the smallest atom of the series) was already large enough to establish the preferred conformation or that the transition state conformer was predominantly transoid. Although the high selectivity of the metal–ammonia reduction can be adequately explained by either the cisoid or transoid geometries, the study with various metals suggested a transoid preference, which is in opposition to the findings[9,10] that ground-state conformations of cyclopropyl methyl ketones are predominantly cisoid. The present work was initiated to settle this discrepancy.

The conformational distributions of several substituted cyclopropyl methyl ketones have been calculated from nmr spectral measurements.[9] Owing to the diamagnetic anisotropy of the cyclopropane ring[11] it has been possible to calculate relative ground-state conformer populations. From nmr and electron diffraction data[10] it has been reported that cyclopropyl methyl ketone exists predominantly as the *s-cis* conformer. By way of comparison, cyclopropylcarboxaldehyde is reported[12] to exist mainly as the *s-trans* conformer. These conformational preferences are thought to be owing to the size of the group attached α to the carbonyl carbon. It is conceivable that metal coordination with the carbonyl oxygen could cause a shift in conformational population from a cisoid distribution in the ground state to a transoid population in the transition state.

The compounds chosen for the present study were cyclopropyl methyl ketone (**1**), 2,2-dimethylcyclopropyl methyl ketone (**2**), and 1-methylcyclopropyl methyl ketone (**3**). The lithium–ammonia reduction of a conjugated cyclopropyl ketone can be viewed as an overall two-electron process to give a carbanion–enolate intermediate.[13] The carbanion generated is sufficiently basic ($pK_a > 50$)[14] to abstract a proton from ammonia ($pK_a \sim 34$), but the enolate that remains ($pK_a \sim 16$) is not basic enough to abstract a second proton from ammonia, and it will remain until a proton source is added



(9) J. L. Pierre and P. Arnaud, *Bull. Soc. Chim. Fr.*, 1690 (1966).

(10) L. S. Bartell, J. P. Guillory, and A. T. Parks, *J. Phys. Chem.*, **69**, 3043 (1965).

(11) H. M. McConnell, *J. Chem. Phys.*, **27**, 226 (1957).

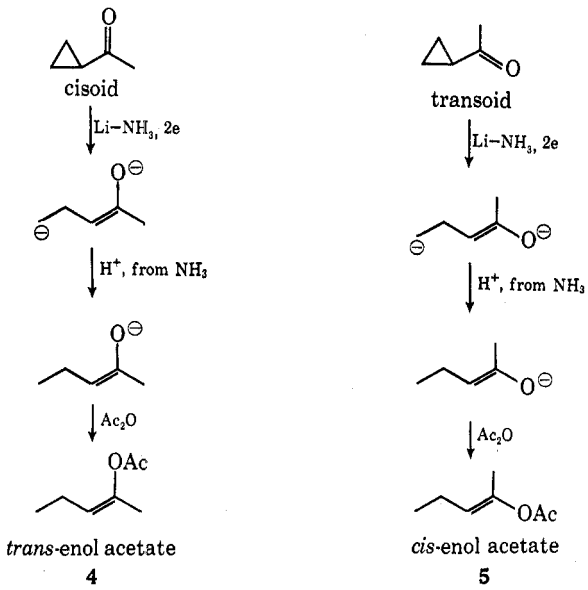
(12) G. J. Karabastos and N. Hsi, *J. Amer. Chem. Soc.*, **87**, 2864 (1965).

(13) Considerable evidence can be found in the literature to support the hypothesis that the β carbon of the cyclopropane ring acquires carbanion character during the reductive process. See (a) D. H. Williams, J. M. Wilson, H. Budzikiewicz, and C. Djerassi, *J. Amer. Chem. Soc.*, **85**, 2091 (1963); (b) M. Fetizon and J. Gore, *Tetrahedron Lett.*, 471 (1966); (c) G. Stork, P. Rosen, N. Goldman, R. V. Coombs, and J. Tsuji, *J. Amer. Chem. Soc.*, **87**, 275 (1965); (d) H. A. Smith, B. J. L. Huff, W. J. Powers, III, and D. Caine, *J. Org. Chem.*, **32**, 2851 (1967).

(14) H. Smith, "Organic Reactions in Liquid Ammonia," Vol. I, part 2, Interscience Publishers, Inc., New York, N. Y., 1963.

or it is trapped by a reagent such as acetic anhydride.[15] The geometry of the lithium enolate thus formed will be related to the original conformer of the cyclopropyl methyl ketone at the time of ring opening provided that no equilibration of the lithium enolate takes place during the trapping process. This sequence is represented in Scheme I.

SCHEME I



The trapping of enolate anions under kinetic and equilibrating conditions has undergone extensive investigation.[15-17] Lithium enolates are particularly resistant to isomeric equilibration under various trapping conditions and have been used to assess the extent of kinetic control in enolate alkylations.[15,18] The trapping of lithium enolates with acetic anhydride leads only to O-acylated products yielding the respective enol acetates. To demonstrate the slowness of isomeric equilibration relative to trapping with acetic anhydride, House and Trost[17] treated a specific enol acetate with methyl lithium to generate the corresponding lithium enolate. When this enolate was reacylated with acetic anhydride, no detectable interconversion to the other geometrical isomer was observed.

It is also of interest to note that House and coworkers[15-17] were able to separate and identify the structures of several enol acetates. The nmr spectra of the isomeric enol acetates show that the vinylic hydrogen β to the acetoxy function is deshielded in the *cis*-enol acetate relative to that of the *trans*-enol acetate.

With this information as background, it was felt that the lithium enolates formed from a lithium in liquid ammonia reduction would provide information about the transition-state conformational populations of various cyclopropyl methyl ketones. The procedure utilized for enolate trapping was essentially that described by House and Kramar.[15] Following the lithium in liquid ammonia reduction, the ammonia was evaporated and replaced with 1,2-dimethoxyethane. The resulting suspension was added to a cold, freshly distilled solution of acetic anhydride. The products were worked up in the usual manner[15] and identified by their nmr spectra in benzene.[15] The reaction products were contaminated with varying amounts of unreacted starting material and hydrolyzed enolate. The results of these experiments are shown in Table I.

TABLE I

ENOL ACETATE COMPOSITION FROM REDUCTIVE OPENING OF CYCLOPROPYL METHYL KETONES

Ketone	*trans*-Enol[a] acetate, %	*cis*-Enol acetate, %	% enol acetate[b] in product mixture
1	4, 82	5, 18	89
2	6, 88	7, 12	33–65[c]
3	10, 70	11, 30	46

[a] The *trans*-enol acetate corresponds to a cisoid conformation. The ratios are normalized to 100%. [b] The remainder of the product mixture included cyclopropyl ketone and hydrolyzed enolate. [c] The ratio of *trans*- to *cis*-enol acetate was calculated from the major bond-breaking path.

As shown in Scheme I the cleavage of cyclopropyl methyl ketone (1) can lead to two isomeric enol acetates **4** and **5**. The results of Table I show that the predominant conformer at the transition state is cisoid. This result is similar to the conformational preference of the ground-state molecule as found by nmr[9] and electron diffraction data[10] as shown in Table II.

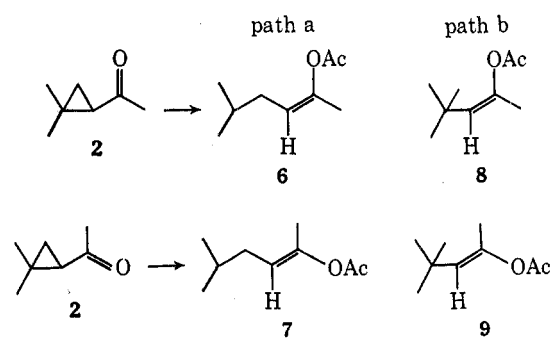
TABLE II

CONFORMATIONAL POPULATIONS OF CYCLOPROPYL METHYL KETONES AS DETERMINED BY VARIOUS METHODS[a]

Method	1	2	3
Electron diffraction[10]	80:20 ± 15%		
Nuclear magnetic resonance[9]	70:30	70:30	50:50
Enolate trapping	82:18	88:12	70:30

[a] The ratio is expressed as cisoid:transoid.

Reduction of 2,2-dimethylcyclopropyl methyl ketone (2) with lithium in liquid ammonia can provide four possible enol acetates **6**, **7**, **8**, and **9**. Enol acetates **6** and **7** are formed from the major reductive path whereas enol acetates **8** and **9** are produced *via* the minor reductive path. The enol acetates **6**, **7**, and **8** were separated on a vpc column (20% XF-1150 cyanosilicone) and were identified by spectral comparisons

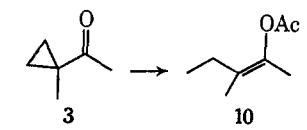


and vpc retention times to independently prepared samples. Enol acetate **9** was not detected in the product mixture, but because of the multiplicity of products its presence could not be ruled out. The result of this trapping experiment clearly shows that the cisoid conformers predominate the transition-state population distribution. Thus, in this case, the transition-state population distribution closely approximates

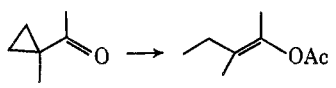
(15) H. O. House and V. Kramar, *J. Org. Chem.*, **28**, 3362 (1963).
(16) H. O. House and B. Trost, *ibid.*, **30**, 1341 (1965).
(17) H. O. House and B. Trost, *ibid.*, **30**, 2502 (1965); see also ref 10c and d.
(18) D. Caine, *ibid.*, **29**, 1868 (1964).

the results reported[9] for the ground-state molecule (see Table II). This fact suggests that the solvated electron-reductive process is very rapid and that little change occurs between the ground-state and transition-state conformations. The insensitivity of the product ratio to a change in the size of the reducing metal is apparently not owing to a transoid geometry.

It had been reported by Pierre and Arnaud[9] that 1-methylcyclopropyl methyl ketone (**3**) exists as a 50:50 mixture of *cis* and *trans* conformers. One might expect



3 **10**



3 **11**

that a nonbonded interaction between the 1-methyl substituent and the α-methyl group would cause a shift toward more transoid conformers in the ground state. The enolate-trapping results suggest this same trend in the transition state.

As mentioned earlier, the reductive cleavage of an unsymmetrically substituted cyclopropyl ketone (such as ketone **2**) can lead to four isomeric enol acetates. If one examines the ratios of the *trans*-enol acetates **6** and **8**, which come from the same conformer *via* path a or path b cleavage, it is possible to evaluate whether one conformer is responsible for path a cleavage and the other conformer responsible for path b cleavage or whether both reductive paths come from the same conformational distribution. If a cisoid conformer were responsible for all path a type cleavage and a transoid conformer for fragmentation through path b, then one would expect to see a marked contrast in the ratios of the *trans*-enol acetates when compared with the overall reduction product ratio. If both cleavages were resulting from the same conformer distribution, then the *trans*-enol acetate ratios should reflect the overall product ratio. These results are summarized in Table III. From these data it is clear that both

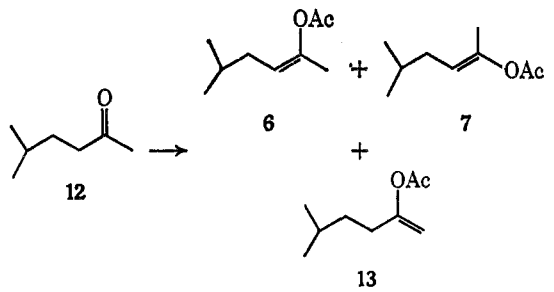
TABLE III

RATIOS OF THE *trans*-ENOL ACETATES 6 AND 8 FROM PATH a OR PATH b CLEAVAGE IN THE LITHIUM–AMMONIA REDUCTION OF KETONE 2

Run	Path a	Path b	Overall product ratio Path a	Path b
1	73	27		
2	80	20		
3	69	31		
Average	77	23	76	24

reductive paths are proceeding from the same conformational equilibrium. The nearly identical ratio of the *trans*-enol acetates to the overall product ratio suggests that the rate of formation of either ring-cleaved product must be of the same order of magnitude.

In order to establish that the enol acetates obtained from this study were kinetic products and properly reflected the conformational equilibrium, the corresponding enol acetates related to isoamyl methyl ketone (**12**) were prepared under kinetic and equilibrating con-



12 **6** **7** **13**

ditions. The enol acetate ratios obtained under these conditions are compared to the ratios observed in the enolate trapping experiments in Table IV. The rela-

TABLE IV

ENOL ACETATE RATIOS OBTAINED UNDER VARIOUS CONDITIONS FROM ISOAMYL METHYL KETONE (12)

Procedure	6	7	13
Kinetic (isopropenyl acetate, H^+)	58	26	16
Equilibrium (acetic anhydride, H^+)	68	29	3
Enolate trapping	88	12	

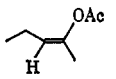
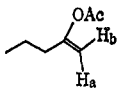
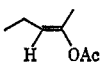
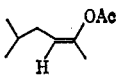
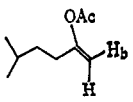
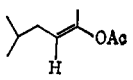
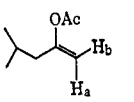
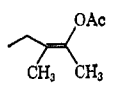
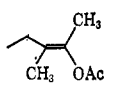
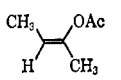
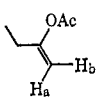
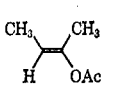
tive amounts of each enol acetate found under kinetic or equilibration conditions are in good agreement with the data reported by House[15] for similar compounds. If equilibration had occurred in the enolate-trapping experiments one would have to conclude that the cisoid conformer is even more predominant than indicated by the observed values. Based on the ground-state populations a completely cisoid conformer is unlikely.

The study of the conformational population of 1-methylcyclopropyl methyl ketone (**3**) presented some interesting complications. The enol acetates **10** and **11** could not be separated on any of the vpc columns at hand (XF-1150 cyanosilicone, SE-30 silicone, and Carbowax 20M). However, the presence of the two isomers was readily apparent when the nmr spectrum in benzene was examined. Two methyl triplets were observed at δ 0.92 and 0.88 in a ratio of 70:30, respectively. The product assignment was made, using the analogy similar to that of House[15] for the β-vinylic hydrogen, on the basis that the isomer with the methyl *cis* to the acetoxy function should be deshielded relative to the isomer with the *trans* methyl–acetoxy relationship. In addition, the vinylic methyl *cis* to the acetoxy group should appear downfield relative to the *trans* methyl. The larger peak (70%) was upfield. Using both peaks it was clear that the major isomer was the *trans*-enol acetate **10** and the minor isomer was *cis*-enol acetate **11**. Double resonance experiments were conducted with the enol acetate mixture. Irradiation of the vinylic methylene region caused a collapse of the two terminal methyl triplets into two singlets. The singlet ratio was 70% **10** to 30% **11**.

In summary, the enolate-trapping experiments clearly show the preference for a cisoid geometry in the transition state of the lithium–ammonia reduction of cyclopropyl methyl ketones. The high bond-breaking selectivity (in the cases where there is a *cis*-2-methyl substituent on the cyclopropane ring) of the process strongly suggests a cisoid *gauche* conformational

TABLE V

ENOL ACETATES. SPECTRAL CHARACTERISTICS

	Structure	Infrared spectrum, ν^{CCl_4} cm^{-1}	Nmr spectrum δ, (benzene) Vinyl H	Nmr spectrum δ, (benzene) Other
4		1750, 1695, 940	4.83	0.86 (t, 3, terminal CH_3, J = 7 Hz)
14		1755, 1665, 870	4.40 H_a 4.60 H_b	0.72 (distorted t, 3 Hz)
5		1750, 1692, 893	5.12	0.83 (t, 3, terminal CH_3, J = 7 Hz)
6		1750, 1692, 935	4.78	0.85 (d, 6, J = 6 Hz)
13		1750, 1660, 870	4.50 H_a 4.68 H_b	0.78 (d, 6, J = 6 Hz)
7		1750, 1690, 910	5.05	0.83 (d, 6, J = 6 Hz)
8		1750, 1695, 943	4.68	1.05 (s, 9)
15		1750, 1660, 870	4.46 H_a 4.75 H_b	0.87 (s, 9)
10		Could not be separated by vpc from the geometric isomer	1.47 (CH_3)	0.92 (t, 3, J = 7 Hz, CH_3–CH_2
11			1.52 (CH_3)	0.88 (t, 3, J = 7 Hz, CH_3–CH_2)
16		1750, 1698	4.78	1.39 (m, 3)
17		1750, 1660	4.50 H_a 4.65 H_b	0.90 (t, 3)
18		1750, 1695	5.06	1.37 (t, 3)

preference rather than a "bisected" geometry in the transition state. It is especially interesting to note the similarity between the transition-state and ground-state conformational populations. This similarity suggests little conformational change between these two states in the lithium–ammonia reduction.

Experimental Section[19]

Enol Acetate Preparations of Aliphatic Methyl Ketones under Kinetic and Equilibrium Conditions.—The procedures described by House and Kramar[15] were followed to prepare the kinetic and equilibrium mixtures of enol acetates from various ketones. The pertinent spectral data are shown in Table V, and the analytical and mass spectral data are tabulated in Table VI.

Kinetic Conditions. 2-Pentanone.—A mixture of 8.6 g (0.1 mol) of 2-pentanone, 20.4 g (0.2 mol) of isopropenyl acetate, and 100 mg of *p*-toluenesulfonic acid monohydrate was stirred at reflux for 27 hr. After the usual work-up[15] the mixture was bulb to bulb distilled under vacuum. The normalized product mixture was composed of 44% *trans*-enol acetate **4** (retention time 18.75 min, 20% XF-1150 cyanosilicone, 150°, 60 psi), 37% 2-acetoxy-1-pentene (**14**) (21 min), and 19% *cis*-enol acetate **5** (24.25 min). The structural assignments were based on the position of the vinylic hydrogen in the nmr spectrum in benzene.

(19) Infrared spectra were recorded on a Perkin-Elmer Model 137 Infracord or a 237 grating spectrophotometer. Nuclear magnetic resonance spectra were determined on a Varian Associates A-60 or HA-100 spectrometer. Mass spectra were recorded with either a Varian Associates M-66 or a modified Consolidated Electronics Corporations Type 21-103C mass spectrometer. An Aerograph A-90 gas chromatograph, equipped with a 10 ft × 0.375 in., 20% XF-1150 cyanosilicone column, was utilized for the separation of isomeric compounds unless indicated otherwise. Product percentages were determined from vpc trace analyses using either an Aerograph 204 or a Hewlett–Packard F & M Model 5720 gas chromatograph, both of which were equipped with a flame-ionization detector. All materials used were either reagent grade or were purified technical grades. The ammonia was dried by refluxing over sodium for a minimum of 30 min and was distilled directly into a flame-dried reaction vessel. The 1,2-dimethoxyethane was dried by distillation from lithium aluminum hydride. Combustion analyses were performed by the Microanalytical Department of the University of California, Berkeley, Calif.

TABLE VI
ENOL ACETATES. ANALYTICAL DATA

Structure	Molecular formula		% Analysis, Calcd	Found	Mol wt, mass spectrum
4	$C_7H_{12}O_2$	C	65.60	65.36	128
		H	9.44	9.62	
14	$C_7H_{12}O_2$	C	65.60	65.54	128
		H	9.44	9.48	
5	$C_7H_{12}O_2$	C	65.60	65.85	128
		H	9.44	9.70	
6	$C_9H_{16}O_2$	C	69.19	69.06	156
		H	10.32	10.52	
13	$C_9H_{16}O_2$	C	69.19	68.84	156
		H	10.32	10.18	
7	$C_9H_{16}O_2$	C	69.19	69.10	156
		H	10.32	10.61	
8	$C_9H_{16}O_2$	C	69.19	69.33	156
		H	10.32	10.40	
15	$C_9H_{16}O_2$	C	69.19	69.28	156
		H	10.32	10.62	
10 and 11	$C_8H_{14}O_2$	C	67.57	67.42	142
		H	9.22	10.11	

ously under a nitrogen atmosphere and was then pipetted into a flask containing 9.4 g (90 mmol) of cold, freshly distilled acetic anhydride (0–5°) which was also stirred under a nitrogen atmosphere. The suspension was stirred magnetically at room temperature for 4 hr. The product mixture, following the usual work-up, was bulb-to-bulb distilled, and the products were separated and identified by vpc and spectral comparisons to the independently prepared samples. The product distribution was as follows: 2% 2-pentanone, 75% *trans*-enol acetate **4**, 6% cyclopropyl methyl ketone (**1**), and 17% *cis*-enol acetate **5**.

Enol Acetates from 2,2-Dimethylcyclopropyl Methyl Ketone (2).—Following the general reduction and enolate-trapping procedure described for cyclopropyl methyl ketone (**1**) three runs were were made with ketone **2**. During the course of these runs it was observed that the 1,2-dimethoxyethane appeared to be reacting with the excess metal present. This reaction was evidenced by the appearance of the monomethyl ether of ethylene glycol and 1-acetoxy-2-methoxyethane in the product mixture. These two products were not included in the product distribution shown in Table VII.

The relative ratio of enol acetates from the major bond cleavage were 88% *trans*-enol acetate **6** and 12% *cis*-enol acetate **7**. The average of the *trans*-enol acetates **6** and **8** ratios were 73% *trans*-enol acetate **6** and 27% *trans*-enol acetate **8**.

TABLE VII
ANALYSIS OF REACTION MIXTURE FROM 2,2-DIMETHYLCYCLOPROPYL METHYL KETONES

Identification	Relative retention time, min	Relative %, Run 1[a]	Run 2[b]	Run 3[c]
Neopentyl methyl ketone (**19**)	4.8	2	10	3
2,2-Dimethylcyclopropyl methyl ketone (**2**)	6.5	11	20	22
trans-Enol acetate **8**	8.0	16	6	16
Isoamyl methyl ketone (**12**)	9.0	17	34	12
trans-Enol acetate **6**	11.8	43	24	36
Unknown	13	3	2	5
cis-Enol acetate **7**	16	6	3	5
Unknown	17	2	1	1

[a] Started with 1.12 g (10 mmol) of ketone **2**. [b] Started with 0.56 g (5 mmol) of ketone **2**. [c] Started with 1.68 g (15 mmol) of ketone **2**.

The vinylic hydrogen *cis* to the acetoxy function has been shown[15] to absorb at a lower field than the *trans* vinylic hydrogen.

Isoamyl Methyl Ketone (12).—Similar conditions were employed for the preparation of enol acetates as described for 2-pentanone. The product mixture composition was 27% ketone **12**, 43% *trans*-enol acetate **6**, 11% enol acetate **13**, and 19% *cis*-enol acetate **7**.

Neopentyl Methyl Ketone (19).—The product distribution from neopentyl methyl ketone (**19**) was 69% ketone **19** (retention time 12.25 min), 13% *trans*-enol acetate **8** (17.5 min), and 18% of 2-acetoxy-4,4-dimethyl-1-pentene (**15**) (22.5 min). None of the *cis*-enol acetate **9** could be isolated from the product mixture but when a large injection was made on the vpc column a trailing shoulder was observed on the peak of enol acetate **8**. The amount of this isomer **9** was judged to be less than 1%.

Thermodynamic Conditions.—A solution of 5.6 g (49 mmol) of isoamyl methyl ketone (**12**), 10.2 g (100 mmol) of acetic anhydride, and 55.3 mg of *p*-toluenesulfonic acid monohydrate were allowed to stir under reflux for 22 hr. After a similar work-up to that described for the kinetic procedure, the product distribution was found to be 62% ketone **12** (21 min), 26% *trans*-enol acetate **6** (24 min), 1% enol acetate **13** (29 min), and 11% *cis*-enol acetate **7** (32 min).

Enolate Trapping Experiments. Enol Acetates from Cyclopropyl Methyl Ketone (1).—To a 200-ml portion of ammonia was added 0.234 g (35 mg-atoms) of hexane-washed lithium wire. The blue solution was stirred for 30 min under a nitrogen atmosphere and a solution of 1.016 g (12.1 mmol) of cyclopropyl methyl ketone (**1**) in 5 ml of freshly dried 1,2-dimethoxyethane was added over a 5-min period. The blue color disappeared after 1 hr. An additional 0.03 g (4.6 mg-atom) portion of lithium was added to the flask. The blue color returned and persisted for 30 min. The ammonia was allowed to evaporate (4 hr) and to the white salt that remained was added 100 ml of dry 1,2-dimethoxyethane. The milky white suspension was stirred vigor-

Enol Acetates from 1-Methylcyclopropyl Methyl Ketone (3).—Following the procedure outline previously, 1.29 g (15 mmol) of 1-methylcyclopropyl methyl ketone (**3**) was reduced with 0.44 g (63 mg-atoms) of lithium in 200 ml of ammonia. The enolate suspension in 1,2-dimethoxyethane was added to 15.4 g (151 mmol) of cold acetic anhydride. The mixture was stirred for 2 hr and worked up as previously described. Five products were detected and identified as follows. Product A (1.8 min) was assigned the structure of 3-methyl-2-pentanone on the basis of the following data: ir (CCl_4) 1718 (C=O), 1460, 1355, and 1190 cm^{-1}; mass spectrum (prominant peaks) *m/e* 100, 85, 72, 57, and 43 (base peak). Product B (2.8 min) corresponded in retention time to ketone **3**, but the ir spectrum indicated the presence of a minor contaminant (1735, 1245, and 1045 cm^{-1}). No peaks above 98 were observed in the mass spectrum.

The structure of product C (3.3 min) could not be definitively established. The ir spectrum indicated the product to be a cyclopropyl alcohol (3600, 3440, and 3050 cm^{-1}).

Product D (3.7 min) was found to be a mixture of the *trans*- and *cis*-enol acetates **10** and **11**, respectively. They could not be separated on XF-1150 cyanosilicone, SE-30 silicone, or Carbowax 20M columns. When injected on a Carbowax–KOH column, the enol acetates were hydrolyzed to 3-methyl-2-pentanone, which had a retention time coincident with product A. The following data were obtained from the mixture of enol acetates **10** and **11**: ir (CCl_4) 1755, 1370, 1247, 1135, 1010, 915, and 850 cm^{-1}; mass spectrum (prominant peaks) *m/e* 142, 100 (B), 85, and 43.

The nmr spectrum of mixture D showed that the two enol acetates were present in a 70:30 ratio. The major product was assigned as *trans*-2-acetoxy-3-methyl-2-pentene (**10**) based on the following peak positions and relative heights: nmr (CCl_4) δ 1.47 (m, 3, $CH_3C{=}C$) and 0.92 (t, 3, J = 7 Hz, CH_3CH_2). The minor product was assigned the structure of *cis*-2-acetoxy-3-methyl-2-pentene (**11**) on these peaks: δ 1.52 (m, 3, $CH_3C{=}C$)

and 0.88 (t, 3, J = 7 Hz, CH_3CH_2). Irradiation of the methylene region, in a double resonance experiment, collapsed the two terminal methyl triplets (δ 0.92 and 0.88) into two singlets. The ratio of the two singlets was 70:30 as observed previously for the two triplets.

The structure of 1-methano-2-methyl-3-acetoxy-3-butene (4.3 min) was tentatively assigned to product E on the following data: ir (CCl_4) 1780 (C=O), 1670 (C=C), 1220, 1150, 1020, 965, 955, and 900 cm^{-1}. In the mass spectrum, peaks were observed at m/e of 140, 125, 112, 98 (B), and 83. Injection of the enol acetate on the Carbowax–KOH column (hydrolysis) gave a peak which corresponded to the retention time of the starting cyclopropyl ketone **3**.

Registry No.—**4**, 24471-77-0; **5**, 24471-78-1; **6**, 24471-79-2; **7**, 24471-80-5; **8**, 24471-81-6; **10**, 24471-82-7; **11**, 24471-83-8; **13**, 24471-84-9; **14**, 10499-83-9; **15**, 1541-05-5; **16**, 15984-03-9; **17**, 10500-08-0; **18**, 15984-02-8.

Cyclopentadienones from 1,2,4-Cyclopentanetriones, 2-Cyclopentene-1,4-diones, and 3-Cyclopentene-1,2-diones

CURTIS F. SHELEY[1] AND HAROLD SHECHTER

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210

Received September 11, 1969

Cyclopentadienones may be prepared by enolization of 1,2,4-cyclopentanetriones, 2-cyclopentane-1,4-diones, and 3-cyclopentene-1,2-diones. 2,5-Diphenyl-1,2,4-cyclopentanetrione (**1b**) reacts with 1 and with 2 equiv of sodium hydride to give the corresponding mono- (**5b**) and dianions (**4b**). Dienolate **4b** is converted by benzoyl chloride into 3-benzoyloxy-2,5-diphenyl-2-cyclopentene-1,4-dione (**6**). 3,4-Dibenzoyloxy-2,5-diphenylcyclopentadienone (**10a**), 3,4-di-*p*-anisoyloxy-2,5-diphenylcyclopentadienone (**10b**), and 3,4-diacetoxy-2,5-diphenylcyclopentadienone (**10c**) result from reactions of **1b** with the appropriate acid chlorides in triethylamine. The structures of **10a–c** are established by reaction with N-phenylmaleimide and from the nmr of the resulting 2-norbornen-7-ones (**12a, d, e**). Cyclopentadienone **10b** and benzyne yield 2,3-di-*p*-anisoyloxy-1,4-diphenylnaphthalene (**18**). 3-Methoxy-2,5-diphenyl-2-cyclopentene-1,4-dione (**19**), prepared from **1b** and diazomethane, reacts with sodium hydride to give monoanion **20**, which with *p*-anisoyl chloride results in 4-*p*-anisoyloxy-3-methoxy-2,5-diphenylcyclopentadienone (**10d**). 3-Phenyl-1,2,4-cyclopentanetrione (**1c**), 3-methyl-1,2,4-cyclopentanetrione (**1d**), and 1,2,4-cyclopentanetrione (**1a**) are converted by diazomethane into their corresponding 3-methoxy-2-cyclopentene-1,4-diones (**21, 24**, and **25**). Acid- and base-catalyzed deuterium exchange into **19, 21, 24**, and **25** reveal that the 2-cyclopentene-1,4-diones are converted into hydroxycyclopentadienones and their conjugate bases. Enolization of 3-cyclopentene-1,2-diones has been investigated. Deuterium incorporation into 4-phenyl-3-cyclopentene-1,2-dione (**29a**), 3,4-diphenyl-3-cyclopentene-1,2-dione (**29b**), and 4-methyl-3-cyclopentene-1,2-dione (**29c**) in acid solution and into **29a** and **20b** in basic environments indicate that these systems are converted into their 2-hydroxycyclopentadienones (**31a–c**) and their cyclopentadienone enolates (**30a,b**). Dione **29b** has been prepared by nitrosation of 3,4-diphenyl-2-cyclopentene-1-one (**32**) to 1-oximino-4,5-diphenyl-3-cyclopentene-1,2-dione (**33**), conversion of **33** by formaldehyde in acid solution into 4,5-diphenyl-3-cyclopentene-1,2-dione (**34**), and isomerization of **34** by hot hydrochloric acid to **29b**. The previous structural assignment to 2-oximino-3,4-diphenyl-3-cyclopentene-1,2-dione is incorrect and **34** is a new cyclopentene-1,2-dione.

Cyclopentadienone is a highly reactive monomer whose isolation is yet to be accomplished.[2] Many tetraaryl- and tetraalkylcyclopentadienones[2c,d] and certain tri- and disubstituted cyclopentadienones such as 2,3,5-triphenylcyclopentadienone, 2,3,5-tri-*t*-butylcyclopentadienone,[3a] cyclooctatetraeno-4-methylcyclopentadienone,[3b] 2,5-diphenylcyclopentadienone,[3c] and 2,4-di-*t*-butylcyclopentadienone,[3d] cyclopentadienones containing delocalizing or bulky groups in 2 and/or 5 positions, are stable at 20–30° or may be generated at moderately elevated temperatures. 3-*t*-Butylcyclopentadienone has been prepared; it dimerizes rapidly, however, at −20°.[3d]

A variety of approaches have been used for synthesis or generation of cyclopentadienones.[2d] Of present interest is that cyclopentenediones and cyclopentanetriones are potentially capable of enolizing to substituted cyclopentadienones.[4,5] DePuy, *et al.*, reported on the synthesis and reactions of 2-cyclopentene-1,4-dione[5] and presented evidence for its enolization to 3-hydroxycyclopentadienone and its enolate.[5] Such enolizations to give cyclopentadienone derivatives have had little other study and, as a consequence, serve as the basis for the present investigation.

1,2,4-Cyclopentanetrione (**1a**)[6] exists as its monoenol (**2a**) and as such is a moderately strong acid (pK_a = 3.0), undergoing conversion into its monoenolate (**5a**). A second enolization would give 3,4-dihydroxycyclopentadienone (**3a**) and in a sufficiently basic environment its cyclopentadienone dianion **4a**. Strong electron-donating groups are expected to stabilize cyclopentadienones. Present attempts to demonstrate the existence of **3a** spectroscopically and of **4a** by reaction of **2a** with strong bases have been ambiguous (see Experimental Section). Additional experiments with this system have been deferred, and work with 3,4-diphenyl-

(1) (a) Abstracted in part from the Ph.D. dissertation of C. F. S., The Ohio State University, Columbus, Ohio, 1966. (b) This research was supported by grants from the Union Carbide Chemical Corp., the American Oil Co., the National Science Foundation, and The Ohio State University.

(2) (a) C. H. DePuy, M. Isaks, K. L. Eilers, and G. F. Morris, *J. Org. Chem.*, **29**, 3503 (1964). (b) For reviews of cyclopentadienones, see (c) C. F. H. Allen and S. A. VanAllan, *J. Amer. Chem. Soc.*, **72**, 5165 (1950); (d) M. A. Ogliaruso, M. G. Romanelli, and E. I. Becker, *Chem. Rev.*, **65**, 261 (1965).

(3) (a) C. Hoogzand and W. Hübel, *Tetrahedron Lett.*, 639 (1961); (b) R. Breslow, W. Vitals, and K. Wandell, *ibid.*, 365 (1965); (c) V. Kruerke and W. Hübel, *Chem. Ber.*, **94**, 2829 (1961); (d) E. W. Garbisch and R. F. Sprecher, *J. Amer. Chem. Soc.*, **88**, 3433 (1966).

(4) (a) F. Kögl, H. Becker, G. deVoss, and E. Wirth, *Justus Liebigs Ann. Chem.*, **465**, 243 (1928); (b) C. F. Koelsch and T. A. Geissman, *J. Org. Chem.*, **3**, 480 (1938);

(5) C. H. DePuy and E. F. Zaweski, *J. Amer. Chem. Soc.*, **79**, 3923 (1957); C. H. DePuy and E. F. Zaweski, *ibid.*, **81**, 4920 (1959); C. H. DePuy and P. R. Wells, *ibid.*, **82**, 2909 (1960).

(6) J. H. Boothe, R. G. Wilkinson, S. Kushner, and J. H. Wilkinson, *ibid.*, **75**, 1732 (1953).