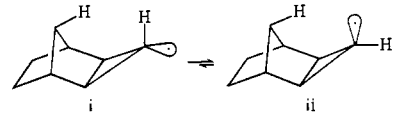
(26) (a) P. G. Gassman and A. F. Fentiman, Jr., *J. Am. Chem. Soc.*, **92**, 2551 (1970); (b) M. S. Baird and C. B. Reese, *J. Chem. Soc., Chem. Commun.*, **523** (1972).
(27) A. de Meijere has discovered radical chlorination with *tert*-butyl hypochlorite to be a useful route to introduction of chlorine at the C-1 bridgehead position of bicyclo[2.2.2]octane and bicyclo[3.3.2]decane systems to which at least one cyclopropane unit has been fused, such as trishomobarrelene, trishomobullvalene, and tricyclo[3.2.2.$0^{2,4}$]nonane. A. de Meijere, O. Schallner, and C. Weitemeyer, *Angew. Chem., Int. Ed. Engl.*, **11**, 56 (1972), and a private communication.
(28) Photochlorination of norbornane with *tert*-butyl hypochlorite in CCl_4 gives 1-chloro, 7-chloro, and a mixture of *exo*- and *endo*-2-chloronorbornane in a ratio of 1.6:2.2:96.2, T. D. Ziebarth, unpublished observation.
(29) For a discussion and suggestive evidence supporting a colinear transition state for hydrogen atom transfer reactions, see J. W. Wilt in "Free Radicals," Vol. I, J. K. Kochi, Ed., Wiley, New York, N.Y., 1973, pp 378–398.
(30) Recent work of J. S. Filippo, Jr., and G. M. Anderson, *J. Org. Chem.*, **39**, 473 (1974), demonstrates only a very mild preference for abstraction of chlorine from *exo*-2-norbornyl chloride relative to chlorine atom abstraction from *endo*-2-norbornyl chloride, $k_{exo}/k_{endo} = 1.4$.
(31) G. C. Fettis and J. H. Knox in "Progress in Reaction Kinetics," Vol. 2, G. Porter, Ed., MacMillan, New York, N.Y., 1964; C. Walling and P. S. Fredricks, *J. Am. Chem. Soc.*, **84**, 3326 (1962).
(32) In a complementary study, we have found that in the equilibrium of I ⇌ II, II is favored by 100:1 or greater at −78°: P. K. Freeman, L. L. Hutchinson, and J. N. Blazevich, *J. Org. Chem.*, **39**, 3606 (1974).



i ii

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(34) H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.*, **81**, 4256 (1959).
(35) E. LeGoff, *J. Org. Chem.*, **29**, 2048 (1964).
(36) C. Walling and B. B. Jacknow, *J. Am. Chem. Soc.*, **82**, 6108 (1960).
(37) E. S. Huyser, *J. Am. Chem. Soc.*, **82**, 394 (1960).
(38) W. J. Blaedel and V. W. Meloche, "Elementary Quantitative Analysis," Harper & Row, New York, N.Y., 1963, p 640.

Aliphatic Semidiones. XXVIII. Formation of Bicyclo[3.2.0]hept-2-ene-6,7-semidiones from Bicyclo[3.2.0] and -[2.2.1] Precursors[1,2]

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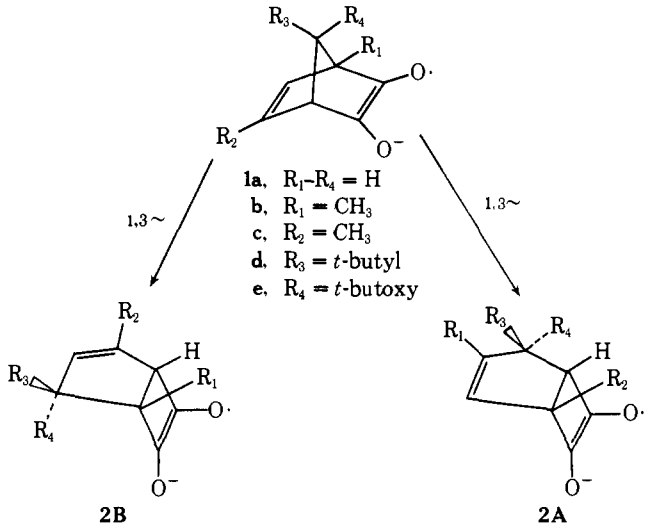
Abstract: The preparation of bicyclo[2.2.1]hept-5-ene-2,3-semidione and bicyclo[3.2.0]hept-2-ene-6,7-semidione are reported. In dimethyl sulfoxide solution containing potassium *tert*-butoxide, 3-hydroxybicyclo[2.2.1]hept-5-en-2-one yields the isomeric bicyclo[3.2.0] semidione. Under similar conditions, 3-*endo*-dimethyl-*tert*-butylsiloxybicyclo[2.2.1]hept-5-en-2-one yielded mainly the semidione in the bicyclo[2.2.1] system. It is argued that when rearrangement occurs it probably involves a symmetrical intermediate, possibly the enediol dianion. Once formed, the semidione radical anions do not seem to undergo rearrangement. 1- or 5-methylbicyclo[2.2.1]hept-5-en-2,3-acyloins each give mixtures of the two possible methyl substituted bicyclo[3.2.0]hept-2-ene-6,7-semidiones. The same mixture of semidiones was also formed from 1-methylbicyclo[3.2.0]hept-2-en-6,7-acyloin, indicating that the rearrangement is reversible.

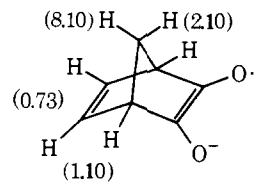
An interest in evaluating the magnitude of through-space delocalization of the π-electron systems in norbornadiene derivatives led us to investigate the synthesis of **1a**. Our initial attempt at the synthesis of **1** was thwarted by the apparent rearrangement of **1** to **2**.[2] We have subsequently shown that **1** can be detected by the treatment of the *endo-tert*-butyldimethylsiloxynorborn-5-en-2-one and other difficultly hydrolyzed derivatives of 3-hydroxynorborn-5-en-2-one with base and DMSO or by electrolysis of the diketone in the esr cavity.[3] The esr spectra of **1** indicated that perhaps 15% of the unpaired electron is transferred by delocalization to the vinyl bridge, a result in agreement with the photoelectron spectrum of norbornadiene[4] or norbornenone.[5] We now present evidence concerning the mechanism and the scope of the rearrangement of **1** to **2** which is formally a 1,3-sigmatropic rearrangement.



1a, R_1–R_4 = H
b, R_1 = CH_3
c, R_2 = CH_3
d, R_3 = *t*-butyl
e, R_4 = *t*-butoxy

1,3~ 1,3~

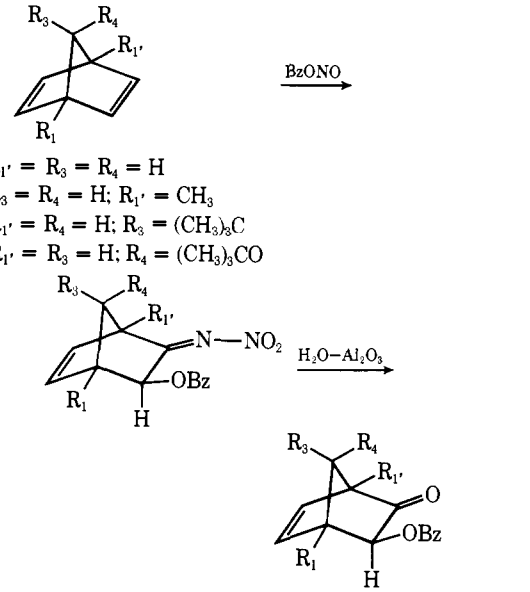
2B **2A**



1a
(a^H in G)

Synthesis of Semidione Precursors. Norbornadienes **3a–c** were converted to the *exo*-3-benzoyloxynorbornen-2-ones **4a–e** by reaction with benzoyl nitrite followed by hydrolysis, Scheme I. An additional series of bicyclo[2.2.1]heptene

Scheme I

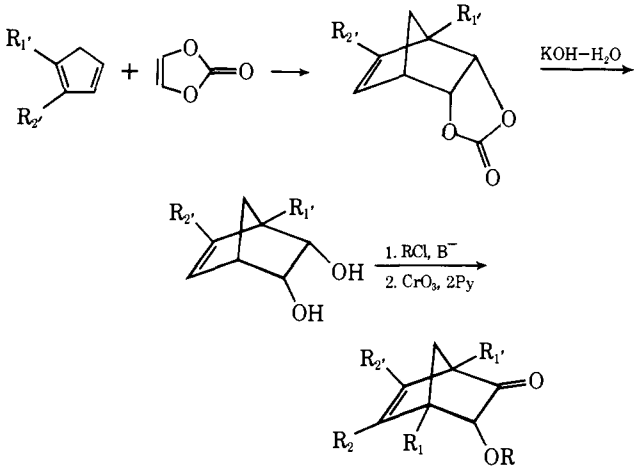


3a, $R_1 = R_1' = R_3 = R_4 = H$
b, $R_1 = R_3 = R_4 = H$; $R_1' = CH_3$
d, $R_1 = R_1' = R_4 = H$; $R_3 = (CH_3)_3C$
e, $R_1 = R_1' = R_3 = H$; $R_4 = (CH_3)_3CO$

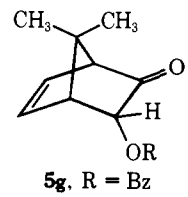
4a, $R_1 = R_1' = R_3 = R_4 = H$
b, $R_1 = R_3 = R_4 = H$; $R_1' = CH_3$
c, $R_1' = R_3 = R_4 = H$; $R_1 = CH_3$
d, $R_1 = R_1' = R_4 = H$; $R_3 = (CH_3)_3C$
e, $R_1 = R_1' R_3 = H$; $R_4 = (CH_3)_3CO$

derivatives **5** was prepared by the Diels-Alder reaction of vinylene carbonate with cyclopentadienes, Scheme II.

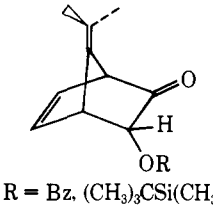
Scheme II



5a, R, R_1, R_1', R_2, R_2' = H
b, R_1, R_1', R_2, R_2' = H; R = Bz, Ac, $(CH_3)_3CSi(CH_3)_2$-
c, R_1' = CH_3, $R_1 = R_2 = R_2'$ = H; R = Ac, $(CH_3)CSi(CH_3)_2$-
d, R_1 = CH_3; $R_1' = R_2 = R_2'$ = H; R = Ac, $(CH_3)_3CSi(CH_3)_2$-
e, R_2' = CH_3; $R_1 = R_1' = R_2$ = H; R = Bz, Ac, $(CH_3)_3CSi(CH_3)_2$-
f, R_2 = CH_3; $R_1 = R_1' = R_2'$ = H; R = Bz, Ac, $(CH_3)_3CSi(CH_3)_2$-

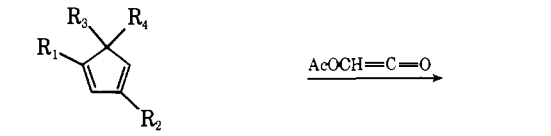


5g, R = Bz

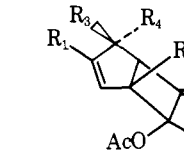


5h, R = Bz, $(CH_3)_3CSi(CH_3)_2$-

Scheme III



6a, R_1-R_4 = H
b, (mixture), R_1 = CH_3; R_2-R_4 = H; R_2 = CH_3; R_1, R_3, R_4 = H
c, R_4 = CH_3; R_1-R_3 = H
d, $R_1 = R_2$ = H; R_3, R_4 = $(CH_3)_2C$=

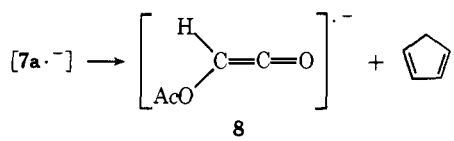


7a, R_1-R_4 = H
b, R_1 = CH_3; R_2-R_4 = H
c, R_2 = CH_3; R_1, R_3, R_4 = H
d, $R_1 = R_2$ = H; R_3, R_4 = $(CH_3)_2C$=

Direct precursors to the bicyclo[3.2.0]hept-2-ene-6,7-semidiones were the corresponding acetoxy ketones formed by the addition of acetoxyketene to the appropriate cyclopentadiene (Scheme III).

Generation of Radical Anions. Treatment of **4a, 5a, 5b,** or **7a** (exo or endo) with potassium *tert*-butoxide in DMSO solution gave esr signals of unstable intermediates best detected in a flow system.[6] Very fast flow rates of a few seconds between mixing and detection were complicated in some cases by the presence of radicals or radical anions other than **1** or **2** or in some cases by low signal intensities or by insufficient quantities of reactants to obtain a resolved esr spectrum.

The hydroxy ketone **5a** gave a maximum radical concentration ~10 sec after treatment with base. A well-resolved spectrum 3 min after mixing indicated only the presence of the [3.2.0]semidione **2** (*i.e.*, like Figure 1a). We were unable to obtain any esr signal from the corresponding [2.2.1]dione at slow or fast flow. The *exo*-benzoyloxy ketone **4a** gave an esr signal (Figure 1a) of the rearranged semidione which was strongest at ~4 min after mixing. For both **5a** and **4a,** the esr spectra observed at periods as short as 10 sec after mixing appeared to indicate predominately if not solely the rearranged species **2.** The same spectrum was observed starting from the exo or endo acetates **7a.** Here at 5-15 sec after treatment with base, a mixture of **2** and a radical with a^H = 12 G plus other unresolved hfs was detected. At 3 min after mixing, the esr is essentially superimposable on that obtained from **5a.** One possibility for the unknown radical with the doublet splitting is **8.** However,



8

we have been unsuccessful in generating this radical from any other acetoxyketene precursor, such as acetoxyacetyl chloride in basic solution.

The endo benzoyloxy or acetoxy ketones **5b** at 10 sec after mixing with base gave an unidentified radical (anion?) with a^H = 3.1 (1), 0.75 (2) G. After 3 min, this paramagnetic species had disappeared, and a mixture of

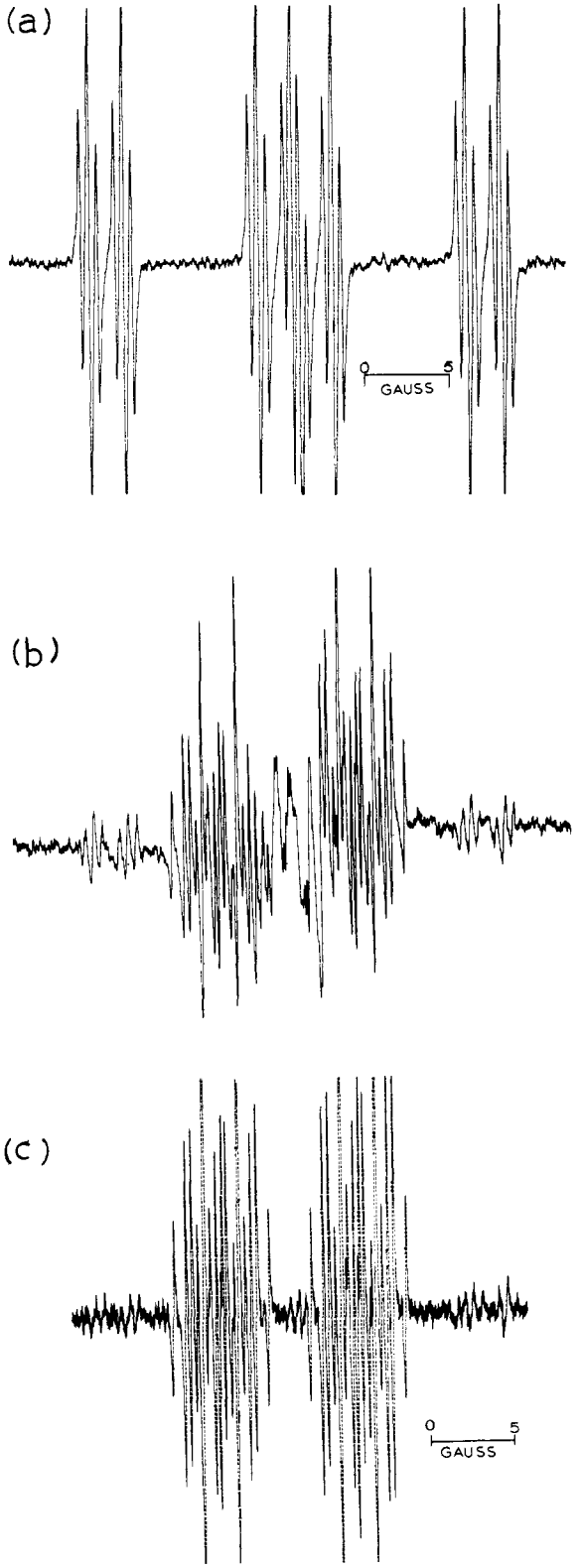
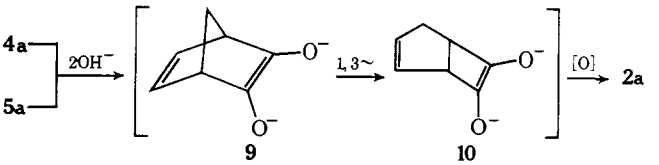


Figure 1. First derivative esr spectra observed in DMSO containing 0.05 *M* potassium *tert*-butoxide ~4 min after preparation of solutions containing 0.025 *M* of (a) *exo*, 3-benzoyloxybicyclo[2.2.1]hept-5-en-2-one, (b) *endo*, 3-benzoyloxybicyclo[2.2.1]hept-5-en-2-one, (c) *endo*, 3-dimethyl-*tert*-butylsiloxybicyclo[2.2.1]hept-5-en-2-one.

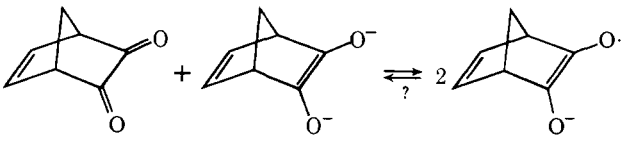
radical anions **1a** and **2a** remained, Figure 1b. The maximum concentration of **2a** was reached in ~10 min from these endo esters and was much less than the maximum concentration of **2a** observed from the exo benzoate.

The *endo*-dimethyl-*tert*-butylsiloxy derivative **5b** formed radical anions more slowly but also gave a higher ratio of **1/2** (Figure 1c). These results suggested to us that we were dealing with a situation in which **4** or **5** → **1** → **2**.[2] However, we have been unable to verify the conversion of **1** to **2**. Indeed, the ratio of **1/2** seems to be independent of time. For **4a** or **5a**, the ratio of **1/2** < 0.02 was observed at either 10 sec or 3 min of reaction with base. With the endo benzoate, roughly the same ratio of **1/2** ≃ 1 was observed between 5 and 20 min after the reaction was commenced. Stopped-flow experiments on reaction products from the endo acetate or endo silyl ether did not indicate any pronounced change in the ratio of **1/2** as the total radical anion concentration passed through a maximum and declined to an unmeasurable quantity in ~30 min. The data suggest some intermediate, whose formation is structure dependent, is responsible for the ratio of **1/2** observed. The acyloin **5a** and the exo benzoate **4a** are rapidly converted to predominately **2**. The dianion **9** seems a likely intermediate from these precursors and may well be responsible for the rearranged product observed.

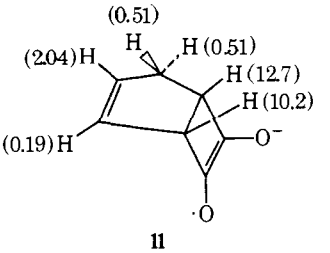


The endo acetate or benzoate and particularly the *endo*-dimethyl-*tert*-butylsiloxy derivative may be more slowly converted to the dianion by potassium *tert*-butoxide. In fact, one might expect enolization now to be the predominant reaction with base. Oxidation followed by reaction with base could yield directly the unrearranged semidione, or perhaps oxygenation to give the dione will divert **9** from the rearrangement pathway to yield **1** (Scheme IV).

It is our conclusion that the dianion **9** and the radical anion **1** having different electron distributions and electron densities can react in different manners. A corollary of our conclusion that **1** is not converted to **2** is that the equilibrium between semidione and diketone plus dianion must lie far on the side of the radical anion.



Evidence for Reversibility of the Interconversion 1 ⇄ 2. The rearrangement of a bicyclo[2.2.1]heptadiene derivative to a bicyclo[3.2.0]heptadiene seemed surprising and suggested that the reverse reaction might occur also. We thus synthesized the methyl derivatives **4b–d**, **5c–f**, and **7b–c**. The analysis of esr spectra for the observed bicyclo[3.2.0]hept-2-ene-6,7-semidiones was facilitated by the very large hfs of the cyclobutane bridgehead hydrogen atoms, **11**.

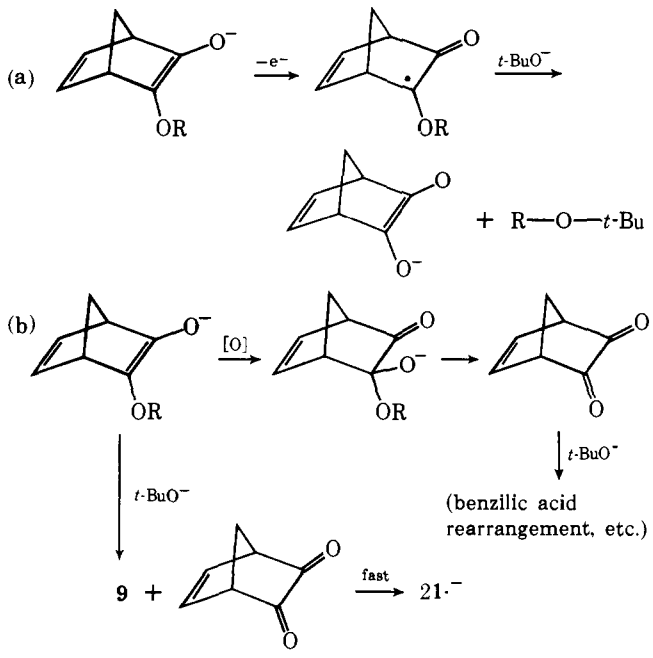


11

(a^H in G)

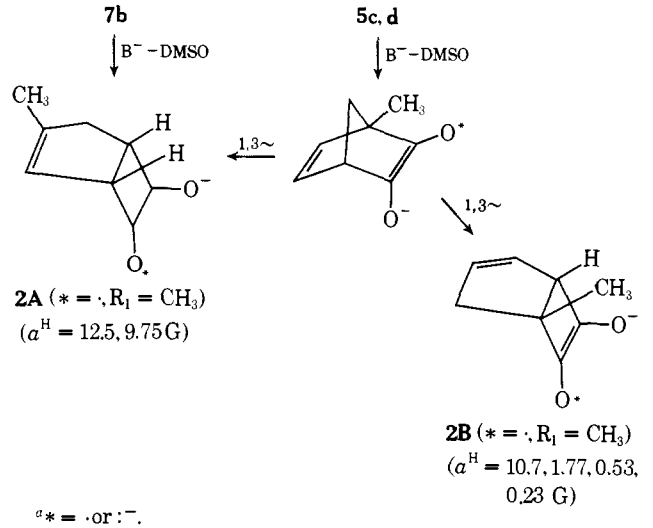
The endo acetate or silyl ether in the bicyclo[2.2.1]heptenone system with a bridgehead methyl (**5c,d**) upon treatment with base gave a mixture of two radical anions (Fig-

Scheme IV



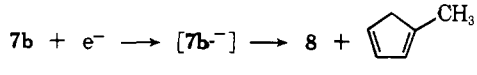
ure 2a) after a reaction time of a few minutes. The paramagnetic species with a^H = 10.7 (1), 1.77 (1), 0.53 (1), and 0.23 (1) G is consistent with the rearranged bicyclo[3.2.0]heptenesemidione, **2B** ($R_1 = CH_3$, R_2-R_4 = H). The other radical anion with a^H = 12.5, 9.75 G is consistent with the isomeric rearrangement product **2A** (R = CH_3, R_2-R_4 = H). It appears as if the processes of Scheme V apply. At reaction times of <1 min, the endo acetate gave a different esr spectrum which may well involve the unrearranged radical **1b.**

Scheme V[a]



[a] * = · or :⁻.

Treatment of **7b** with potassium *tert*-butoxide in DMSO gave a mixture of radicals at a short reaction time in which the spectrum assigned to **2A,** $R_1 = CH_3$, could be detected, but in which the predominant species was one with a single doublet splitting, a^H = 12.5 G, but without the hyperfine splitting observed in Figure 2a for **2B,** $R_1 = CH_3$. This species may be the same one observed previously starting from **7a.** The same doublet of a^H = 12.5 G was observed starting from the exo benzoates in the bicyclo[2.2.1] series, **4b,c.**



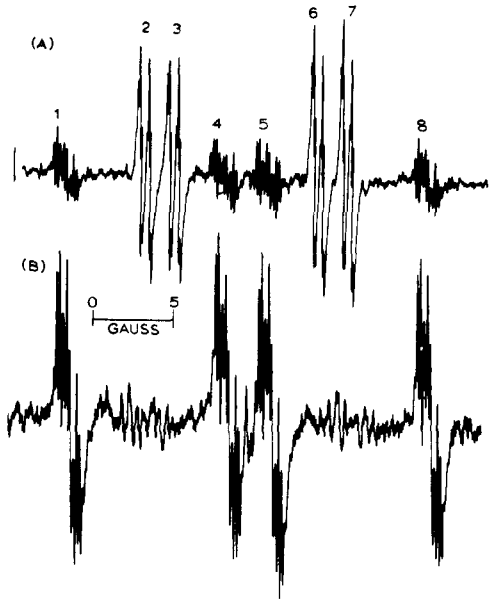


Figure 2. Esr spectra of mixtures of **2A** ($R_1 = CH_3$) and **2B** ($R_1 = CH_3$) formed from **5c,d** (A) or **7b** (B) in DMSO containing 0.05 *M* potassium *tert*-butoxide. Multiplets 1,4,5, and 8 are assigned to **2A** and 2,3,6,7 to **2B.**

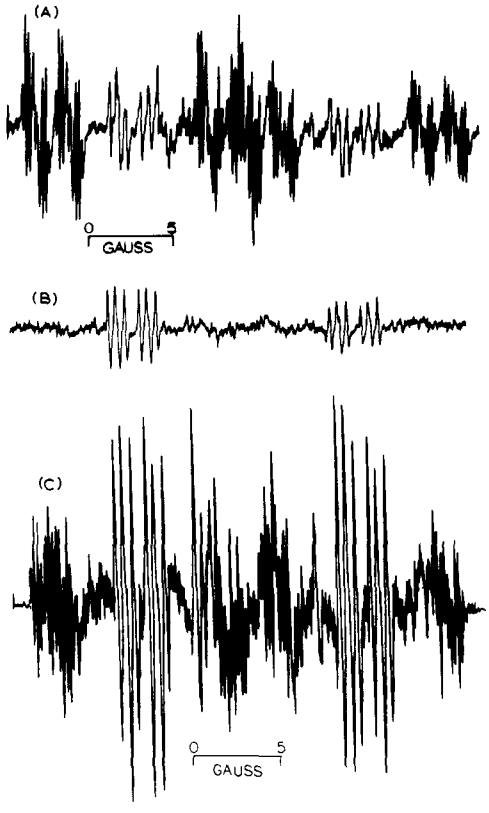
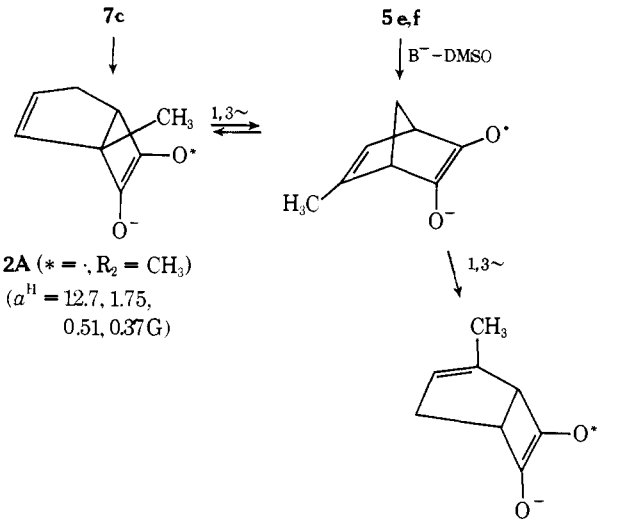


Figure 3. First derivative esr spectra observed in DMSO at 25° in the presence of 0.05 *M* potassium *tert*-butoxide: (A) mixture of **2A** ($R_2 = CH_3$) and **2B** ($R_2 = CH_3$) observed from 5- and 6-methyl-*endo*,3-acetoxybicyclo[2.2.1]hept-5-en-2-one (**5e,f**); (B) **2A** ($R_2 = CH_3$) observed immediately after treatment of 1-methyl-*endo*,7-acetoxybicyclo[3.2.0]hept-2-en-6-one (**7c**) with base; (C) mixture of **2A** ($R_2 = CH_3$) and **2B** ($R_2 = CH_3$) obtained from **7c** under static or stopped-flow conditions.

The endo acetates in the bicyclo[2.2.1] system with a methyl group substituted on the double bond (**5e** or **5f**), or the corresponding benzoates, gave a mixture of radical anions whose spectrum we analyze to be a mixture of the two bicyclo[3.2.0]heptenesemidiones (Scheme VI), Figure 3a.

Scheme VI[a]



[a] * = · or :⁻.

The bicyclo[3.2.0]heptene precursor methylated at a bridgehead position, **7c,** was isolated from the reaction of acetoxyketene with methylcyclopentadiene(s). Up to 10 min after treatment of **7c** with potassium *tert*-butoxide in DMSO, only the semidione **2A**·⁻ could be detected (Figure 3b). By 20 min of reaction time, the concentration of **2A**·⁻ had decreased considerably, and now **2B**·⁻ was clearly discernible (Figure 3c). Unfortunately a direct precursor to **2B,** $R_2 = CH_3$, has not yet been synthesized. Nevertheless, the reversibility of the rearrangement, *i.e.*, **2A** → **1** → **2B,** seems established.

Rearrangement of 7-Substituted Bicyclo[2.2.1]heptadiene Derivatives. 7-Substituted bicycloheptenones **4d, 4e, 5g, 5h,**

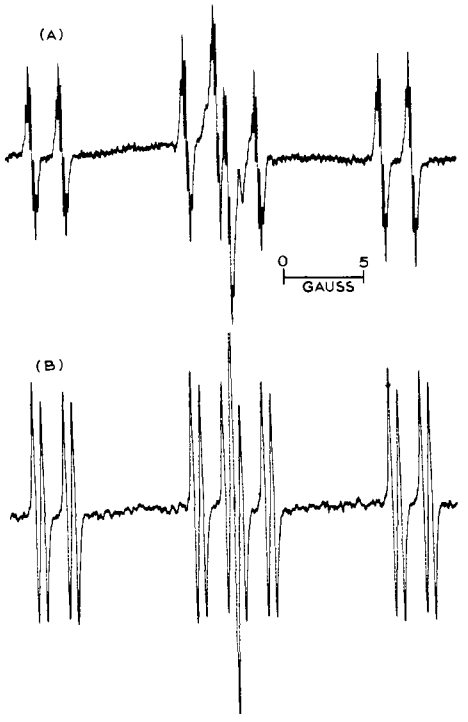


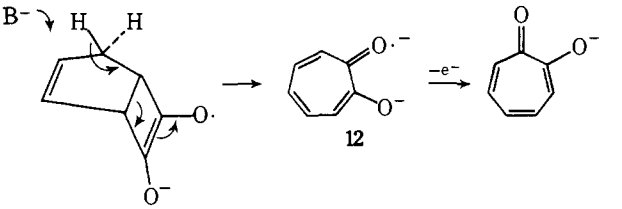
Figure 4. First derivative esr spectra in DMSO solution: (A) 4,4-dimethylbicyclo[3.2.0]hept-2-ene-6,7-semidione prepared from **5g**; (B) *endo*,4-*tert*-butoxybicyclo[3.2.0]hept-2-ene-6,7-semidione prepared from **4d.**

Table I. Observed Hfsc for **2A** in DMSO, 25°

Substituents	a^H, G H-1	H-2 (vinyl)	H-3 (vinyl)	H-4 (methylene)	H-5
None	10.2	0.10	2.04	0.51 (2)	12.7
1-Methyl		*a*	1.75	0.51, 0.37	12.7
2-Methyl	9.87	0.19[b]	1.94	0.52, 0.43	12.9
3-Methyl	9.75	*c*	*c*	*c*	12.5
4,4-Dimethyl	9.62	0.27	1.90	0.12 (6)[b]	12.15
exo-4-*tert*-Butyl	9.97	0.08	1.93	0.57 (1)	12.4
endo-4-*tert*-Butoxy	10.13	*a*	1.90	0.50 (1)	11.5
5-Methyl	10.7	0.23	1.77	0.53, 0.23	0.115[b]
4-Isopropylidene	8.85	0.20	2.10	0.095 (6)[b]	13.3

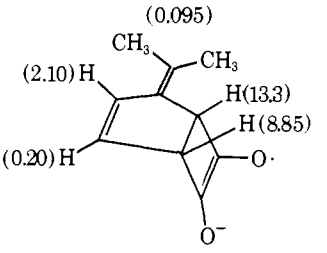
[a] Not observed. [b] Methyl hfs. [c] Not resolved, $\Sigma a^H \cong 1.7$ G.

and **7d** were investigated. Now the rearrangement products **2A** and **2B** will be enantiomers. As expected, only a single paramagnetic species was observed upon treatment of the acyloin derivatives with base in DMSO. Figure 4 gives the esr spectra of **2,** with $R_3 = R_4 = CH_3$, $R_1 = R_2 = H$ and with $R_3 = (CH_3)_3C$-, $R_1 = R_2 = R_4 = H$. The hfsc constants are given in Table I. These semidiones are much more stable than the bicyclo[3.2.0]hept-2-ene-6,7-semidiones without substitution at C-4. This suggests that at least one of the routes for semidione destruction involves removal of a proton from C-4 (exo position). We do not expect to see **12,** because we have made many attempts without success to reduce α-tropolone or its salts to radical anions with alkali metals at low temperatures.



12

The isopropylidene derivatives **5h**-siloxy ether and **7d** gave the same semidione which we identify as **13.** Semidione **13** was the only observed product from **5h**-siloxy



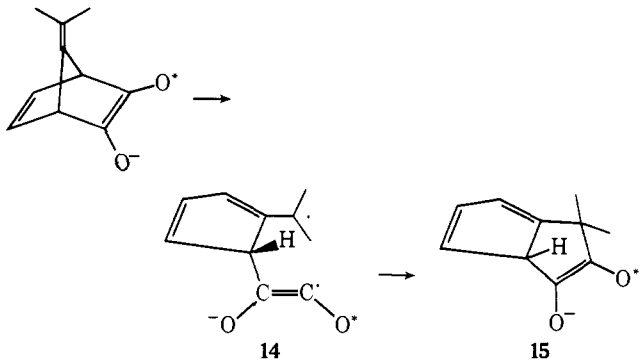
13

ether. However, from **7d** an additional esr signal from a species with a 12-G doublet was observed. Apparently this is the same species observed from **7a** and **7b** and tentatively assigned to **8.**

Mechanism of the Rearrangement. The formation of **13** from **5h**-siloxy ether has perhaps some implications in regard to the mechanism of the rearrangement of the bicyclo[2.2.1]heptadiene derivative. If the reaction occurs stepwise in a nonconcerted manner (*via* **14**), it would appear likely that rearrangement involving the isopropylidene group would occur, *e.g.*, Scheme VII.

Semidione **15** (* = ·) should be a stable semidione with only one significant hfsc (the α-bridehead hydrogen atom). The absence of **15** is thus partial evidence against intermediates such as **14** and in favor of a concerted 1,3-sigmatropic rearrangement from C (1) to C (4) which would be free of the steric effect of the methyl groups in the isopropylidene substituent.

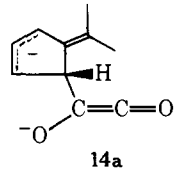
Scheme VII[a]



14 15

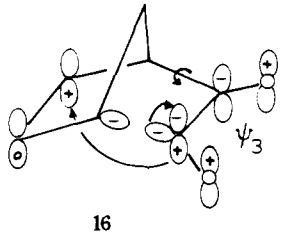
[a] * = · or :⁻

It seems that rearrangement from the acyloin derivatives before conversion to the radical anion or dianion is eliminated by the observation that **5c** and **5d** or **5e** and **5f** gave the same esr spectra. This suggests a symmetrical intermediate such as **1**·⁻ or the dianion and excludes a photochemical or other rearrangement of the unrearranged keto esters. The 2-ketonorbornenes do undergo photochemical rearrangement to bicyclo[3.2.0]hept-2-en-7-ones,[7-9] and it has been shown that this process is at least partially reversible upon thermolysis.[9] The photochemical 1,3-acyl migration of 1,4,4-trimethylbicyclo[3.2.0]hept-6-en-2-one to 4,4,6-trimethylbicyclo[3.2.0]hept-6-en-2-one[10-12] and other β,γ-unsaturated ketones,[13-15] represents a similar process. Even more pertinent is the recent report by Rubin and Weiner that photolysis of bicyclo[2.2.1]heptenedione and benzobicyclo[2.2.2]octadienedione yields the rearranged bicyclo-[3.2.0]hept-6-ene-6,7-dione and 2,3-benzo[4.2.0]octa-2,4-diene-7,8-dione prior to photochemical decarbonylation.[15] In the radical anion **1** or the dianion (* = :⁻ in Schemes V and VI), electrons have been added to the LUMO of the diketone system, and these intermediates have some similarity to the π* excited state for ketone photolysis. However, we are faced with the perplexing situation that the dianion rearranges, but the radical anion apparently does not, or at least the dianion rearranges much more rapidly than the radical anion. Possibly the dianion rearranges *via* a transition state which allows separation of the negative charges, and this charge separation provides a driving force not present in the radical anion. Intermediate or transition state **14a** is an interesting possibility which seems to be consistent with the rearrangement proceeding to **13** rather than to **15.**



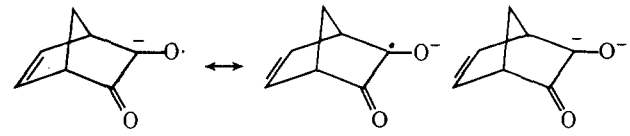
14a

Another possible rationalization involves the formation of a transition state for a concerted rearrangement having a sextet of electrons. The concerted 1,3-migration would involve transition state **16.**[16] The argument can be advanced



16

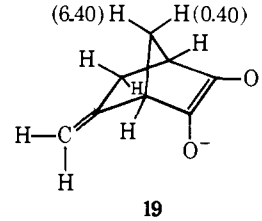
that a pair of electrons in the carbonyl p_z orbital will be more readily available in the dianion **18** than in the semidione radical anion **17** where carbon and oxygen spin densities are nearly equal (*i.e.*, $\rho_C = 0.25$).[17]



17a, 25% **17b**, 25% **18**

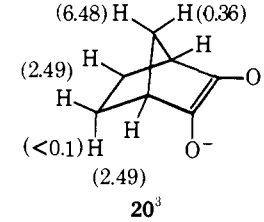
Side Reactions during Semidione Formation. We have previously noted the participation of the methylsulfinyl carbanion (CH_3SOCH_2:⁻) in the formation of radical anions in DMSO solutions of potassium *tert*-butoxide. Thus monoalkyl or -aryl glyoxals yield methyl semidiones,[17-19] and anthracene yields the 9,10-dimethylanthracene radical anion.[20]

We observed an unexpected esr signal from the *endo*-dimethyl-*tert*-butylsiloxy ethers **5e,f** at reaction times of 30 min. One interpretation of these spectra is that the methylsulfinyl carbanion has reacted with the $\Delta^{5,6}$ double bond in **5e,f** either by addition or by allylic rearrangement. Perhaps these processes become possible, because the siloxy ketones are only slowly solvolyzed affording ample time for reaction. From **5e,f,** a complex well-resolved esr spectrum was observed which we feel probably indicates **19.** Note the



19

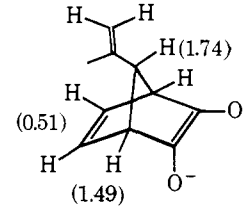
(a^H = 0.20(2H), 0.52(1H), 2.8(1H), 3.1(1H), 3.7(1H) G)



20[3]

(a^H in G)

close correspondence between the hfsc's of **19** and **20.** Treatment of **5h**-benzoate (mixture of exo and endo isomers) with potassium *tert*-butoxide gave **13** between 10 and 30 sec after the reactants had been mixed. At reaction periods of 40–70 sec, another species predominated. The hfsc suggest structure **21.** A similar isomerization appears

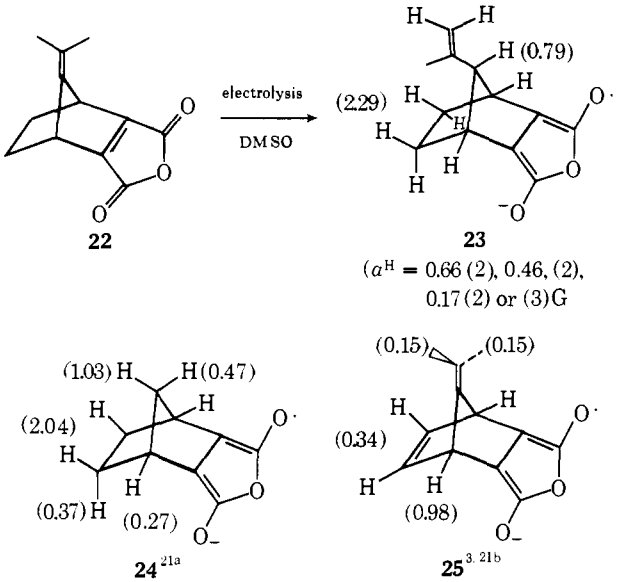


21

(a^H in G)

to be involved in the electrolysis of **22.** The hfsc of the radical anion are not consistent with presence of the isopropylidene group and suggest structure **23** by comparison with **24** and **25.**

There is no indication that semifuraquinones such as **23** undergo rearrangements similar to **1** ⇄ **2.** There seems to be an interaction with the isopropenyl group of **21** not detected for **23.** We have previously pointed out that the semidione and semifuraquinone spin labels have similar electron densities but different symmetries of the HOMO.[3] This results in compensation of delocalization and spin polarization effects for the *anti*-7-alkyl groups in semidiones, such as **21,** but fairly strong and stereoselective interaction for the *anti*-7-alkyl groups in the semifuraquinones (such as



22 23

(a^H = 0.66 (2), 0.46, (2), 0.17 (2) or (3) G

24[21a] 25[3,21b]

23) where spin polarization effects are the only spin interaction mechanism.

Experimental Section

Detection of Esr Signals. Semidiones were prepared by mixing deoxygenated DMSO solutions 0.025 *M* in ketonic precursor and 0.05 *M* in potassium *tert*-butoxide in a flow cell with a volume of ~0.05 ml between the point of mixing and detection. Solutions were placed in disposable polyethylene syringes mounted in a Compact Infusion Pump Model 975 (Harvard Apparatus Co., Inc.). The syringes were connected to the quartz liquid flow mixing chamber (Varian Associates V-4549A) by polyethylene tubing which was replaced after each experiment. Spectra were recorded on a Varian E-3 spectrometer and simulated by use of a Japan Electron Optics Co. JNM-RA-1 spectrum accumulator.

General Procedures. Diels-Alder reactions with vinylene carbonate or dichlorovinylene carbonate were performed in a 125-ml suction flask utilizing 25 g of toluene per 0.1 mol of the diene. After the flask was sealed at Dry-Ice temperature, the solutions were heated in an oil bath.

Addition of benzoyl nitrite typically involved the dropwise addition of 0.05 mol of the olefin in 40 ml of carbon tetrachloride over a period of ~20 min to a solution of 0.10 mol of benzoyl nitrite in 60 ml of carbon tetrachloride at 0°. The mixture was warmed to room temperature and filtered to remove benzoic acid before dilution to 300 ml with carbon tetrachloride. At this point, 50 g of Woelm grade III alumina (6% water) was added and stirring continued at 65–70° until the ir band at 1590 cm^{-1} (=NNO_2) had disappeared (6–12 hr). The solution was filtered, the alumina was extracted with methylene chloride, and the organic solutions were extracted twice with 60 ml of 7% aqueous $NaHCO_3$ and once with 50 ml of saturated NaCl before drying over $MgSO_4$.

The *in situ* formation and addition of acetoxyketene to cyclopentadienes employed a solution of 0.09 mol of acetoxyacetyl chloride in 20 ml of ether which was added dropwise to a stirred solution of 1 mol of the cyclopentadiene and 0.095 mol of dry triethylamine (molecular sieves) in 200 ml of ether at −50°. The solution was allowed to warm to 25° and stirred for 6 hr before filtration with the aid of Celite. The desired adduct was isolated by chromatography on silica gel followed by distillation.

Hydrolysis of cyclic carbonates from Diels-Alder reactions was performed by adding 1 g of the carbonate in 10 ml of ether to a rapidly stirred solution of 1 g of potassium hydroxide in 10 ml of water. After the solution was stirred for 2 hr at 25°, the aqueous layer was extracted four times with 10 ml of CH_2Cl_2. The organic phase was washed with 10 ml of saturated aqueous NaCl and dried over $MgSO_4$ before vacuum evaporation of the solvents.

Oxidation of alcohols to ketones employed 8 mmol of CrO_3 and 16 mmol of dry pyridine in 20 ml of CH_2Cl_2. To this dry solution was added 1 mmol of the alcohol with stirring for 20 min. The organic layer was decanted, the residue washed with 10 ml of CCl_4, and the combined organic solution extracted twice with 10 ml of 7% aqueous $NaHCO_3$, once with 10 ml of H_2O, and once with 10 ml of saturated aqueous NaCl before drying over $MgSO_4$. Removal of the solvent *in vacuo* gave a precipitate of residual chromium salts which were removed by treatment with ether followed by filtration. The ether was removed *in vacuo* and the residue immediately purified by column chromatography.

Benzoyl nitrite was conveniently prepared by reaction of sodium benzoate (48 g) in 250 ml of CCl_4 with 36 g of nitrosyl chloride (Matheson Gas Products) at −5° in a nitrogen atmosphere. The stirred solution was warmed to 15° over an 80-min period and filtered, and the product was distilled under vacuum to give 31 g (62%) of material, bp 41–42° (0.35 Torr) [lit.[22] bp 41–42° (0.25 Torr)].

Warning Violent explosions may occur in the distillation of benzoyl nitrite particularly when the distillation is performed in sunlight.

Acetoxyacetyl Chloride.[23] Treatment of technical glycolic acid with acetyl chloride and then with PCl_3 gave the desired product: bp 45–48° (9 Torr) [lit.[23] 54° (14 Torr)]; pmr ($CDCl_3$) δ 2.2 (s, 3), 4.7 (s, 2).

Preparation of Norbornadienes. 1-Methylnorbornadiene[24] was prepared by slowly condensing methylcyclopentadiene (32 g) distilled directly from the dimer through a 40-cm Vigreux column into a Friedrich condenser attached to a flask containing propynoic acid (25 g) in 170 ml of refluxing ethyl acetate. The solution was refluxed for 12 hr after which the solvent was removed under vacuum and the residue dissolved in aqueous Na_2CO_3 (300 ml). After extraction with hexane, the aqueous solution was acidified to give 49 g of a solid extracted by ether. A fraction of this product (16.5 g) was decarboxylated by heating to 220° for 30 min in 30 g of quinoline in the presence of 1 g of copper-chromite catalyst. Distillate was collected from 60 to 155°. This material was washed with 5% hydrochloric acid, dried over $CaCl_2$, and distilled using a spinning band column to give the desired 1-methylnorbornadiene in 8% yield: bp 93° (lit.[24] bp 93.5°); pmr ($CDCl_3$) δ 1.47 (s, 3), 1.9 (s, 2), 3.45 (m, 1), 6.46 (d, 2, J = 5 Hz), 6.7 (d of d, 2, J = 5, 3 Hz). An 11% yield of 2-methylnorbornadiene, bp 103°, was also obtained.

7-*tert*-Butylnorbornadiene was prepared by the procedure of Wittig and Klemp[25] by reaction of *tert*-butyllithium and 7-*tert*-butoxynorbornadiene (Frinton Laboratories) to give material: bp 70–73° (20 Torr) [lit.[25] 64° (20 Torr)]; pmr ($CDCl_3$) δ 0.82 (s, 9), 2.43 (s, 1), 3.40 (m, 2), 6.35 (t, 2, J = 2.5 Hz), 6.83 (t, 2, J = 2.5 Hz).

Preparation of Substituted Cyclopentadienes. 5-Methylcyclopentadiene, prepared in 62% yield by the method of McLean and Haynes,[26] was distilled at 0° (6 Torr) and held below 0° at all times. Its ir spectrum was identical with that reported.[26] **5,5-Dimethylcyclopentadiene** was prepared starting from β,β-dimethylglutaric acid (Aldrich Chemical Co). Conversion to the ester was followed by acyloin condensation in ether in the presence of trimethylchlorosilane[27] to give 97% of 1,2-bis(trimethylsiloxy)-4,4-dimethylcyclopentene: bp 86–87.5° (5 Torr); pmr (CCl_4) δ 0.32 (s, 18), 1.20 (s, 6), 2.11 (s, 4); mass spectrum (70 eV) *m/e* (rel intensity) [calcd for M^+ $C_{13}H_{28}O_2Si_2$, 272 (100), 273 (24.8), 274 (8.1)] 272 (100), 273 (24.8), 274 (9.0). Hydrolysis and dehydration of the bis(trimethylsiloxy)alkene (203 g) in 170 ml of 85% H_3PO_4 occurred readily. After the reactants were mixed, vacuum distillation from an oil bath at 100° (35 Torr) was commenced. During 20 min, the pot temperature was raised to 165°, and a mixture of water and **4,4-dimethyl-2-cyclopenten-1-one** was collected. Separation of the water and redistillation gave 56 g of material: bp 65–68° (35 Torr) [lit.[28] 75° (45 Torr)]; pmr ($CDCl_3$) δ 1.24 (s, 6), 2.1 (s, 2), 5.8 (d, 1, J = 5.5 Hz), 7.3 (d, 1, J = 5.5 Hz). Reduction of this ketone by the literature procedure[28] gave 4,4-dimethyl-2-cyclopenten-1-ol: bp 48–51° (6 Torr) [lit.[28] bp 42° (1.5 Torr)]; pmr ($CDCl_3$) δ 1.03 (s, 3), 1.5 (s, 3), 1.3–2.2 (m, 2), 4.0 (s, 1), 4.7 (m, 1), 5.5 (s, 2). The alcohol was converted to the bromide by hydrogen bromide[28] which was dehydrobrominated to give the desired diene: bp 65° (lit.[28] bp 70°); pmr (CCl_4) δ 1.14 (s, 6), 6.17 (s, 4).

6,6-Dimethylfulvene was prepared by a literature procedure,[29] bp 69–70° (40 Torr) [lit.[29] bp 47° (11 Torr)].

Preparation of 2-Keto-3-*exo*-benzoyloxybicyclo[2.2.1]hept-5-enes (4a–e). Norbornadiene (4.6 g) was converted by the benzoyl nitrite procedure into 6.0 g (53%) of ***exo*,3-benzoyloxybicyclo[2.2.1]hept-5-en-2-one (4a)**, bp 125–135° (0.1 Torr) [lit.[30] bp 85–90°

(0.07 Torr)], which after purification by chromatography on silica gel with benzene (80%)-ethyl acetate (20%) eluent followed by recrystallization from 2-propanol-hexane gave 4.8 g of material, mp 72–73°: ir ($CDCl_3$) 1740, 1275 cm^{-1}; pmr ($CDCl_3$) δ 2.0–2.6 (m, 2, H-7), 3.08 (m, 1, H-4), 3.18 (m, 1, H-1), 4.95 (d, 1, J = 2 Hz, endo H-3; irradiation at δ 2.3 gave s); 6.3 (d of d, 1, J = 4.5, 2.5 Hz, H-6), 6.6 (d of d, 1, J = 4.5, 2.0 Hz, H-5), 7.2–8.3 (m, 5, C_6H_5).

Benzoates **4b** and **4c** were obtained in yields of 10 and 18%, respectively, by treatment of 1-methylnorbornadiene with benzoyl nitrite. The mixture of keto benzoates was chromatographed on 100 g of silica gel/1 g of ketone using CCl_4 (80%)-$CHCl_3$ (20%) eluent which gave the 1-methyl isomer **4b** as the first eluted compound. Analytical data for **1-methyl-*exo*,3-benzoyloxybicyclo[2.2.1]hept-5-en-2-one** follow: ir ($CHCl_3$) 1275, 1610, 1736 cm^{-1}; pmr ($CDCl_3$) δ 1.28 (s, 3, CH_3), 2.1 (d of m, 1, J = 9 Hz, syn H-7), 2.3 (d, 1, J = 9 Hz, anti H-7), 3.1 (m, 1, H-4), 5.1 (d, 1, J = 2 Hz, endo H-3), 6.0 (d, 1, J = 5 Hz, H-6), 6.4 (d of d, 1, J = 5, 3 Hz, H-5), 7.2–8.0 (m, 5, C_6H_5).[31]

For **4-methyl-*exo*,3-benzoyloxybicyclo[2.2.1]hept-5-en-2-one (4c)**, the analytical data were: ir (CCl_4) 1275, 1605, 1740 cm^{-1}; pmr ($CDCl_3$) δ 1.26 (s, 3, CH_3), 2.1 (d of m, 1, J = 9 Hz, syn H-7), 2.3 (d, 1, J = 9 Hz, anti-H-7), 3.1 (m, 1, H-1), 4.9 (d, 1, J = 2 Hz, endo-H-3), 6.0 (d of d, 1, J = 5.5, 3 Hz, H-6), 6.1 (d, 1, J = 5.5 Hz, H-5), 7.2–8.0 (m, 5, C_6H_5).[31]

***exo*,3-Benzoyloxy-*anti*-7-*tert*-butylbicyclo[2.2.1]hept-5-en-2-one** was obtained as crude material in 40% yield from the benzoyl nitrite addition followed by silica gel chromatography using benzene (84%)-ethyl acetate (16%) as the eluent: ir ($CDCl_3$) 1280, 1730, 1765 cm^{-1}; pmr ($CDCl_3$) δ 0.9 (s, $(CH_3)_3C$), 2.7 (s, syn H-7), 3.1 (broad s, H-4), 4.99 (s, 1, CHOBz), 6.0 (d of d, 1, J = 4, 6 Hz, H-6), 6.25 (d of d, 1, J = 3, 6 Hz, H-5), 7.4–8.0 (m, 5, C_6H_5).

***exo*,3-Benzoyloxy-*syn*-7-*tert*-butoxybicyclo[2.2.1]hept-5-en-2-one** was obtained in crude form from the benzoyl nitrite reaction with 7-*tert*-butoxynorbornadiene. The ethereal oxygen apparently has a neighboring group effect and causes the cis-exo addition to occur in the syn fashion. Elution from silica gel by hexane (50%)-benzene (50%) gave material with ir ($CDCl_3$) 1120, 1278, 1727, 1771 cm^{-1}; pmr ($CDCl_3$) δ 1.18 (s, 9, $(CH_3)_3CO$), 1.21 (s, 0.45, $(CH_3)_3CO$ impurity), 3.0 (m, 1, H-1 or H-4), 3.2 (m, 1, H-1 or H-4), 4.3 (q, 1, J = 2.5 Hz, anti H-7), 5.0 (d, 1, J = 2.5 Hz, endo H-3), 6.0 (d of d of d, 1, J = 1, 3, 5 Hz, H-6), 6.4 (d of d, 1, J = 3, 5 Hz, H-5), 7.3–8.1 (m, 5, C_6H_5); mass spectrum (70 eV) *m/e* (rel intensity) M^+ 300 (0), 226 (18), 122 (73), 105 (100), 77 (24).

Preparation of Derivatives 5b of *endo*-3-Hydroxybicyclo[2.2.1]hept-5-en-2-one (5a). The Diels–Alder reaction of vinylene carbonate followed by carbonate hydrolysis yielded *endo,cis*-bicyclo[2.2.1]hept-5-ene-2,3-diol, mp 168–170° (lit.[32a] mp 176°), whose pmr spectrum was in agreement with the literature values.[32b] The glycol was converted into the benzoyl, acetyl, dimethyl-*tert*-butylsilyl, and α-tetrahydropyranyl ether derivatives which were oxidized to the ketones **5b** and in the case of the α-tetrahydropyranyl ether further hydrolyzed to **5a**.

***endo,cis*-3-Benzoyloxybicyclo[2.2.1]hept-5-en-2-ol** was prepared by refluxing the diol (16.5 mmol) with benzoyl chloride (25 mmol) and pyridine (25 mmol) in benzene for 17 hr followed by vacuum evaporation of the solvent and chromatography on silica gel with benzene (80%)-ethyl acetate (20%) eluent to give 2.6 g of material: bp 128–133° (0.21 Torr); ir ($CDCl_3$) 1121, 1280, 1724, 3590 cm^{-1}; pmr ($CDCl_3$) δ 1.35 (d of m, J = 10 Hz, anti H-7), 1.6 (d of t, 1, J = 2, 10 Hz, syn H-7), 2.2 (s, 1, OH), 3.2 (m, 2, H-1,4), 4.45 (d of d, 1, J = 3.5, 7 Hz, CHOH), 5.30 (d of d, 1, J = 3.5, 7 Hz, CHOBz), 6.35 (m, 2, CH=CH), 7.3–8.1 (m, 5, C_6H_5); mass spectrum (16 eV) *m/e* (rel intensity) M^+ 230 (1), 164 (35), 108 (80), 105 (100), 77 (100).[31a]

***endo*,3-Benzoyloxybicyclo[2.2.1]hept-5-en-2-one** was prepared by oxidation of the alcohol with CrO_3·2Py according to the general procedure in 74% yield. Chromatography on silica gel with benzene (80%)-ethyl acetate (20%) eluent gave material: mp 34–36°; bp 160–180° (0.15 Torr); ir ($CDCl_3$) 1130, 1278, 1731, 1770 cm^{-1}; pmr ($CDCl_3$) δ 2.1 (d of m, 1, J = 10 Hz, H-7) 2.3 (d of m, 1, J = 10 Hz, irradiation at δ 3.4 gave d, J = 10 Hz, H-7), 3.3 (m, 2, H-1,4), 5.3 (d, 1, J = 4 Hz, irradiation at δ 3.4 gave s, CHOBz), 6.3 (d of m, 1, J = 5.5 Hz; irradiation at δ 3.4 gave d, J = 5.5 Hz, H-6), 6.5 (d of d, 1, J = 2.5, 5.5 Hz, irradiation at δ 3.4 gave d, J = 5.5 Hz, H-5), 7.2–8.1 (m, 5, C_6H_5); mass spectrum (16 eV) *m/e* (rel intensity) M^+ 228 (2), 105 (100), 77 (46), 51 (12).[31a]

In a similar manner, ***endo*,3-acetoxybicyclo[2.2.1]hept-5-en-2-one** was prepared from the diol and acetic anhydride followed by glpc isolation of the acetoxy alcohol and purification of the acetoxy ketone by chromatography on silica gel to give material: bp 70–71° (0.5 Torr); ir ($CDCl_3$) 1077, 1250, 1745, 1765 cm^{-1}; pmr ($CDCl_3$) δ 1.9–2.4 (m, 2, CH_2), 2.09 (s, 3, CH_3), 3.22 (m, 2, H-1,4), 5.1 (d, 1, J = 3.5 Hz collapsed by irradiation at δ 3.22, CHOAc), 6.2 (m, 1, irradiation at δ 3.22 gave 5.5 Hz, d, H-6), 6.5 (d of d, 1, J = 3, 5.5 Hz irradiation at δ 3.22 collapsed 3 Hz, d, H-5); mass spectrum (70 eV) *m/e* (rel intensity) M^+ 166 (3), 124 (11), 66 (21), 43 (100).[31a]

***endo*,3-*tert*-Butyldimethylsiloxybicyclo[2.2.1]hept-3-en-2-one** was prepared from the diol by reaction with *tert*-butyldimethylchlorosilane in the presence of imidazole in DMF.[33] The siloxy ether was distilled, bp 60–69° (0.13 Torr), oxidized by the general procedure, and chromatographed from silica gel by benzene to give the desired ketone: ir ($CDCl_3$) 1133, 1757 cm^{-1}; pmr ($CDCl_3$) δ 0.2 (s, 6, CH_3Si), 1.0 (s, 9, CH_3C), 1.9 (d, 1, J = 10 Hz, H-7), 2.3 (d of t, 1, J = 2, 10 Hz, H-7), 3.1 (m, 2, H-1,4), 4.0 (d, 1, J = 4 Hz, CHOSi), 6.1 (m, 1, H-6), 6.5 (d of d, 1, J = 3, 5 Hz, H-5); mass spectrum (16 eV) *m/e* (rel intensity) M^+ 238 (0), 181 (29), 151 (64), 75 (100), 73 (28).[31a]

The **α-tetrahydropyranyl ether of *endo*,3-hydroxybicyclo[2.2.1]hept-5-en-2-one** was prepared from reaction of the diol with dihydropyran in ether at −40° in the presence of a trace of concentrated hydrochloric acid to give the hydroxy ether, bp 100–105° (0.09 Torr), which was oxidized to the keto ether and purified by silica gel chromatography with benzene eluent and by distillation to give material: bp 100° (0.10 Torr); ir ($CDCl_3$) 1041, 1082, 1139, 1764 cm^{-1}; pmr δ 1.4–2.0 (m, $CH_2CH_2CH_2$, syn H-7), 2.4 (d of q, 1, J = 10 Hz, anti-H-7), 3.1 (m, 2, H-1,4), 3.3–4.3 (pair of d superimposed on a m, 3, J = 3.5 Hz collapsed by irradiation at δ 3.1 to give s at δ 4.01 and 4.14, diastereomeric CHOTHP, CH_2O), 4.8 (m, 1, OCHO), 6.13 (m, 1, irradiation at δ 3.1 gave a pair of d, J = 5.5 Hz, H-6 in diastereomeric mixture), 6.47 and 6.58 (pair of d of d, 1, J = 5.5 Hz upon irradiation at δ 3.1, H-5 in diastereomeric mixture); mass spectrum (16 eV) *m/e* (rel intensity) M^+ 224 (0), 67 (31), 55 (39).[31a]

***endo*,3-Hydroxybicyclo[2.2.1]hept-5-en-2-one** was prepared by hydrolyzing the THP ether (1.11 g) in 40 ml of ether stirred vigorously with 6 ml of 5% hydrochloric acid for 8 min at 25°. The ether solution was washed with 10 ml of saturated aqueous NaCl, dried ($MgSO_4$), evaporated under vacuum, and chromatographed on 90 g of silica gel using benzene (75%)-ethyl acetate (25%) eluent. The major fraction eluted was fractionally sublimed at 80–90° (0.1 Torr) in a Hickman still to give 75 mg (11%) of the desired α-ketol: mp 68–74°; ir ($CDCl_3$) 1072, 1757; pmr ($CDCl_3$) δ 2.0 (d, 1, J = 10 Hz, H-7), 2.3 (d of t, 1, J = 1.5, 10 Hz, H-7), 3.15 (m, 2, H-1,4), 3.6 (s, 1, OH), 4.1 (d, 1, J = 4 Hz, irradiation at δ 3.15 gave s, C*H*OH), 6.1 (m, 1, irradiation at δ 3.15 gave d of m, J = 5.5 Hz, H-6), 6.6 (d of d, 1, J = 3, 5.5 Hz, irradiation at δ 3.15 gave d, J = 5.5 Hz, H-5).[31b]

Preparation of 5c–e from 1- and 5-Methyl-*endo,cis*-bicyclo[2.2.1]hept-5-ene-2,3-diol Carbonate. Vinylene carbonate (10 g) and technical methylcyclopentadiene dimer (11 g) at 170° for 16 hr gave 17 g of a mixture of Diels–Alder adducts, bp 103–106° (0.15 Torr). Hydrolysis yielded a mixture of diols which were either separated by glpc or converted to mixtures of **5c–e** and then separated by glpc. The mixture of methylnorbornene diols was separated on a 6 ft × 0.75 in. 7% Carbowax 6000 column at 140° which yielded the 1-methyl diol (21% overall yield) in 16 min and the 5-methyl diol (41% overall yield) in 21 min. The 1-methyl diol had mp 54.5–55.5°; pmr ($CDCl_3$) δ 1.1 (d of m, 1, syn H-7), 1.3 (s, 3, CH_3), 1.6 (d of m, 1, J = 10 Hz, anti H-7), 2.4 (m, 2, OH), 2.9 (m, 1, H-4), 3.7 (m, 1, in D_2O J = 7.5 Hz, H-5), 4.2 (m, 1, in D_2O J = 4.5, 7.5 Hz, H-2), 6.0 (d, 1, J = 7 Hz, H-6), 6.2 (d of d, 1, J = 7, 3 Hz, H-5).[31a]

The 5-methyl isomer was an oil: pmr ($CDCl_3$) δ 1.11 (d of t, 1, J = 2.5, 10 Hz, irradiation at δ 2.8 gave d, J = 10 Hz, syn H-7), 1.5 (d of t, 1, J = 1, 10 Hz, irradiation at δ 2.8 gave d, J = 10 Hz, anti-H-7), 2.8 (m, 2, H-1,4), 2.35 (s, 2, OH), 4.2 (s, 2, C*H*OH), 5.75 (s, 1, CH=C).

Anal. Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.58. Found: C, 68.62; H, 8.61.

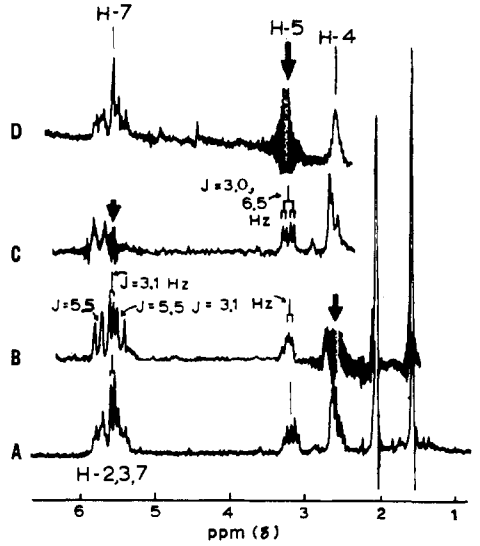


Figure 5. The 60-MHz pmr spectrum of *endo*,7-acetoxy-1-methylbicyclo[3.2.0]hept-2-en-6-one: (A) normal spectrum; (B) irradiation of H-4 methylene, J_{57} = 3.1, J_{23} = 5.5 Hz; (C) irradiation at H-7, J_{45} = 3.0, 6.5 Hz; (D) irradiation at H-5, H-7 uncoupled.

The synthesis of acetates **5c–f** was achieved by monoacetylation of the mixture of diols by 1.1 equiv of acetic anhydride in benzene to give a mixture of hydroxy acetates, bp 65–72° (0.07 Torr). Oxidation gave the keto esters, bp 75–85° (0.18 Torr), which upon glpc on a 9 ft × 0.75 in. 7% Carbowax 6000 column at 145° gave: (1) a mixture of **5c** and **5d**, retention time 12 min, 5% overall yield; (2) **5e**, retention time 15 min, 11% overall yield; and (3) **5f**, retention time 16.5 min, 6% overall yield. A lower retention time was observed for the 6-methyl isomer **5e** than for the 5-methyl compound **5f** for all 2-endo substituents, *i.e.*, acetoxy, benzoyloxy, and *tert*-butyldimethylsiloxy. The mixture of **5c** and **5d** had bp 75° (0.18 Torr); pmr δ 2.0–2.4 (s at 2.07 and m, 5, CH_3CO_2, CH_2), 3.1 (m, 1, H-1 and H-4), 5.1 (s and d, 1, CHOAc), 5.7–6.4 (m, 2, CH=CH).[31a]

6-Methyl-*endo*,3-acetoxybicyclo[2.2.1]hept-5-en-2-one (5e) had bp 70° (0.15 Torr); pmr δ 1.9–2.3 (m, 2, CH_2), 1.8 (d, 1, J = 1.8 Hz collapsed by irradiation at δ 5.8, CH_3C=C), 1.99 (s, 3, CH_3CO_2), 2.9 (m, 2, H-1,4), 4.90 (d, 1, J = 4 Hz collapsed by irradiation at δ 2.9, CHOAc), 5.80 (m, 1, H-5).[31a]

5-Methyl-*endo*,3-acetoxybicyclo[2.2.1]hept-5-en-2-one (5f), mp 60–71°, was contaminated with ~10% of the isomer **5e**: pmr 1.8–2.1 (m, 2, CH_2), 1.8 (d, 3, J = 1.8 Hz, CH_3C=C), 2.06 (s, 3, CH_3CO_2), 3.00 (m, 2, H-1,4), 5.00 (d, 1, J = 4 Hz collapsed by irradiation at δ 3.00, CHOAc), 5.60 (m, 1, H-6).[31a]

A mixture of **1- and 4-methyl-*endo,cis*-3-*tert*-butyldimethylsiloxy-2-bicyclo[2.2.1]hept-5-en-2-ones (5c,d)** was obtained by silylation of the pure 1-methyl-2,3-diol followed by oxidation of the purified siloxy alcohols to give material with bp 58° (0.09 Torr); ir ($CDCl_3$) 850, 1263, 1753 cm^{-1}; pmr ($CDCl_3$) δ 0.23 (s, 6, CH_3Si), 1.01 (s, 9, $(CH_3)_3C$), 1.31 (s, 1.9, 4-CH_3), 1.38 (s, 1.2, 1-CH_3), 1.7–2.3 (m, 2, CH_2), 2.9–3.1 (m, 1, H-1,4), 3.7 (s, 0.6, H-3), 4.0 (d, 0.4, J = 3.5 Hz, H-3), 5.7–6.5 (m, 2, CH=CH).

***endo*,3-*tert*-Butyldimethylsiloxy-5-methylbicyclo[2.2.1]hept-5-en-2-one (5f)** was separated by glpc in 22% yield from the four isomeric siloxy ketones obtained by monosilylation of the mixture of 1- and 5-methyl 2,3-diols followed by oxidation. Material isolated from the 9 ft × 0.75 in. 7% Carbowax 6000 column at 110° had: bp 58° (0.08 Torr); pmr ($CDCl_3$) δ 0.23 (s, 6, CH_3Si), 1.0 (s, 9, $(CH_3)_3C$), 2.03 (d, 3, J = 1.8 Hz collapsed by irradiation at δ 5.7, CH_3C=C), 2.00 (d of m, 1, J = 10 Hz, syn H-7), 2.3 (d of d of d, 1, J = 10 Hz, anti H-7), 2.85 (m, 1, unaffected by irradiation at δ 5.7, H-4), 3.00 (m, 1, sharpened by irradiation at δ 5.7, H-1), 4.10 (d, 1, J = 3.5 Hz collapsed by irradiation at δ 2.85, CHOSi), 5.7 (m, 1, CH=C).[31a]

A mixture of **5- and 6-methyl-*endo*,3-benzoyloxybicyclo[2.2.1]hept-5-en-2-one (5e,f)** was prepared by benzoylation of the 5-methyl-2,3-diol with benzoyl chloride (1.25 equiv) and pyridine (1.25 equiv) in benzene followed by oxidation of the purified benzoyloxy alcohols to give a mixture of isomers which could be separated by glpc on a 6 ft × 0.75 in. Carbowax 6000 column at 145° with a retention time of 28 min for the 5-methyl **5f** and 36 min for the 6-methyl isomer **5e**. The mixture of the two isomers used for esr work had: bp 130–145° (0.14 Torr); pmr ($CDCl_3$) δ 1.8 (pair of d, 3, J = 1.8 Hz, CH_3C=C), 2.1 (d of m, 1, J = 10 Hz, syn H-7), 2.3 (d of m, 1, J = 10 Hz, anti H-7), 3.2 (m, 2, H-1,4), 5.3 (m, 1, CHOBz), 5.6 (m, 0.5, H-6), 5.8 (m, 0.5, H-5), 7.2–8.2 (m, 5, C_6H_5).[31a]

***endo,cis*-7,7-Dimethylbicyclo[2.2.1]hept-5-ene-2,3-diol carbonate, precursor to 5g,** was prepared in 51% yield from the Diels–Alder reaction in bromobenzene at 155° for 24 hr, mp 74.5–74.8°. Hydrolysis yielded the diol which was benzoylated without isolation to yield ***endo,cis*-3-benzoyloxy-7,7-dimethylbicyclo[2.2.1]-hept-5-en-2-ol** purified by chromatography on silica gel and recrystallized from ether to give material with mp 133–134°; pmr ($CDCl_3$) δ 1 (s, 3, CH_3), 1.08 (s, 3, CH_3), 1.5 (s, 1, OH), 2.7 (m, 2, H-1,4), 4.7 (m, 1, C*H*OH), 5.6 (d of d, 1, J = 3.5, 7.0 Hz, J = 3.5 Hz collapsed by irradiation at δ 2.7, CHOBz), 6.2 (m, 2, CH=CH), 7.1–7.9 (m, 5, C_6H_5).[31a]

Oxidation of the benzoyloxy alcohol gave ***endo*,3-benzoyloxy-7,7-dimethylbicyclo[2.2.1]hept-5-en-2-one (5g)**: mp 95.5–97.0°; pmr ($CDCl_3$) δ 1.18 (s, 3, CH_3), 1.26 (s, 3, CH_3), 2.9 (m, 2, H-1,4), 5.5 (d, 1, J = 3.5 Hz collapsed by irradiation at δ 2.9, H-3), 6.0 (m, 1, irradiation at δ 2.9 gave d, J = 5.5 Hz, H-6), 6.4 (m, 1, irradiation at δ 2.9 gave d, J = 5.5 Hz, H-5), 7.2–8.0 (m, 5, C_6H_5).[31a]

A mixture of *exo*- and *endo*,7-isopropylidenebicyclo[2.2.1]hept-5-ene-2,3-diol carbonates was prepared,[34] mp of exo isomer 70–72° (lit.[34] 74–76°). Hydrolysis, silylation with *tert*-butyldimethylchlorosilane and chromatography on silica gel using hexane (94%)–ethyl acetate (6%) eluent gave a mixture of the exo,-cis and endo,cis siloxy ethers, bp 85–97° (0.09 Torr). Oxidation followed by silica gel chromatography and glpc on a 6 ft × 0.75 in. 7% Carbowax 6000 column at 140° gave the pure ***endo*,3-*tert*-butyldimethylsiloxy-7-isopropylidenebicyclo[2.2.1]hept-5-en-2-one:** bp 85–92° (0.13 Torr); pmr ($CDCl_3$) δ 0.29 (s, 6, C*H*$_3$Si), 1.07 (s, 9, $(CH_3)_3C$), 1.76 and 1.81 (s, 6, $(CH_3)_2C$=C), 3.7 (m, 2, H-1,4), 4.0 (d, 1, J = 3.5 Hz, CHOSi), 6.3 (m, 1, H-6), 6.6 (d of d, 1, J = 2.5, 5.1 Hz, H-5).[31a]

In a similar fashion, a mixture of ***endo*- and *exo*,3-benzoyloxy-7-isopropylidenebicyclo[2.2.1]hept-5-en-2-one** was prepared and purified by chromatography on silica gel and distillation to give material: bp 155–160° (0.13 Torr); pmr ($CDCl_3$) δ 1.7–1.8 (s, s, s, 6, $(CH_3)_2C$=C), 3.6–3.9 (m, 2, H-1,4), 4.98 (s, 0.5, endo H-3), 5.17 (d, 0.5, collapsed by irradiation at δ 3.92, exo H-3), 6.3 (m, 1, H-6), 6.5 (d of d, 1, J = 5.2, 2.8 Hz, H-5), 7.2–8.0 (m, 5, C_6H_5).[31a]

7-Isopropylidenebicyclo[2.2.1]hept-2-ene-2,3-dicarboxylic anhydride (22) was prepared from dimethyl 7-isopropylidenebicyclo[2.-2.1]hept-2-ene-2,3-dicarboxylate,[35] mp 56–60° (lit.[35] mp 64–65°). The ester was saponified with 20% aqueous KOH and the crude diacid refluxed for 12 hr in benzene with a ten-fold excess of acetic anhydride to give material sublimable at 110° (0.2 Torr) which was purified by chromatography on silica gel to give the desired anhydride: mp 112.5–114.0°; pmr ($CHCl_3$) δ 1.20–2.11 (m, 4), 1.64 (s, 6), 3.88–3.97 (m, 2).[31a]

Acetoxyketene–Cyclopentadiene Adducts 7a–d. Acetoxyketene (0.09 mol) and cyclopentadiene (1.0 mol) gave 9.3 g (62%) of product, bp 76–80° (0.2 Torr). Preparative glpc using a 6 ft × 0.75 in. 7% Carbowax 6000 column at 135° gave 0.32 g of ***exo*,7-acetoxybicyclo[3.2.0]hept-2-en-6-one,** retention time 16 min: ir ($CDCl_3$) 1228, 1614, 1753, 1796 cm^{-1}; pmr ($CDCl_3$) δ 2.08 (s, 3, CH_3), 2.6 (m, 2, CH_2), 3.4 (m, 1, H-1), 4.0 (m, 1, H-5), 4.82 (t, 1, J = 3.5 Hz, endo-H-7), 5.8 (s, 2, CH=CH).[31a]

***endo*,7-Acetoxybicyclo[3.2.0]hept-2-en-6-one (7a)** was the major product (6.95 g), retention time 24 min: ir ($CDCl_3$) 1230, 1609, 1740, 1791 cm^{-1}; pmr ($CDCl_3$) δ 2.03 (s, 3, CH_3), 2.55 (m, 2, CH_2), 3.5–4.0 (m, 2, H-1.5); (exo) δ 5.5–6.0 (d and m, 3, J = 5.5 Hz, d collapsed to s by irradiation at δ 3.6, H-2,3, exo-H-7).[31a]

Reaction of 55 g (0.69 mol) of 5-methyl-1,3-cyclopentadiene in 50 ml of ether with 0.09 mol of acetoxyketene gave 9.1 g (56%) of a mixture of exo (4%) and endo (96%) isomers, bp 84–85° (0.30 Torr), which could be separated by glpc on a 6 ft × 7% Carbowax 6000 column at 148°.

***exo*,7-Acetoxy-3-methylbicyclo[3.2.0]hept-2-en-6-one** had a retention time of 21 min: pmr ($CDCl_3$) δ 1.74 (m, 3, CH_3), 2.07 (s,

3, CH_3CO_2), 2.5 (m, 2, CH_2), 3.2-3.5 (m, 1, H-1), 3.8-4.2 (m, 1, H-5), 4.82 (t, 1, J = 3.5 Hz, endo H-7), 5.4 (m, 1, H-2).

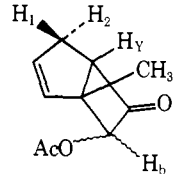
***endo*,7-Acetoxy-3-methylbicyclo[3.2.0]hept-2-en-6-one (7b)** had a retention time of 31 min: pmr ($CDCl_3$) δ 1.80 (s, 3, CH_3), 2.09 (s, 3, CH_3CO_2), 2.4 (m, 2, CH_2), 2.8-3.3 (m, 2, H-1,5), 5.6 (d of d, 1, J = 3.1, 7.7 Hz, exo H-7).

Addition of acetoxyketene to methylcyclopentadiene obtained by cracking the commercial dimer gave the exo and endo isomers of 7-acetoxy-3-methylbicyclo[3.2.0]hept-2-en-6-one and a third isomer (5% overall yield) with a lower retention time of 12 min: ir ($CDCl_3$) 1230, 1618, 1755, 1799 cm^{-1}; pmr ($CDCl_3$) δ 1.60 (s, 3, CH_3), 2.09 (s, 3, CH_3CO_2), 2.6 (m, 2, CH_2), 3.20 (m, 1, J_{57} = 3.1, $J_{54\text{-exo}}$ = 6.5, $J_{54\text{-endo}}$ = 3.0 Hz, H-5), 5.58 (d, 1, J = 3.1 Hz, exo H-7), 5.7 (m, 2, CH=CH); mass spectrum (70 eV) *m/e*, M^+ 80. The assigned structure on the basis of the pmr was ***endo*,7-acetoxy-1-methylbicyclo[3.2.0]hept-2-en-6-one** by comparison with model compounds (see Appendix).

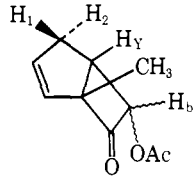
Addition of acetoxyketene to 6,6-dimethylfulvene gave 20% ***endo*,7-acetoxy-4-isopropylidene-bicyclo[3.2.0]hept-2-en-6-one (7d)**: bp 106-108° (0.15 Torr); pmr ($CDCl_3$) 1.78 (s, 6, $(CH_3)_2C$=), 2.02 (s, 3, CH_3CO_2), 3.8-4.2 (m, 2, irradiation at δ 5.8 gave AB q, J_{15} = 7 Hz, H-1,5), 5.7 (d, 1, J = 6 Hz collapsed by irradiation at δ 6.4, H-2), 5.7 (d of d, 1, J = 3, 8 Hz, exo H-7), 6.4 (d, 1, J = 6 Hz collapsed by irradiation at δ 5.7, H-3); %C 0.47% in excess of calculated value.[31a]

Appendix

Structure proof for ***endo*,7-acetoxy-1-methylbicyclo-[3.2.0]hept-2-en-6-one (7c).** The pmr spectrum, Figure 5, shows a multiplet for one hydrogen atom between δ 3 and 4, whereas acetoxy ketones **7a,b,d** had multiplets from two hydrogen atoms in this area. Moreover, at δ 5.4-5.9 there is a three-hydrogen multiplet easily ascribed to —CH=CH— and —CH(OAc)C(=O)—. Decoupling experiments (Figure 5) demonstrated that the bridgehead proton (δ 3.0-3.5) was coupled to the C-4 methylene group (J = 3.0, 6.5 Hz) and to —CH(OAc)— (J = 3.1 Hz). Two possible structures consistent with this splitting pattern are **26** and **27**.

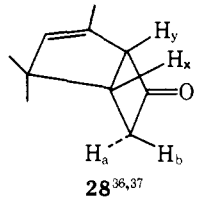


26



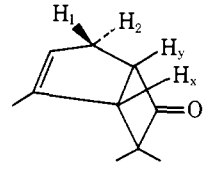
27

The magnitude of J_{by} = 3.1 Hz excludes **27** (either exo or endo) by comparison with **28** (J_{ax} = 6, J_{bx} = 8.1 Hz).



28[36,37]

(J_{ax} = 6.0, J_{ay} = 2.4, J_{bx} = 8.1, J_{by} = 4.0 Hz)



29[36]

(J_{1y} = 3.0, J_{2y} = 8.0, J_{xy} = 8.0 Hz)

Structure **26** (endo acetate) is consistent with **28** with J_{by} (**26**) = 3.1, J_{by} (**28**) = 4.0, J_{y1} (**26**) = 3.0, J_{y1} (**29**) = 3.0, J_{y2} (**26**) = 6.5, J_{y2} (**29**) = 8.0 Hz. Further support for the endo-acetoxy structure arises from the fact that the olefinic region of Figure 5 is quite similar to the observed patterns for **7a** (endo acetate), whereas for the isomeric exo acetate, the olefinic protons nearly form a singlet.

References and Notes

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