(−)-(3S)-IVa, 16451-50-6; (+)-(3R)-IVb, 16451-51-7; (−)-(3S)-IVb, 16451-52-8; V, 16451-53-9; (+)-(3R)-VIa, 16451-54-0; (−)-(3S)-VIa, 16451-55-1; (+)-(3R)-VIb, 16451-56-2; (−)-(3S)-VIb, 16451-57-3; (+)-(3R)-VII, 16503-30-3; (−)-(3S)-VII, 16462-50-3; (+)-(3R)-VIIIb, 16503-31-4.

The Stereochemistry of Methylene Transfer from Sulfonium Ylides to Unsaturated Bicyclic Ketones[1]

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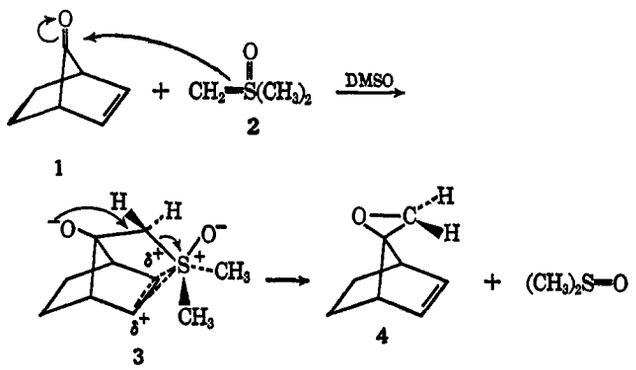
In contrast to other nucleophilic reagents, dimethyloxosulfonium methylide attacks dehydronorcamphor predominantly from the *endo* direction to yield a 71:29 ratio of spiro[norborn-2-en-*exo*- and -*endo*-5,2′-oxacyclopropanes]. Dimethylsulfonium methylide, however, produces the same two oxides in a 6:94 ratio. Both the oxosulfonium and the sulfonium ylide attack norcamphor preponderantly from the *exo* side to yield spiro[norbornan-*exo*- and -*endo*-2,2′-oxacyclopropanes] in a 10:88 or 5:95 ratio, respectively. Competitive rate studies have been used to demonstrate that dehydronorcamphor exhibits an enhanced *endo* and decreased *exo* reactivity toward the oxosulfonium ylide. Participation by the π electrons of the double bond has been suggested as the cause of this unusual kinetic and stereochemical effect.

During the course of some synthetic investigations undertaken in connection with another problem, it was observed that the reaction of norbornen-7-one (**1**) with dimethyloxosulfonium methylide (**2**) occurs in a stereospecific manner to yield spiro[norbornen-*anti*-7,2′-oxacyclopropane] (**4**)[2] and suggested that π-electron participation *via* the intermediate **3**[3-5] might be responsible for the preferential *syn* addition, *viz.*



However, since the *syn* side of a 7-substituted norbornene is apparently less sterically hindered than the *anti*—the irreversible reaction of norbornen-7-one (**1**) with a mixed-metal hydride or an organometallic produces an *anti* alcohol predominantly,[2] while equilibration of the mixed 7-carbomethoxynorbornenes with methanolic sodium methoxide yields more *syn* than *anti* ester[6]—a steric factor could not be ruled out as the cause of the observed stereospecificity. To test these ideas and to learn more of the path by which sulfur ylides react with ketones to yield epoxides, we have extended our investigations to include the ketones norcamphor (**13**), dehydronorcamphor (**5**), and norbornan-7-one (**18**) and the ylide dimethylsulfonium methylide (**12**).[7]

Results

The reaction of dehydronorcamphor (**5**) at 25° with a 10% excess of dimethyloxosulfonium methylide (**2**)[7] in dimethyl sulfoxide (DMSO) yields a mixture containing 65% spiro[norbornen-*exo*-5,2′-oxacyclopropane] (**7**), 27% spiro[norbornen-*endo*-5,2′-oxacyclopropane] (**9**), and 8% the unreacted ketone, **5**. The composition of the product mixture was determined by gas–liquid partition chromatography (glpc) on a basic Quadrol/SAIB column[8] at 115°, conditions which permit analysis of the reactive unsaturated *anti* oxide, **4**,[2] without rearrangement. The major products, **7** and **9**, respectively, were identified from their analyses and infrared and nmr spectra (see Experimental Section) and by their reduction with lithium aluminum hydride to the known[9] unsaturated alcohols 5-methylnorbornen-*exo*- and -*endo*-5-ols (**10** and **11**), respectively (Chart I).

At a lower temperature **5** reacts with an ~20% excess of dimethylsulfonium methylide (**12**) in DMSO to yield a mixture containing 6% the unsaturated *exo* oxide **7** and 94% the unsaturated *endo* oxide **9**.

$$\underset{}{5} + \underset{12}{CH_2{=}S(CH_3)_2} \longrightarrow 7\ (6\%) + 9\ (94\%)$$

In contrast to dehydronorcamphor (**5**), norcamphor (**13**) reacts with **2** to produce a mixture containing about 10% spiro[norbornan-*exo*-2,2′-oxacyclopropane] (**15**), at least 88% spiro[norbornan-*endo*-2,2′-oxacyclopropane] (**17**), and less than 2% unreacted norcamphor (**13**). Since the two saturated oxides, **15** and **17**, which constitute at least 98% (by glpc) of the distilled reaction product could not be separated by glpc, they were collected together, and their relative proportion

(1) Portions of this work have been presented before the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966, Abstracts, p 8K.

(2) R. K. Bly and R. S. Bly, *J. Org. Chem.*, **28**, 3165 (1963).

(3) We represent this intermediate as charge delocalized purely as a matter of convenience and analogy,[4] but do not intend to imply that our experimental results permit us to distinguish it from a tricyclic charge-localized structure(s).

(4) Analogous structures have been suggested to accommodate the observed stability of positively charged carbon,[5a-c] and sulfur[5d] exocyclic, *syn* and β to the 5 or 7 position of 2-norbornene.

(5) (a) E. L. Allred and T. J. Maricich, *Tetrahedron Lett.*, 949 (1963); (b) R. M. Hawthorne, Jr., Ph.D. Dissertation, Rutgers, 1963, part II; (c) R. S. Bly, R. K. Bly, A. O. Bedenbaugh, and O. R. Vail, *J. Amer. Chem. Soc.*, **89**, 880 (1967); (d) P. Wilder, Jr., and L. A. Feliu-Otero, *J. Org. Chem.* **31**, 4264 (1966).

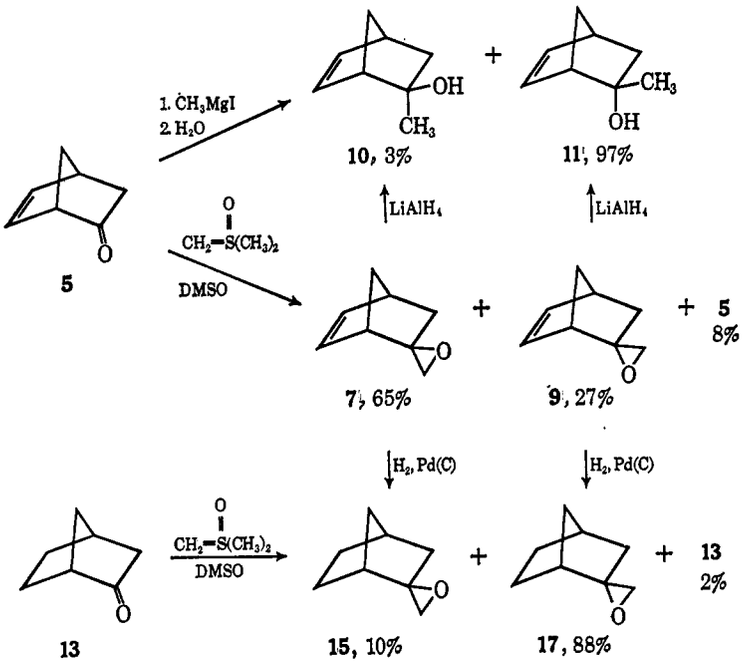
(6) R. R. Sauers and R. M. Hawthorne, Jr., *ibid.*, **29**, 1685 (1964).

(7) E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **87**, 1353 (1965).

(8) The preparation and properties of this liquid phase have been described earlier; *cf.* J. A. Broderick, "Aerograph Research Notes," Wilkins Instrument and Research, Walnut Creek, Calif., Fall Issue, 1960.

(9) (a) N. J. Toivonen and P. J. Mälkönen, *Suomen Kemistilehti*, *B*, **32**, 277 (1959); (b) *ibid.*, **33**, 53 (1960).

CHART I

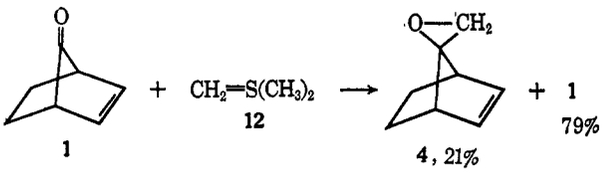


was determined by nmr spectroscopy. The oxirane-type hydrogens of authentic **15**, prepared by catalytic hydrogenation of **7**, appear as a two-hydrogen singlet at δ 2.61, while the corresponding hydrogens of the saturated *endo* oxide **17**, prepared in a similar manner from **9**, appear as an AB-type quartet[10] (H_A, δ 2.72; H_B, δ 2.54; J_{AB} = 5.8 cps) centered at 2.63. The collected reaction mixture from **13** is revealed by integration of its nmr spectrum to consist of nine parts **17** and one part **15** (Chart I).

Norcamphor (**13**) reacts with dimethylsulfonium methylide (**12**) to give a mixture of 2% **15**, 41% **17**, and 57% unreacted ketone **13**.

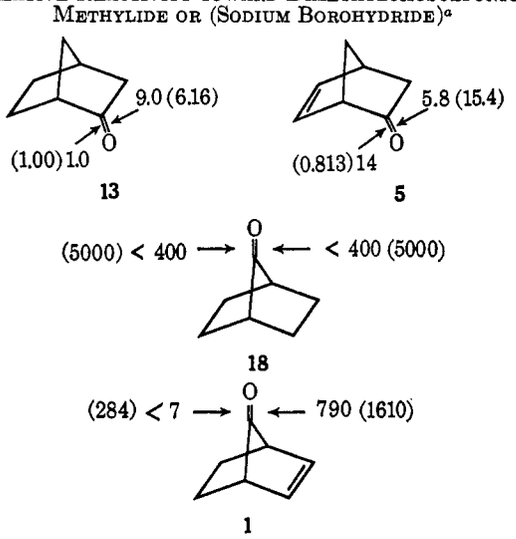
$$13 + 12 \longrightarrow 15 + 17 + 13$$

Norbornen-7-one (**1**), in analogy to its reaction with dimethyloxosulfonium methylide (**2**), yields the unsaturated *anti* oxide, **4**, exclusively, when treated with dimethylsulfonium methylide (**12**), *viz.*



In order to determine the relative reactivity of the ketones **1**, **5**, and **13** toward dimethyloxosulfonium methylide (**2**), known mixtures of **1** and **5** and of **5** and **13** were allowed to react for 1 hr at 26.0° with less than stoichiometric amounts of **2** in DMSO solution.[11] The reaction mixtures were then analyzed by glpc under conditions at which both the unreacted starting ketone and the products were not only stable but completely resolved. The relative rate of reaction of dimethyloxosulfonium methylide at each position of three ketones[11] was calculated from these data[14] and is indicated diagrammatically and compared with that of sodium borohydride[15] in Chart II.

CHART II
RELATIVE REACTIVITY TOWARD DIMETHYLOXOSULFONIUM METHYLIDE OR (SODIUM BOROHYDRIDE)[a]



[a] Calculated from the data of ref 15.

Discussion

Dimethyloxosulfonium methylide (**2**) reacts in an unusual manner with dehydronorcamphor (**5**). Toward the saturated ketone, norcamphor (**13**), dimethyloxosulfonium methylide behaves as do other nucleophiles (Table I) and yields predominantly the product

(10) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, London, 1959, p 89 ff.

(11) Although norbornan-7-one (**18**) was also included in our competitive rate studies, a quantitative comparison of its reactivity toward epoxide formation is not too meaningful because of the large amounts of sulfur-containing by-products which are also formed and because of some uncertainty about the origin of the epoxide, spiro[norbornan-7,2′-oxacyclopropane], which is produced.[12] However, in the sense that less unsaturated ketone (**1**) than saturated ketone (**18**) remains unreacted when an equimolar mixture of the two is allowed to react with insufficient dimethyloxosulfonium methylide in DMSO, norbornen-7-one (**1**) is apparently somewhat more reactive than norbornan-7-one (**18**).[13]

(12) We plan to discuss this reaction in a future publication.

(13) See Chart II.

(14) T. S. Lee in "Technique of Organic Chemistry," Vol. VIII, S. L. Friess and A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1953, p 100 ff.

(15) H. C. Brown and J. Muzzio, *J. Amer. Chem. Soc.*, **88**, 2811 (1966).

TABLE I
PROPORTION OF PRODUCT RESULTING FROM *exo* OR *syn* ATTACK ON SOME BICYCLIC KETONES

Reactant/solvent	% 13	% 5	% 1
$NaBH_4/i$-PrOH[a]	86	95	85
$LiAlH_4/Et_2O$	94[b]	91[b]	86[c]
$LiAlH(t\text{-}OBu)_3/THF$[d]	>92	77	...
CH_3MgI/Et_2O	100[e]	97[f]	100[g]
C_2H_5MgBr/Et_2O[h]	...	100	...
$(CH_3)_2CHMgBr/Et_2O$[h]	...	100	...
C_6H_5MgBr/Et_2O	~100[i]	...	~67[i]
$CH_2{=}CHMgBr$[k]	...	...	~75
$n\text{-}C_4H_9Li/C_7H_{16}$[c]	...	...	61
$(CH_3)_2S{=}CH_2$[f]	95	94	100
$(CH_3)_2\overset{\overset{O}{\|}}{S}{=}CH_2$	90[f]	29[f]	100[g]

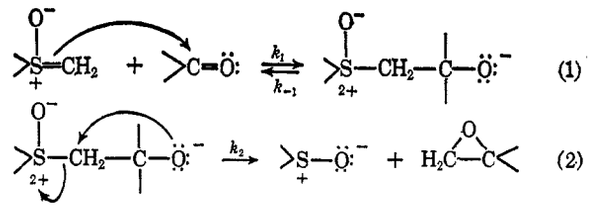
[a] See ref 15. [b] S. Beckmann and R. Mezger, *Chem. Ber.*, **89**, 2738 (1956). [c] R. K. Bly, unpublished work. [d] C. H. DePuy and P. R. Story, *J. Amer. Chem. Soc.*, **82**, 627 (1960). [e] N. J. Toivonen, E. Siltanen, and K. Ojala, *Ann. Acad. Sci. Fennicae*, AII No. 64 (1955). [f] This work. [g] See ref 2. [h] S. J. Cristol and P. K. Freeman, Abstracts of the 133rd National Meeting of the American Chemical Society, San Francisco, Calif., April 13–18, 1958, p 6N; P. K. Freeman, *Dissertation Abstr.*, **20**, 2012 (1958). [i] This and other aryl Grignard reagents apparently react exclusively from the *exo* side; *cf.* D. C. Kleinfelter and P. Schleyer, *J. Org. Chem.*, **26**, 3740 (1961); and H. C. Brown, F. S. Chloupek, and M.-H. Rei, *J. Amer. Chem. Soc.*, **86**, 1246 (1964). [j] Private communication from P. G. Gassman, Department of Chemistry, The Ohio State University. [k] J. A. Berson and M. Jones, Jr., *ibid.*, **86**, 5019 (1964).

of *exo* attack, *viz.*, the saturated *endo* oxide **17**. Mixed-metal hydrides and Grignard reagents also react in this manner with the *unsaturated* ketone, dehydronorcamphor (**5**), *i.e.*, approach exclusively or predominantly from the *exo* side to produce an *endo* alcohol (Table I). Dimethyloxosulfonium methylide (**2**), however, reacts with this ketone preferentially from the *endo* side to yield the unsaturated *exo* oxide **7**, predominantly. Furthermore, while with sodium borohydride in isopropyl alcohol the actual rate of *exo* addition *increases* and that of *endo* addition *decreases* slightly in passing from norcamphor (**13**) to dehydronorcamphor (**5**) (Chart II),[15] with dimethyloxosulfonium methylide (**2**) the opposite is true: *endo* attack becomes 14 times more facile while *exo* addition occurs only 0.64 times as fast (Chart II).

A similar kinetic effect may also be apparent in the attack of the oxosulfonium ylide **2** on norbornen-7-one (**1**). This ylide appears to be somewhat more reactive toward the unsaturated ketone **1** than toward the saturated norbornan-7-one (**18**).[11] In this respect it contrasts sharply with sodium borohydride which reacts ten times more rapidly with **18** (Chart II).[15]

Although the exact course of the reaction of oxosulfonium ylides with ketones has not yet been established,[7] it is now thought to consist of eq 1, a reversible nucleophilic addition by the "methylene" carbon of the ylide at the electron-deficient carbonyl carbon of the ketone to form a betaine intermediate, followed by eq 2, an irreversible intramolecular nucleophilic displacement of the sulfoxide by the oxide of the betaine.[16]

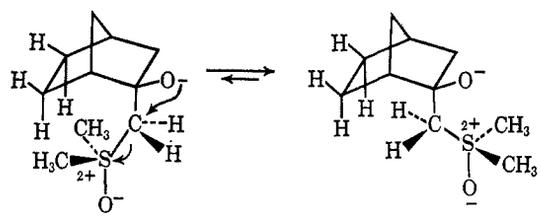
(16) The current status of mechanistic thought on sulfonium ylide reactions is summarized in A. W. Johnson, "Ylid Chemistry," Academic Press Inc., New York, N. Y., 1966, Chapter 9.



(1)

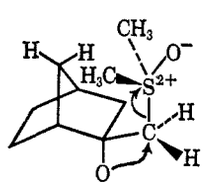
(2)

In the case of dissymmetric bicyclic ketones, such as **1**, **5**, and **13**, two modes of reaction are possible. With norcamphor (**13**) the observed ratio of *exo/endo* attack is 9.0:1.0 (Chart II) and probably reflects the fact that not only is *exo* attack sterically more favorable than *endo*, *e.g.*, $(k_1)_{exo} > (k_1)_{endo}$, but that, because of repulsions between the methyl groups and the *endo* hydrogens at C-5 and C-6, the *endo*-betaine **14** is less favorably



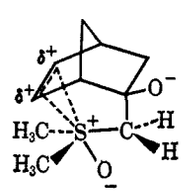
14

oriented for displacement of dimethyl sulfoxide than is the *exo*-betaine **16**, *i.e.*, $(k_2)_{exo} > (k_2)_{endo}$.



16

With dehydronorcamphor (**5**) *exo/endo* attack occurs in the ratio of 5.8:14 or 0.24:1.0 (Chart II). It is suspected that this greatly enhanced preference for *endo* (axial) attack may be due to π-electron participation[3] by the reactive double bond of the ketone which increases both $(k_1/k_{-1})_{endo}$ with respect to $(k_1/k_{-1})_{exo}$ by stabilizing the increased positive charge on sulfur in the *endo*-transition state and intermediate *endo*-betaine **6**[3] of eq 1, and $(k_2)_{endo}$ with respect to $(k_2)_{exo}$ by fixing the *endo*-betaine **6** in the most favorable conformation for intramolecular displacement of dimethyl sulfoxide, eq 2.



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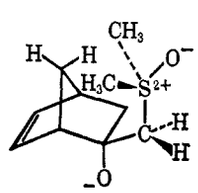


8

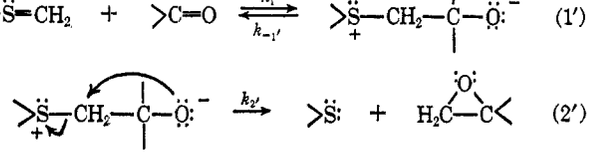
It is doubtful that this preference for methylene transfer from **2** to the *endo* side of dehydronorcamphor (**5**) could derive from steric effects alone. Not only does this ketone exhibit a strong kinetic preference for *exo* attack by other nucleophiles (Table I), but there is apparently little difference in the thermodynamic stability of most *exo*- or *endo*-5-substituted norbor-

nenes.[17] Hence, in the absence of π-electron participation by the double bond, it is unlikely that a strong bias for reversible *exo* attack in eq 1 would be overridden by an even greater tendency for irreversible *endo*-methylene product formation in eq 2.

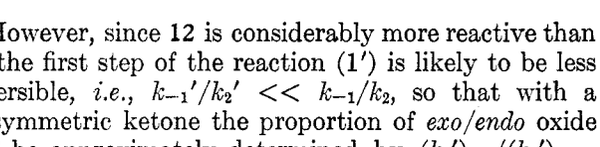
Nor is it believed that the effect of the double bond can be predominantly inductive in nature. Brown and Muzzio[15] have clearly demonstrated that with respect to norcamphor (**13**) *exo* attack by borohydride ion is enhanced in dehydronorcamphor (**5**) while *endo* attack is suppressed (Chart II). They have suggested that the electron-withdrawing inductive effect of the double bond is responsible for the enhanced "*exo* reactivity" of **5**. Assuming that their explanation is correct, it is clearly not possible to attribute both the enhanced *exo* reactivity of **5** toward the nucleophile borohydride and its enhanced "*endo* reactivity" toward the nucleophile dimethyloxosulfonium methylide (**2**) to this same inductive effect.[18]

In the case of norbornen-7-one (**1**) the preference for methylene transfer from **2** to the side of the double bond is even more pronounced, *i.e.*, >100:1. Here too, the effect of the double bond is to decrease the rate of *syn* attack by borohydride ion while apparently increasing the *syn* reactivity of **1** toward attack by the oxosulfonium ylide **2** (Chart II). Again we suspect that the latter reaction is accompanied by π-electron participation whose effect is to increase the forward rates of both steps by stabilizing the developing positive charge on sulfur and holding the intermediate *syn*-betaine **3** in the best conformation for the internal displacement of dimethyl sulfoxide. Since **1** is extremely reactive toward nucleophiles,[2,11] and since *syn* attack is also the sterically as well as the electronically favored process (Table I), the over-all reaction is quite rapid and highly stereospecific.

The reaction of dimethylsulfonium methylide (**12**) with a ketone may probably, in analogy to dimethyloxosulfonium methylide (**2**), be considered as a two-step reaction,[16] *viz.*



(1′)



(2′)

However, since **12** is considerably more reactive than **2**,[7] the first step of the reaction (1′) is likely to be less reversible, *i.e.*, $k_{-1}'/k_2' << k_{-1}/k_2$, so that with a dissymmetric ketone the proportion of *exo*/*endo* oxide will be approximately determined by $(k_1')_{exo}/(k_1')_{endo}$. Also because of its higher reactivity the course of the reaction of the sulfonium ylide **12** with a ketone is less likely to be influenced by small differences in the stabilities of the intermediate betaines. In other words, the transition state of **1** will be reached earlier in the reaction than that of **1**, and hence will be less susceptible to the effect of π-electron participation.[19] Under the circumstances it is probably not surprising that the sulfonium ylide reacts by the sterically favored process in each case, *e.g.*, transfers methylene from the *exo* side of both **5** and **13** and from the *syn* side of **1** (Table I).

(17) (a) A. C. Cope, E. Ciganek, and N. A. Le Bel, *J. Amer. Chem. Soc.*, **81**, 2799 (1959); (b) J. A. Berson and D. A. Ben-Efraim, *ibid.*, **81**, 4083 (1959).

(18) *E.g.*, since the steric factors in *exo* addition (eq 1) to either **5** or **13** are essentially identical (*cf.* **8** and **16**), the electron-withdrawing inductive effect of the double bond could only increase the absolute rate of *exo*-nucleophilic attack upon **5** with respect to a similar attack upon **13**.

(19) G. S. Hammond, *ibid.*, **77**, 334 (1955).

Experimental Section[20]

Dehydronorcamphor (5).—Although dehydronorcamphor has been known for many years[21a] the authors believe that the following preparation is generally superior to any of the published methods[21] because it proceeds in 35% over-all yield in two steps from commercially available starting materials.

Forty grams (0.16 mol) of aluminum *t*-butoxide was added in one portion to a warm solution of 23.2 g (0.168 mol) of norborn-5-en-2-yl formates[22] and 40 g (0.37 mol) of *p*-benzoquinone in 350 ml of dry benzene. The mixture was refluxed for 24 hr with stirring and then cooled to room temperature. Hydrochloric acid (3 *N*, 100 ml) was added, and, after filtration through a Celite mat, the aqueous layer was discarded. The benzene layer was washed successively with six 200-ml portions of 3 *N* hydrochloric acid, six 200-ml portions of aqueous 5% sodium hydroxide, and finally two 100-ml portions of saturated sodium chloride solution. The benzene was removed by distillation at atmospheric pressure, and the residue was distilled under reduced pressure to yield 11.2 g (0.104 mol, 62%) of ketone, bp 55–57° (10 mm). A glpc analysis of the distillate on the 8-ft UCON column[20] (column temp, 100°; helium flow, 85 ml/min) showed it to be greater than 98% pure; its infrared and nmr spectra are identical with those of authentic dehydronorcamphor prepared in the usual manner.[21c]

5-Methylnorborn-2-en-*exo*- and -*endo*-5-ol (10 and 11, Respectively).—To a solution of methylmagnesium iodide, prepared in the usual manner from 2.0 g (0.082 g-atom) of magnesium turnings and 12.7 g (0.0883 mol) of methyl iodide in 100 ml of anhydrous ether, was slowly added a solution of 2.0 g (0.019 mol) of dehydronorcamphor (**5**) in 25 ml of anhydrous ether. After the addition was complete, the reaction mixture was heated at gentle reflux for 1 hr and cooled the complex was decomposed by the addition of water and wet sodium sulfate. The precipitated salts were removed by filtration, and the ethereal solution was dried over anhydrous sodium sulfate and concentrated. The residue was distilled through a short-path distillation apparatus to yield 1.40 g (0.0113 mol, 60%) of the tertiary alcohols. Analysis of the distillate by glpc on the 8-ft UCON column[20] (column temp, 100°; helium flow, 120 ml/min) showed two components. The **first** (retention time, 4.3 min; rel abundance, 97%) has an ir spectrum (CCl_4) identical with that of *exo*-5-methylnorborn-2-en-*endo*-5-ol.[9b] Its nmr spectrum (CCl_4) has resonances at δ 6.42–5.99, octet (2 $-CH{=}CH-$); 2.88–2.67, broad singlet (1 $\geqslant C-H$, bridgehead); 2.67–2.49, broad singlet (1 $\geqslant C-H$, bridgehead); 1.92–1.73, perturbed doublet (1 $>CHH$); 1.73–1.57, perturbed doublet (2 $>CHH$); 1.57–1.46, perturbed, concentration dependent singlet (1 $\geqslant C-OH$); 1.42, singlet (3 $-CH_3$); 1.27–0.90, perturbed doublet (1 $>CHH$). In dilute

(20) Melting and boiling points are uncorrected. Microanalyses were performed by either Bernhardt Mikroanalitisches Laboratorium, Mülheim, Germany, or Galbraith Laboratories, Inc., Knoxville, Tenn. The mass spectral analysis was performed by the Morgan-Schaffer Corp., Montreal. The infrared spectra were determined on a Perkin-Elmer grating spectrophotometer Model 337, except for the high-dilution spectra which were run on a Perkin-Elmer Model 521 using 1-cm quartz cells. The nmr spectra were determined on a Varian A-60 spectrophotometer at ~35° using tetramethylsilane (δ 0.00) and/or chloroform (δ 7.31) as internal standards in carbon tetrachloride. The glpc analyses, which were not corrected for differences in thermal conductivity of the components, were carried out on an F & M Model 500 linear temperature-programmed gas chromatograph using an 8 ft × 0.25 in. coiled copper tube packed with 20% water-insoluble UCON on 60–80 mesh Chromosorb P, or 12 ft × 0.25 in. copper tubes packed with 20% of a 2:1 mixture of Quadrol/SAIB[8] on 60–80 mesh, nonacid-washed Chromosorb P or with 20% diethyleneglycol succinate (DEGS) on nonacid-washed Chromosorb P. The preparative glpc's were carried out on an Aerograph Autoprep Model 600 using a 10 ft × 0.375 in. coiled aluminum tube packed with 20% Quadrol/SAIB (2:1)[8] on 60–80 mesh, nonacid-washed Chromosorb P.

(21) (a) K. Alder and H. Rickert, *Ann. Chim.*, **543**, 19 (1940); (b) P. D. Bartlett and B. E. Tate, *J. Amer. Chem. Soc.*, **78**, 2473 (1956); (c) S. J. Cristol and P. K. Freeman, *ibid.*, **83**, 4427 (1961); (d) H. Krieger, *Suomen Kemistilehti, B*, **38**, 68 (1965).

(22) Prepared in 65% yield, as described by Alder and Rickert,[21a] from freshly cracked cyclopentadiene and vinyl formate (Columbia Organic Chemical Co.).

solution (CCl_4), its ir spectrum exhibits an absorption at 3595 cm^{-1} (π- - - H-O) (lit.[23] 3591 cm^{-1}). The **second** (retention time, 5.6 min; rel abundance, 3%) has an infrared spectrum (CCl_4) in good agreement with the published spectrum of *endo*-5-methylnorborn-2-en-*exo*-5-ol (**10**)[9b] and shows resonances in the nmr (CCl_4) at δ 6.06, multiplet (2 -C*H*=C*H*-); 2.92–2.50, broad singlet (1 >C-*H*, bridgehead) superimposed on a singlet at 2.85 whose position is concentration dependent (1 >C-O*H*); 2.60–2.13, broad singlet (1 >C-*H*), bridgehead); 2.13–0.93, broad complex multiplet superimposed on a sharp singlet at 1.21 (4 >C*HH* + 3 -CH_3), and exhibits a nonbonded O-H stretch at 3612 cm^{-1} (lit.[23] 3611 cm^{-1}) in its high-dilution (CCl_4) infrared spectrum.

The Reaction of Dehydronorcamphor (5) with Dimethyloxosulfonium Methylide (2).[7]—Trimethyloxosulfonium iodide[24] (11 g, 0.051 mol) was added to a dry-nitrogen-blanketed, stirred suspension of 1.20 g (0.0500 mol) of sodium hydride (available as a 53% dispersion in mineral oil from Metal Hydrides, Inc.) in 40 ml of dimethyl sulfoxide (DMSO). When the evolution of hydrogen had ceased, a solution of 5.40 g (0.0500 mol) of dehydronorcamphor (**5**) in 20 ml of DMSO was added dropwise over a period of 15 min with cooling. The reaction mixture was stirred at room temperature for 2 hr, at 50–60° for 1 hr, cooled, diluted with 100 ml of water, and extracted with three 50-ml portions of pentane. The pentane extracts were combined, washed with water, dried over anhydrous sodium sulfate, concentrated, and distilled under reduced pressure to yield 4.33 g of product, bp 46.5–49° (8.75 mm).

A glpc analysis on the 12-ft Quadrol/SAIB column[8,20] (column temp, 115°; helium flow, 100 ml/min) revealed the presence of three cleanly separated components[25] which were collected individually and identified as follows. The **first** component (retention time, 19.5 mm; relative abundance, 65%) shows infrared bands (CCl_4) at 3152, 3071, 726, 707 (-CH=CH-); 3045, 1465, 1452, 549, 520 (>C(-CH$_2$-O)?); and 1022, 918, 905 cm^{-1} (C-O?); and nmr resonances (CCl_4) at δ 6.14, octet (1 -C*H*=CH- + 1 -CH=C*H*-); 3.05–2.76, broad singlet (1 >C-*H*, bridgehead); 2.63, singlet (2 >C(-C*H*$_2$-O)); 2.32–2.09, broad singlet (1 >C-*H*, bridgehead); 1.92–1.07, complex multiplet (2 >C*HH*); 1.66–1.48, complex multiplet (2 >C*HH*).

Anal. Calcd for $C_8H_{10}O$: C, 78.65; H, 8.25. Found: C, 78.79; H, 8.40.

The authors believed this component to be a spiro[norborn-2-ene-5,2′-oxacyclopropane]. To test this a 95-mg (0.78 mmol) sample was reduced with a stirred slurry of 45 mg (1.2 mmol) of lithium aluminum hydride in 2 ml of anhydrous ether. After 6 hr at reflux, the cooled reaction mixture was hydrolyzed with 15% aqueous sodium hydroxide.[26] The precipitated salts were removed by filtration, and the ethereal solution was dried over sodium sulfate and evaporated to dryness at reduced pressure. Sublimation of the residue at 60° (90 mm) gave 21 mg (0.17 mmol, 22%) of white needles, mp 51–53° (lit.[9b] mp 54.8–55.8°). The retention time of this material on the 8-ft UCON column[20] (column temp, 100°; helium flow, 75 ml/min) and its infrared and nmr spectra are identical with those of the authentic *endo*-5-methylnorborn-2-en-*exo*-5-ol (**10**). We conclude that this **first** component is spiro[norborn-2-en-*exo*-5,2′-oxacyclopropane] (**7**).

The **second** component (retention time, 25.1 min; rel abundance, 27%) exhibits infrared bands (CCl_4) at 3140, 3066, 719, 711 (-CH=CH-); 3038, 1466, 1448, 559, 505 (>C(-CH$_2$-O)?); 1026, 885, 851 cm^{-1} (C-O?); and nmr resonances (CCl_4) at δ 6.73–6.06, complex multiplet (2 -C*H*=C*H*-); 3.09–2.90, broad singlet (1 >C-*H*, bridgehead); 2.84, singlet (2 >C(-C*H*$_2$-O)); 2.53–2.34, broad singlet (1 >C-*H*, bridgehead); 2.20–1.80, quartet (1 >C*H*H); 1.80–1.58, multiplet (2 >C*HH*); 1.42–1.00, perturbed doublet (1 >C*H*H).

Anal. Calcd for $C_8H_{10}O$: C, 78.65; H, 8.25. Found: C, 78.81; H, 8.25.

It was believed that this **second** component was also a spiro-[norborn-2-en-5,2′-oxacyclopropane], and hence of *endo* configuration (**9**). This was confirmed by reduction of a 15-mg (0.12 mmol) sample with 12 mg (0.32 mmol) of lithium aluminum hydride as before. The 3.3 mg (0.024 mmol, 20%) of collected product (8-ft UCON column) was identical in every respect with the authentic *exo*-5-methylnorborn-2-en-*endo*-5-ol (**11**).

The retention time and the infrared and nmr spectra of the **third** component (retention time, 29.9 min; rel abundance, 8%) are identical with those of authentic dehydronorcamphor (**5**).

Samples of the two oxides (components 1 and 2) were collected for the reduction and rearrangement studies from the 10-ft Quadrol/SAIB column[20] (column temp, 125°; helium flow, 210 ml/min) on an Autoprep. Neither was rearranged under these conditions.[25]

The Reaction of Dehydronorcamphor (5) with Dimethylsulfonium Methylide (12).[7]—A suspension of 1.44 g (0.060 mol) of dry-nitrogen-blanketed sodium hydride in 30 ml of DMSO was heated at 70–75° for 45 min. The solution was cooled to room temperature, diluted with an equal volume of dry tetrahydrofuran (to prevent freezing), and then cooled in an ice–salt bath. With stirring, a solution of 12.2 g (0.0617 mol) of trimethylsulfonium iodide[7] in 50 ml of DMSO was added over a period of about 3 min. The reaction mixture was stirred for another minute before adding neat 5.04 g (0.0466 mol) of dehydronorcamphor (**5**). Stirring was continued at ice–salt temperature for 7 min and then for an additional 60 min with no further external cooling. The reaction mixture was then diluted with an equal volume of water (*CAUTION!*), and the product was extracted with four 50-ml portions of pentane. The combined extract was washed with water, dried over anhydrous sodium sulfate, concentrated at atmospheric pressure, and distilled under vacuum to yield 3.48 g of product, bp 50–53° (9 mm), which, by glpc analysis, consists of 6% spiro[norborn-2-en-*exo*-5,2′-oxacyclopropane] (**7**) and 94% spiro[norborn-2-en-*endo*-5,2′-oxacyclopropane] (**9**). No unreacted ketone **5** could be detected.

The Reaction of Norborn-2-en-7-one (1) with Dimethylsulfonium Methylide (12).—In the manner described previously, 6.1 g (0.031 mol) of trimethylsulfonium iodide[7] was treated with 0.72 g (0.030 mol) of sodium hydride followed by 2.70 g (0.0250 mol) of norborn-2-en-7-one (**1**) to yield 1.10 g of distilled product which glpc on the 12-ft Quadrol/SAIB column[20] (column temp, 115°; helium flow, 110 ml/min) revealed to consist of 21% spiro-[norborn-2-en-*anti*-7,2′-oxacyclopropane] (**4**) and 79% unreacted ketone. The spectra of the collected oxide were identical with those described previously.[2] No unsaturated *syn* oxide could be detected.

Spiro[norbornan-*exo*-2,2′-oxacyclopropane] (15).—A solution of 212 mg (1.74 mmol) of spiro[norborn-2-en-*exo*-5,2′-oxacyclopropane] (**7**) in 15 ml of ethyl acetate was hydrogenated at atmospheric pressure using 16 mg of 5% palladium on carbon as a catalyst. The first 1.03 equiv (44.0 ml, 1.80 mmol) of hydrogen was absorbed in 30 min, after which time the rate of hydrogen uptake decreased sharply. The reaction was stopped at this point, the catalyst was removed by filtration, and the solvent was stripped by distillation at atmospheric pressure through a 0.5 × 15 cm wire-spiral-packed column. Distillation of the residue at 10 mm in a short-path still (bath temp, 85°) yielded 163 mg (1.32 mmol, 76%) of the colorless liquid, saturated *exo* oxide **15**. Its infrared spectrum (CCl_4) shows no bands attributable to a double bond or a hydroxyl group but has absorptions at 3046, 1468, 1450, 528 (>C(-CH$_2$-O)?), 943 cm^{-1} (C-O?); nmr (CCl_4), δ 2.61, singlet (2 >C(-C*H*$_2$-O)); 2.50–2.24, broad singlet (1 >C-*H*, bridgehead); 1.86–1.00, complex multiplet (1 >C-*H*, bridgehead + 8 >C*HH*).

Anal. Calcd for $C_8H_{12}O$: C, 77.34; H, 9.74. Found: C, 77.01; H, 9.68.

Spiro[norbornan-*endo*-2,2′-oxacyclopropane] (17).—A 160-mg (1.31 mmol) sample of spiro[norborn-2-en-*endo*-5,2′-oxacyclopropane] (**9**) was hydrogenated in the same manner to yield 105 mg (0.846 mmol, 65%) of distilled (bath temp, 75°; pressure, 14 mm) saturated *endo* oxide **17**: infrared (CCl_4) 3045, 1468, 1455, 517 (>C(-CH$_2$-O)?); 1060, 961, 951 cm^{-1} (C-O?); nmr, (CCl_4) δ 2.72, asymmetric doublet (1 >C(-C*H*$_A$H$_B$-O)); 2.54, asymmetric doublet (1 >C(-CH$_A$*H*$_B$-O)—taken together these two doublets constitute a typical AB-type quartet,[10] J_{AB} = 5.8 cps, centered at δ 2.63; 2.46–2.17, broad singlet (1 >C-*H*, bridgehead); complex multiplet (1 >C-*H*, bridgehead + 8 >C*HH*).

(23) P. Hirsjarvi and K. Salo, *Suomen Kemistilehti, B*, **32**, 280 (1959).

(24) R. Kuhn and H. Trischmann, *Ann. Chim.*, **611**, 117 (1958).

(25) We have observed that an accumulation of acidic residues in the injection port of the gas chromatograph can cause the epoxides to rearrange to aldehyde. In order to obtain reproducible analytical results it was necessary to wash the injection port with base prior to the analysis of this mixture.

(26) V. M. Micović and M. L. Mihailović, *J. Org. Chem.*, **18**, 1190 (1953).

Anal. Calcd for $C_8H_{12}O$: C, 77.34; H, 9.74. Found: C, 76.88; H, 10.11;[27] mol wt (by mass spectrometry)[20] 124.

The Reaction of Norcamphor (13) with Dimethyloxosulfonium Methylide (2).[7]—In the manner described previously a 5.30-g (0.0482 mol) sample of norcamphor (**13**) was allowed to react with an ~10% excess of dimethyloxosulfonium methylide in DMSO. Distillation of the product, bp 59–59.5° (14 mm), gave 4.00 g of clear liquid which was shown by glpc on the 12-ft Quadrol/SAIB column[20] (column temp, 125°; helium flow, 90 ml/min) to consist of at least two components. The **first** peak (retention time, 10.2 min; rel abundance, >98%) was shown by analysis of its infrared and nmr spectra (see Results) to be due to a 1:10 mixture of the saturated spiro[norbornan-*exo*- and -*endo*-2,2′-oxacyclopropanes] (**15** and **17**), respectively, while the **second** component (retention time, 17.4 min; relative abundance, <2%) was identical in all respects with the starting ketone **13**.

The Reaction of Norcamphor (13) with Dimethylsulfonium Methylide (12).—A 5.50-g (0.0500 mol) sample of norcamphor (**13**) was allowed to react in the manner described previously with a solution of the ylide generated from 1.2 g (0.050 mol) of sodium hydride and 11.3 g (0.0571 mol) of trimethylsulfonium iodide[7] in DMSO. The 4.1 g of distilled product was shown by glpc on the 12-ft Quadrol/SAIB column[20] (column temp, 125°; helium flow, 90 ml/min) to consist of at least two components. The **first** component (retention time, 10.2 min; relative abundance, 43%) was shown by nmr to consist of 95% spiro[norbornan-*endo*-2,2′-oxacyclopropane] (**17**) and 5% spiro[norbornan-*exo*-2,2′-oxacyclopropane] (**15**). The **second** peak (retention time, 17.4 min; relative abundance, 57%) was identified as unreacted starting material (**13**) by its retention time and its infrared and nmr spectra.

Competitive Reaction Rates. A. Of Dimethyloxosulfonium Methylide (2) with Norcamphor (13) and Dehydronorcamphor (5).—A solution of 0.025 mol of ylide in 20 ml of DMSO was prepared as described previously and allowed to come to thermal equilibrium in an oil bath at 25.0°. A similarly thermostated solution containing 0.044 mol of ketone [42.8% dehydronorcamphor (**5**), 57.2% norcamphor (**13**) by glpc] in 10 ml of DMSO was added to the solution of ylide over a 10-min period. After the addition had been completed, the mixture was stirred for 1 additional hr, decomposed by the addition of 50 ml of water, and extracted with three 25-ml portions of pentane. The combined extract was washed with water, dried over anhydrous sodium sulfate, and concentrated by distillation of the solvent at atmospheric pressure through a 15-cm, wire-spiral-packed column. The concentrate was analyzed by glpc on the 12-ft Quadrol/SAIB column[20,25] (injection port temp 155°;[28] column temp, 115°; helium flow, 90 ml/min). The mixture contained 2.9 parts spiro[norbornan-2,2′-oxacyclopropanes] [10% *exo* (**15**) to 90% *endo* (**17**) *vide supra*], 3.2 parts spiro[norborn-2-en-5,2′-oxacyclopropanes] [71% *exo* (**7**) to 29% *endo* (**9**), *vide supra*], 1.0 part dehydronorcamphor (**5**), and 3.0 parts norcamphor (**13**). The relative reactivities calculated[14] from these data are shown in Chart II.

B. Of Dimethyloxosulfonium Methylide (2) with Norbornen-7-one (1) and Dehydronorcamphor (5).—The product concentrate from a similar experiment using a mixture of 62.4% norbornen-7-one (**1**) and 37.6% dehydronorcamphor (**5**) consisted of 22.6 parts spiro[norbornen-*anti*-7,2′-oxacyclopropane] (**4**), 1.0 part spiro[norborn-2-en-5,2′-oxacyclopropanes] (71% **7**, 29% **9** as before), 3.9 parts norbornen-7-one (**1**),[28] and 23.0 parts dehydronorcamphor (**5**). The calculated[14] relative reactivities are shown in Chart II.

C. Of Dimethyloxosulfonium Methylide (2) with Norbornen-7-one (1) and Norbornan-7-one (18).—In a similar manner a solution of 1.08 g (0.0100 mol) of norbornene-7-one (**1**) and 1.10 g (0.0100 mol) of norbornan-7-one (**18**) in 30 ml of DMSO was added to a solution of ylide prepared by the reaction of 0.24 g (0.010 mol) of sodium hydride and 2.2 g (0.0095 mol) of trimethyloxosulfonium iodide in 10 ml of DMSO. The reaction mixture was stirred overnight before being diluted with 70 ml of water. The resulting white sulfur-containing precipitate, after being washed with water and several portions of pentane, amounted to 0.562 g.[12]

The aqueous filtrate was extracted with five 20-ml portions of pentane which were combined with the previous pentane washings, washed further with saturated sodium chloride, dried over anhydrous sodium sulfate, and concentrated to 5 ml as before. A glpc analysis of the concentrate, *vide supra*, revealed the presence of 78.6 parts spiro[norborn-2-en-*anti*-7,2′-oxacyclopropane] (**4**), 5.2 parts norbornen-7-one (**1**), 9.6 parts spiro[norbornan-7,2′-oxacyclopropane], and 6.6 parts norbornan-7-one (**18**). The approximate relative reactivity of the two ketones is shown in Chart II.[11]

Registry No.—**7**, 16282-08-9; **9**, 16282-09-0; **10**, 3212-13-3; **11**, 3212-14-4; **15**, 16282-10-3; **17**, 16282-11-4.

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(27) Considerable difficulty was experienced in obtaining good analytical data on this material. The mean of seven carbon–hydrogen determinations carried out by two different laboratories[20] over a 27-month period is C, 76.67 ± 0.28; H, 9.90 ± 0.33. The value reported in the text is the best of these individual determinations. We suspect that the difficulty arises from the demonstrably facile rearrangement of the epoxide to norbornancarboxaldehyde which is partially oxidized and/or hydrated prior to weighing.

(28) Norbornen-7-one does not decarbonylate under these glpc conditions.