The extract was dried and evaporated. The residue was recrystallized to give pure compounds 11.

4-(Ethoxycarbonyl)-5-hydroxy-6-methyl-1,3-diphenyl-1,6-dihydropyridazine (11a): 80%; mp 84 °C (ethanol); IR ($CHCl_3$) 2800–2600, 1655, 1610 cm^{-1}; UV (EtOH) (ϵ) 246 (19400), 304 (8900), 369 nm (5200); ^1H NMR ($CDCl_3$) δ 0.82 (t, 3 H, J = 7 Hz), 1.23 (d, 3 H, J = 7 Hz), 3.75–4.28 (m, 16 lines, 2 H), 4.94 (q, 1 H, J = 7 Hz), 6.76–7.20 (m, 8 H), 12.70 (broad, 1 H).

4-(Ethoxycarbonyl)-5-hydroxy-1,6-dimethyl-3-phenyl-1,6-dihydropyridazine (11d): 65%; mp 123 °C (CH_3CN); IR ($CHCl_3$) 2800–2600, 1650, 1610 cm^{-1}; UV (EtOH) (ϵ) 247 (13100), 307 nm (7400); ^1H NMR ($CDCl_3$) δ 0.86 (t, 3 H, J = 7 Hz), 1.25 (d, 3 H, J = 7 Hz), 3.11 (s, 3 H), 3.78 (q, 1 H, J = 7 Hz), 3.73–4.23 (m, 2 H), 7.16–7.60 (m, 5 H), 12.5 (broad, 1 H).

1-Benzyl-4-(ethoxycarbonyl)-5-hydroxy-6-methyl-3-phenyl-1,6-dihydropyridazine (11g): 50%; mp 117 °C (hexane); IR ($CHCl_3$) 2800–2600, 1640, 1610 cm^{-1}; UV (EtOH) (ϵ) 244 (13800), 310 nm (8500); ^1H NMR ($CDCl_3$) δ 0.83 (t, 3 H, J = 7 Hz), 1.20 (d, 3 H, J = 7 Hz), 3.83 (q, 1 H, J = 7 Hz), 3.75–4.31 (m, 2 H), 4.46 and 4.78 (d, AB, 2 H, J_{AB} = 14.5 Hz), 7.25–7.55 (m, 10 H), 13.0 (broad, 1 H).

General Preparation of 5-(Ethoxycarbonyl)-3-methyl-6-phenyl-1,2-disubstituted-1,2,3,4-tetrahydropyridazin-4-ones (12a and 12d). Dimethyl sulfate (1 mL, 1.35 g, 10.6 mmol) was added to a stirred solution of **11a** or **11d** (5 mmol) in 2 N potassium hydroxide (10 mL, 20 mmol). After 35 min of stirring, the mixture was extracted with methylene chloride (3 × 15 mL). The organic phases were washed with 2 N potassium hydroxide, followed by water, and dried ($MgSO_4$). Evaporation of the solvent afforded the crude compounds which were recrystallized.

5-(Ethoxycarbonyl)-1,3-dimethyl-2,6-diphenyl-1,2,3,4-tetrahydropyridazin-4-one (12a): 50%; mp 128 °C [hexane–ethyl acetate (1:1)]; IR ($CHCl_3$) 1715, 1650, 1600 cm^{-1}; UV (EtOH) (ϵ) 243 (17300), 314 nm (11000); ^1H NMR ($CDCl_3$) δ 0.70 (t, 3 H, J = 7 Hz), 1.50 (d, 3 H, J = 7 Hz), 3.06 (s, 3 H, 3.73 (q, 2 H, J = 7 Hz), 4.18 (q, 1 H, J = 7 Hz), 6.87–7.58 (m, 10 H).

5-(Ethoxycarbonyl)-1,2,3-trimethyl-6-phenyl-1,2,3,4-tetrahydropyridazin-4-one (12d): 49%; mp 187 °C (acetone); IR ($CHCl_3$) 1710, 1625 cm^{-1}; UV (EtOH) (ϵ) 247 (14200), 315 nm (8600); ^1H NMR ($CDCl_3$) δ 0.78 (t, 3 H, J = 7 Hz), 1.50 (d, 3 H, J = 7 Hz), 3.33 (s, 3 H), 3.48 (s, 3 H), 3.78 (q, 1 H, J = 7 Hz), 3.97 (q, 2 H, J = 7 Hz), 7.57 (s, 5 H).

4-(Ethoxycarbonyl)-5-methoxy-6-methyl-1,3-diphenyl-1,6-dihydropyridazine (13a). To a solution of **11a** (1.67 g, 5 mmol) in 5 mL of methanol was added an excess of ethereal diazomethane. After 2 h, TLC indicated complete disappearance of the starting material. Evaporation of the solvent and then recrystallization afforded **13a** (1.12 g, 56%): mp 92 °C (hexane); IR ($CHCl_3$) 1720, 1635 cm^{-1}; UV (EtOH) (ϵ) 247 (22600), 290 (5150), 373 nm (10600); ^1H NMR ($CDCl_3$) δ 0.85 (t, 3 H, J = 7 Hz), 1.23 (d, 3 H, J = 7 Hz), 4.00 (s, 3 H), 4.03 (q, 2 H, J = 7 Hz), 5.08 (q, 1 H, J = 7 Hz), 6.97–8.00 (m, 10 H).

4-(Ethoxycarbonyl)-5-methoxy-1,6-dimethyl-3-phenyl-1,6-dihydropyridazine (13d). Evaporation of the solvent as described for **13a** afforded an isomeric mixture of **13d** and **12d** in a ratio 45:55 (from its NMR spectra). The mixture was chromatographed on silica gel. Elution with ethyl acetate gave only **13d** as a viscous oil (0.30 g, 20%): IR ($CHCl_3$) 1720, 1630 cm^{-1}; UV λ_{max} (EtOH) (ϵ) 246 (13400), 336 nm (2700); ^1H NMR ($CDCl_3$) δ 0.80 (t, 3 H, J = 7 Hz), 1.12 (d, 3 Hz, J = 7 Hz), 3.17 (s, 3 H), 3.92 (s, 3 H), 3.97 (q, 2 H, J = 7 Hz), 4.03 (q, 1 H, J = 7 Hz), 7.32–7.75 (m, 5 H).

Satisfactory analytical data (±0.3%) for C, H, and N were recorded for compounds **7**, **8** 11, 12, and 13.

Registry No. **1a**, 53252-56-5; **1b**, 62879-96-3; **1c**, 62879-97-4; **2a**, 62538-35-6; **3a**, 70864-67-4; **3b**, 70864-68-5; **3c**, 70864-69-6; **3d**, 70864-70-9; **3e**, 70864-71-0; **3f**, 70864-72-1; **3g**, 70864-73-2; **4g**, 65942-86-1; **5d**, 70864-74-3; **5g**, 70864-75-4; **6d**, 65942-85-0; **6g**, 65942-87-2; **7**, 70864-76-5; **8**, 70864-77-6; **10**, 66823-25-4; **11a**, 70864-78-7; **11d**, 70864-79-8; **11g**, 70864-80-1; **12a**, 70864-81-2; **12d**, 70864-82-3; **13a**, 70864-83-4; **13d**, 70864-84-5; phenylhydrazine, 100-63-0; benzylhydrazine, 555-96-4; methylhydrazine, 60-34-4.

Supplementary Material Available: Spectroscopic data (UV, IR, ^1H NMR) for **3a–c,e,f** (1 page). Ordering information is given on any current masthead page.

Mono- and Bishomobenzotropones. 1. Synthesis and Nuclear Magnetic Resonance Spectra of 2,3-Benzo-6,7-monohomotropone and 2,3-Benzo-*trans*-4,5:6,7-bishomotropone

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The reaction of 2,3-benzotropone with dimethyloxosulfonium methylide has been observed to be nonselective and affords as the major products 2,3-benzo-6,7-monohomotropone and 2,3-benzo-*trans*-4,5:6,7-bishomotropone in yields of 35 and 28%, respectively. Structural characterization of these compounds has been established by extensive NMR analysis. Determination of the mechanism for this nonselective addition of Corey's reagent to an unsymmetrical seven-membered-ring conjugated ketone has also been attempted.

Synthesis

In 1962 Corey reported[1c] the first reaction of dimethyloxosulfonium methylide (1) with a seven-membered-ring conjugated ketone, eucarvone (2), and isolated, as the only product from this reaction, the cyclopropyl ketone 3 (eq 1). Corey[1e] used the results of this reaction to establish the selectivity of 1 as a methylene-transfer agent, since methylene transfer occurred only to the α,β rather than the γ,δ double bond. He qualified the selectivity observed for 1 in this reaction indicating that a partial shielding effect of the *gem*-dimethyl groups at C_δ may have prevented methylene transfer to the γ,δ double bond. Since this initial report by Corey, dimethylsulfonium methylides (4)[2] have been added to unsym-

(1) (a) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, 84, 866 (1962); (b) *ibid.*, 84, 867 (1962); (c) *ibid.*, 84, 3782 (1962); (d) *ibid.*, 87, 1345 (1965); (e) *ibid.*, 87, 1353 (1965).

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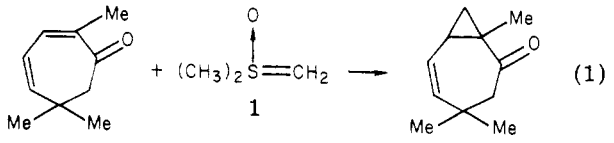


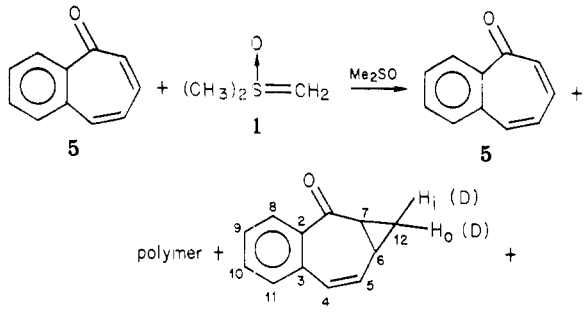
2 1 3 (1)

$(CH_3)_2SCHCOR$
R = OC_2H_5, C_6H_5, p-BrC_6H_4

4

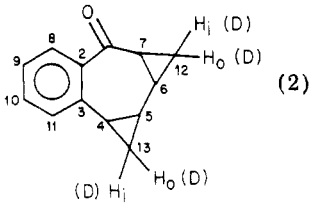
metrical seven-membered-ring conjugated ketones, while both dimethylsulfonium methylides (4)[3a] and dimethyloxosulfonium methylide (1)[3a-c] have been added to symmetrical seven-membered-ring conjugated ketones. However, until recently[4] Corey's original work was the only report of methylene transfer to an unsymmetrical seven-membered-ring conjugated ketone using dimethyloxosulfonium methylide (1). We now report another example of the reaction of an unsymmetrical seven-membered-ring conjugated ketone with 1 where no selectivity of methylene transfer is observed.

Reaction of a 1:1 molar ratio of dimethyloxosulfonium methylide (1)[1] and 2,3-benzotropone (5)[5] afforded 2,3-benzo-6,7-monohomotropone (6) and 2,3-benzo-*trans*-4,5:6,7-bishomotropone (7) in 35 and 28% yields, respectively, in addition to 10% uncharacterized polymer and 27% of recovered starting material (eq 2). Isolation



5 1 5

6
D, 6-d_2



7
D, 7-d_4

of the products from this reaction mixture was accomplished by column chromatography on silica gel, using carbon tetrachloride as eluent. Four distinct bands were obtained corresponding to, in order, polymer, bishomotropone 7, monohomotropone 6, and benzotropone 5. The infrared spectrum of 6 exhibited a strong carbonyl band at 1660 cm^{-1} while the infrared spectrum of 7 exhibited a strong carbonyl band at 1650 cm^{-1}. In addition to the above spectra and satisfactory analyses, 6 and 7 were also converted to their 2,4-dinitrophenylhydrazone derivatives in quantitative and 38% yield, respectively.

In order to help establish the proton assignments for 6 and 7 as well as the orientation of the cyclopropyl groups in 7, we also synthesized their cyclopropyl-d_2- and -d_4-labeled analogues by using dimethyloxosulfonium-d_6 methylide-d_2.

Reaction of a 1:1 molar ratio of 2,3-benzotropone (5) and dimethyloxosulfonium-d_6 methylide-d_2 afforded 35% of 2,3-benzo-6,7-monohomotropone-d_2 (6-d_2), 24.9% of 2,3-benzo-*trans*-4,5:6,7-bishomotropone-d_4 (7-d_4), 29.9% of recovered unreacted 2,3-benzotropone (5), and 10% of the same uncharacterized polymer as discussed above. Separation of this product mixture was accomplished by column chromatography on silica gel, using carbon tetrachloride as eluent. The order of elution of the components from this chromatography was the same as that for the proton analogues.

Mechanism

On the basis of the results of the ylide reaction, it appears that the bishomotropone 7 arises from the subsequent reaction of initially formed monohomotropone 6 with more dimethyloxosulfonium methylide (1). This is especially probable since the benzotropone was added to ylide 1, the latter being present in excess at the initial stages of the reaction. In order to observe if ylide 1 was the limiting reagent for the production of 7, we carried out a reaction with a 1:4 molar ratio of benzotropone 5 to ylide 1 which resulted in the production of 28% of 6, 53% of 7, and 19% of polymer, with no unreacted benzotropone remaining. These proportions of products decreased with a concomitant increase in the amount of polymer formed when the ratio of 5 to 1 was increased above 1:4.

In an effort to establish the mechanistic course of this reaction, we allowed a mixture containing 28% of 5, 40% of 6, and 32% of 7 (polymer being removed by treatment with cyclohexane) to react with a large excess of 1. Product analysis of this reaction showed the presence of 52% of 6, 44% of 7, and 4% of polymer and no benzotropone. Since the increase in the amount of 6 and 7 in this reaction mixture can be accounted for strictly on the basis of the disappearance of 5, these results indicate that the bishomotropone 7 is probably being formed by reaction of ylide 1 with benzotropone 5 and not from reaction of 6 with additional ylide 1. To definitely establish this pathway, we attempted to react pure monohomotropone 6 with ylide 1 in a 1:2 molar ratio, but a 92% recovery of unreacted monohomotropone 6 was obtained.

Examination of the infrared and NMR spectra of the polymer obtained from the initial reaction of 5 with 1 showed the presence of a carbonyl group, a benzene ring, and aliphatic protons but no cyclopropyl protons. These results, in addition to the fact that no polymer was obtained from the reaction of monohomotropone 6 with ylide 1, suggest that this polymeric material results from reaction of benzotropone 5 or bishomotropone 7 with ylide 1. In order to establish the source of the polymer, we carried out a final reaction with a 1:2 molar ratio of bishomotropone 7 to ylide 1 and found that a 95% recovery of starting material was obtained with no trace of polymeric material.

The results from these reactions suggest the following mechanism. First, the polymer must indeed come only from the reaction of benzotropone 5 and ylide 1, since no polymer was obtained when either 6 or 7 was independently treated with ylide 1. Second, the reaction of benzotropone 5 with dimethyloxosulfonium methylide (1) must initially give rise to the α,β-monohomotropone 6 as

(2) Y. Sugimura and N. Soma, *Tetrahedron Lett.*, 1721 (1970).
(3) (a) Y. Sugimura, N. Soma, and Y. Kishida, *Tetrahedron Lett.*, 91 (1971); (b) R. E. Harmon, R. Suder, and S. K. Gupta, *J. Chem. Soc., Chem. Commun.*, 472 (1972); (c) H. A. Corver and R. F. Childs, *J. Am. Chem. Soc.*, **94**, 6201 (1972).
(4) (a) M. Oda, Y. Ito, and Y. Kitahara, *Tetrahedron Lett.*, 977 (1978); (b) L. A. Paquette, G. D. Ewing, S. V. Ley, H. C. Berk, and S. G. Traynor, *J. Org. Chem.*, **43**, 4712 (1978).
(5) (a) E. W. Collington and G. Jones, *J. Chem. Soc., Chem. Commun.*, 958 (1968); (b) *J. Chem. Soc.*, 2656 (1969).

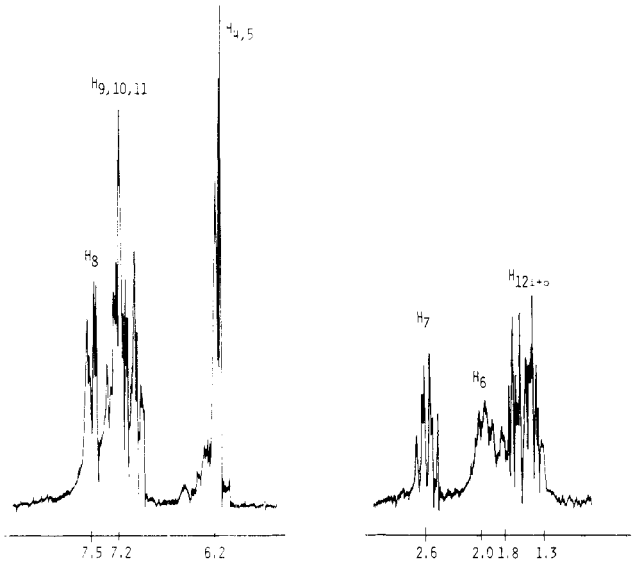
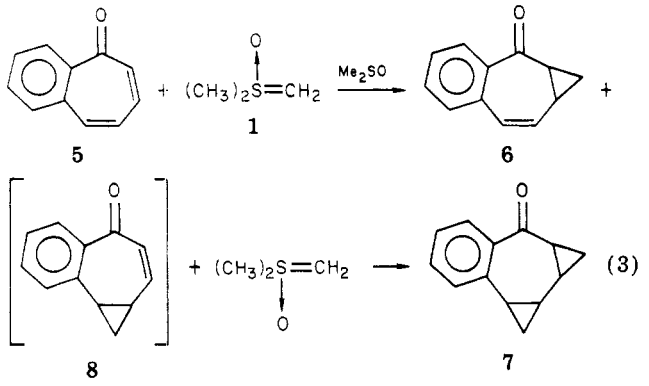


Figure 1. NMR spectrum of 2,3-benzo-6,7-monohomotropone (**6**).

well as the γ,δ-monohomotropone **8**, and subsequently only the γ,δ-monohomotropone **8** reacts with ylide **1** to give the bishomotropone **7** (eq 3). In the initial stages of the



reaction of **5** with **1** attack of ylide **1** can occur at either double bond in the benzotropone **5** since the electronic effects of the carbonyl group must be felt by the γ,δ double bond through the α,β double bond. This carbonyl electronic effect is not transmitted to the γ,δ double bond through the benzene ring double bonds, however, since the α,β-monohomotropone **6** did not afford bishomotropone **7** upon further reaction with ylide **1**. If ylide attack occurs on the α,β double bond of **5** to give **6**, the reaction stops. However, if ylide attack occurs on the γ,δ double bond of **5**, it gives rise to **10** with the electronic effect of the carbonyl group still affecting the α,β double bond, and this molecule reacts further with ylide affording **7**. This mechanism along with the observed NMR helps substantiate the structure for the isolated monohomotropone as the α,β-monohomotropone **6** and not its isomer **8**.

NMR Spectra

The 100-MHz proton NMR spectra of the monohomotropone **6** and its deuterio analogue **6**-d_2 in $CDCl_3$ are shown in Figure 1 and 2, respectively. It can be seen that the aromatic protons H_{8-11} for both **6** and **6**-d_2 have the same chemical shifts with essentially the same multiplicity. The same is true for the vinyl protons $H_{4,5}$. As expected, the major change in the two spectra occurs in the cyclopropyl region. The assignment for the cyclopropyl protons in the undeuterated **6** was made on the basis of the following observations: first, H_7, being closer to the carbonyl group, is expected to experience more of a deshielding

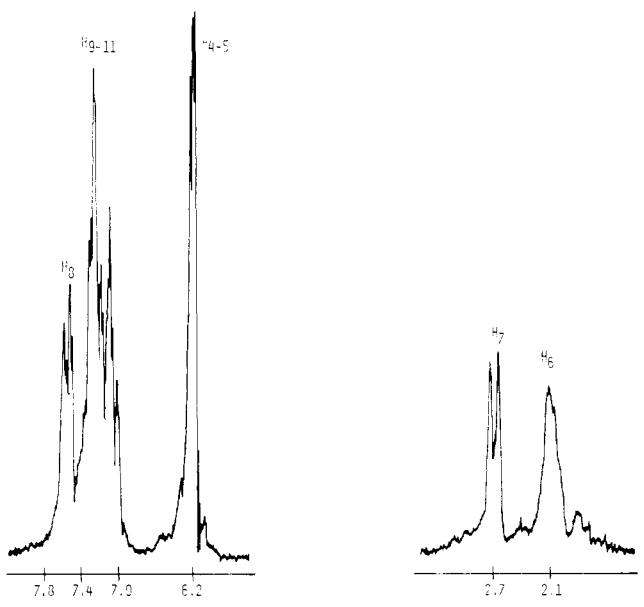


Figure 2. NMR spectrum of 2,3-benzo-6,7-monohomotropone-d_2 (**6**-d_2).

Table I. Chemical Shifts and Coupling Constants for Monohomotropone 6[a]

ν_4	614.6	$J_{4,5}$	11.85	$J_{6,7}$	8.96
ν_5	620.1	$J_{4,6}$	0.72	$J_{6,12i}$	6.67
ν_6	195.3	$J_{4,7}$	0.0	$J_{6,12o}$	8.56
ν_7	259.4	$J_{4,12i}$	0.0	$J_{7,12i}$	6.18
ν_{12i}	140.5	$J_{4,12o}$	0.0	$J_{7,12o}$	8.57
ν_{12o}	159.4	$J_{5,6}$	7.13	$J_{12i,12o}$	−4.54
		$J_{5,7}$	−0.04		
		$J_{5,12i}$	−0.03		
		$J_{5,12o}$	−0.10		

[a] 100-MHz NMR, 5% in $CDCl_3$, ambient temperature. Shifts are reported in hertz; all are downfield relative to Me_4Si.

effect than H_6, and second, and more important, the splitting of H_7 is expected to be less extensive than that of H_6, owing to the fact that H_7 is strongly coupled to three protons, H_6, H_{12i}, and H_{12o}, whereas H_6 is strongly coupled to four, H_5, H_7, H_{12i}, and H_{12o}.

This assignment of H_7 was confirmed by observation of the NMR spectrum of its deuterio analogue **6**-d_2. This compound was expected to show a much simpler splitting pattern since both H_{12i} and H_{12o} have now been replaced by deuterium. The NMR spectrum of **6**-d_2 (Figure 2) exhibits a doublet at 2.7 ppm corresponding to H_7, which is expected since H_7 is now neighboring only one proton, H_6. The doublet is broadened by coupling to the deuterium atoms. Proton 6 shows a more complex pattern, resulting from coupling to both deuterium atoms, H_5 and H_7, and virtual coupling to H_4.

The signals appearing between 1.4 and 1.8 ppm in the NMR spectrum of **6** clearly belong to H_{12i} and H_{12o}, since both of these protons, and their associated NMR signals, are absent in **6**-d_2.

The NMR spectrum of the six aliphatic protons in **6** was analyzed in detail with the aid of computer program LAON3.[6] Using information gained from the spectrum of **6**-d_2 and coupling constant correlations found in the literature,[7] we were able to conclusively assign all chemical

(6) (a) S. Castellano and A. A. Bothner-By, *J. Chem. Phys.*, **41**, 3863 (1964); (b) R. J. Abraham, "Analysis of High Resolution NMR Spectra", Elsevier, Amsterdam, 1971.

(7) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed., Pergamon Press, Oxford, England, 1969.

Table II. Chemical Shifts and Coupling Constants for Bishomotropone 7[a]

ν_4	384.3	$J_{4,5}$	9.05	$J_{5,6}$	4.53	$J_{6,12i}$	7.20	$J_{7,13o}$	0.0
ν_5	377.7	$J_{4,6}$	0.43	$J_{5,7}$	0.12	$J_{6,12o}$	8.46	$J_{12i,12o}$	−4.64
ν_6	468.3	$J_{4,7}$	0.10	$J_{5,12i}$	0.0	$J_{6,13i}$	0.0	$J_{12i,13i}$	0.0
ν_7	556.7	$J_{4,12i}$	0.0	$J_{5,12o}$	0.0	$J_{6,13o}$	0.0	$J_{12i,13o}$	0.0
ν_{12i}	350.6	$J_{4,12o}$	0.0	$J_{5,13i}$	6.39	$J_{7,12i}$	5.61	$J_{12o,13i}$	0.0
ν_{12o}	223.5	$J_{4,13i}$	6.31	$J_{5,13o}$	8.41	$J_{7,12o}$	8.16	$J_{12o,13o}$	0.72
ν_{13i}	184.6	$J_{4,13o}$	9.29	$J_{6,7}$	9.96	$J_{7,13i}$	0.0	$J_{13i,13o}$	−4.84
ν_{13o}	276.4								

[a] 300-MHz NMR, 5% in C_6D_6, ambient temperature. Shifts are reported in hertz; all are downfield relative to Me_4Si.

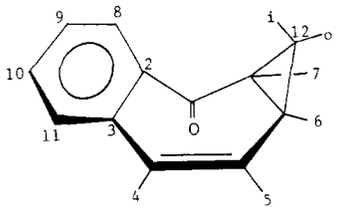


Figure 3.

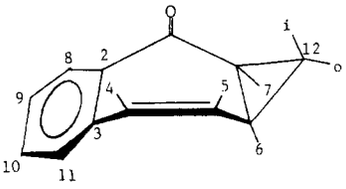


Figure 4.

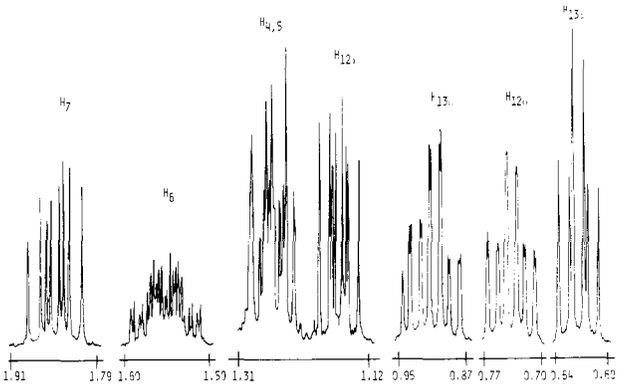


Figure 5. NMR spectrum of 2,3-benzo-*trans*-4,5:6,7-bishomotropone (7).

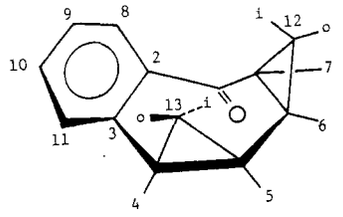


Figure 6.

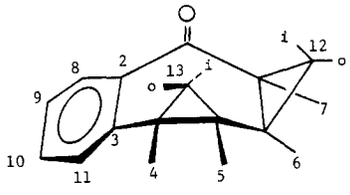


Figure 7.

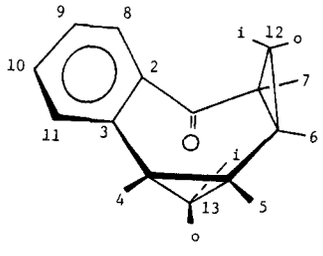


Figure 8.

shifts and coupling constants.[8] The results are shown in Table I. The computer plot using these parameters gave a spectrum with lines having root-mean-square error of 0.04 Hz relative to those of the experimental spectrum. It is felt that the coupling constants are accurate to within ±0.1 Hz with two possible exceptions, $J_{4,6}$ and $J_{5,6}$. We are fairly sure that the sum of these couplings is 7.8–7.9 Hz. However, $J_{4,6}$ may be as large as 1.0 Hz and $J_{5,6}$ may be as small as 6.8 Hz. It is unfortunate that the greatest uncertainty lies in these values, for these two couplings are the most informative with respect to the preferred conformation of the molecule. Even with the above uncertainty, it is clear that the most favorable conformation of **6** is the one with the bond to H_6 orthogonal to the π orbitals of C_4–C_5 (H_5–H_6 eclipsed), for only in this conformation is $J_{4,6}$ expected to be as large as +0.7–1.0 Hz.[9] Furthermore, the magnitude of $J_{5,6}$ is also consistent with this conformation[9,10] (Figure 3). The other reasonable conformation for **6** (Figure 4) would be expected to have a $J_{4,6}$ more negative than −1.0 Hz, owing to the near-parallel orientation of the H_6 bond relative to the π orbitals of C_4–C_5.[11] Finally, the proposed conformation has H_7 located almost in the plane of the carbonyl group, resulting in deshielding of H_7, consistent with experimental observation. The chemical shift of H_7 in the other conformation (Figure 4) would not be expected to be so large, owing to its location in the shielding zone above the plane of the carbonyl group.

NMR analysis of bishomotropone **7** at 100 MHz was not possible, owing to the complexity of the spectrum. However, in C_6D_6 at 300 MHz, the spectrum gave rather well-separated signals for six of the eight aliphatic protons (Figure 5). The specific proton assignment in the aliphatic region was based upon several observations: first, analysis of the deuterated bishomotropone, **7**-d_4, spectrum at 300 MHz; second, spin-decoupling experiments performed on both **7** and **7**-d_4; third, coupling constant correlations;[7] and fourth, solvent-effect studies on the chemical shifts.[13] The 300-MHz spectrum of the eight aliphatic protons of **7** in benzene was analyzed in detail with the aid of computer

(8) Weak coupling of one or more of the aromatic protons to H_4 was deduced from broadening of some of the lines in the vinylic region. This was not explored in detail, and it is not reported in Table I.

(9) E. W. Garbisch, Jr., *J. Am. Chem. Soc.*, **86**, 5561 (1964).

(10) The monohomobenzotropone **6** exists as a single enantiomeric pair with each enantiomer having two possible conformers. The conformations of one enantiomeric pair are shown in Figures 3 and 4.

(11) A negative value for the transoid four-bond coupling of H_4 to H_6 is predicted both for "propenic" coupling[9] and for "butadienic" coupling[12] models for the conformation of **6** shown in Figure 4.

(12) A. A. Bothner-By and D. Juang, *J. Am. Chem. Soc.*, **90**, 2342 (1968).

(13) D. H. Williams and N. S. Bhacca, *Tetrahedron*, **21**, 2021 (1965).

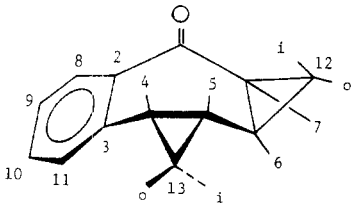


Figure 9.

program LAOCN3.[6] Values for most of the estimated chemical shifts and coupling constants, as required by LAOCN3, were read directly from the spectrum. These values were augmented by information gained from spin-decoupling data, both from **7** and from **7**-d_4. The results of the analysis are shown in Table II. Agreement between experimental and calculated frequencies was quite good, the root-mean-square error being less than 0.06 Hz.

It is felt that the coupling constants are accurate to within ±0.2 Hz and, as such, are useful in drawing stereochemical conclusions about **7**. The most important question to be addressed concerns the cis vs. trans stereochemistry of the two cyclopropane rings.[14] Of lesser importance is the question of conformation. The two possible conformations of the cis form of **7** are shown in Figures 6 and 7, and the corresponding conformations of the trans stereoisomer are shown in Figures 8 and 9. These structures are all chiral, and no significance should be attached to the particular enantiomers shown. In considering cis vs. trans stereochemistry, the three-bond coupling constant between protons 5 and 6 is of particular significance. In both conformations of the cis isomer the dihedral angle between H_5 and H_6 is less than 30°. Assuming that a Karplus-type relationship similar to that in saturated systems can be applied, we would predict a coupling constant of 6–9 Hz for this system. The trans isomer has one conformation with the H_5–H_6 dihedral angle similar to that of the cis form (Figure 8) and a second conformation with an angle of 100–120° (Figure 9). In this case the predicted $J_{5,6}$ will depend on the conformer population, but it should be smaller than the 6–9 Hz predicted for the cis isomer. The measured value for $J_{5,6}$ of 4.53 Hz is clearly more consistent with the trans structure. Further, the magnitude of the coupling constant argues that neither conformation dominates, and the system is in dynamic equilibrium with substantial amounts of both forms present. The long-range coupling of 0.72 Hz between H_{12o} and H_{13o} also supports this conclusion. It is well established that such coupling is associated with a trans–trans zigzag chain of bonds,[15] and only in the trans isomer (Figure 9) is this structural feature found. Furthermore, no other pair of protons has this five-bond trans–trans zigzag path. Consistent with this observation is the fact that all of the other five-bond couplings are zero.

The chemical shifts found for **7** are also consistent with the trans stereochemistry. Note in particular that H_{13i} would be expected to be highly shielded, owing to its positioning above the carbonyl group (Figure 8). On the other hand, H_{12i} is deshielded, for it is in the plane of the carbonyl in the conformation shown in Figure 8. The fact that the conformer shown in Figure 9 is in equilibrium with the conformer shown in Figure 8 is of little importance in these arguments, for none of the protons, H_{12i}, H_{12o}, H_{13i}, H_{13o}, are especially shielded or deshielded here. However, it should be noted that these chemical shifts, while consistent with the trans assignment, do not require it. Similar arguments can be applied to the cis isomer.

(14) Paquette et al.[4b] uses the syn/anti notation.

(15) A. A. Bothner-By and R. K. Harris, *J. Am. Chem. Soc.*, **87**, 3451 (1965).

Experimental Section

General Procedures. Melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected. The infrared spectra were recorded on a Beckman 20A-X recording spectrophotometer using salt plates, while NMR spectra were obtained by using a high-resolution JEOL-100 (100 MHz) or a Varian SC-300 (300 MHz) spectrometer with tetramethylsilane (Me_4Si) as the standard. Mass spectra and exact mass determinations were obtained on a Hitachi Perkin-Elmer RMU-7 mass spectrometer at 70-eV ionizing voltage. Elemental analyses were determined with a Perkin-Elmer 240 C, H, and N analyzer.

6,7,8,9-Tetrahydrobenzocyclohepten-5-one (Benzosuberone). This compound was prepared by the method of Gilmore and Horton[16] or was obtained commercially from Aldrich Chemical Co.: bp 71–72 °C (0.02 mm) (lit.[16] bp 138–139 °C (12 mm)); IR (neat) 3010 (CH), 1675 (C=O) cm^{-1}; NMR (neat) δ 7.7 (2 d, 1 H), 7.2 (m, 3 H), 2.7 (t, 2 H), 2.5 (t, 2 H), 1.6 (m, 4 H).

6,6-Dibromo-6,7,8,9-tetrahydrobenzocyclohepten-5-one and 2,3-Benzotropone (5). These compounds were both prepared by the method of Collington and Jones.[5] The dibromo ketone was obtained in 92% yield as a white solid: mp 41–42 °C (lit.[5] mp 42–44 °C); IR (KBr) 3008 (CH), 1700 (C=O) cm^{-1}; NMR (neat) δ 7.3 (m, 4 H), 2.7 (m, 4 H), 1.9 (m, 2 H). The 2,3-benzotropone (**5**) was obtained in 80% yield as a clear colorless liquid: bp 90–91 °C (0.02 mm) (lit.[5] bp 106 °C (0.04 mm)); IR (neat) 3010 (CH), 1640 (C=O), 1620 (C=C) cm^{-1}; NMR (CCl_4) δ 8.1 (2 d, 1 H), 7.1 (m, 3 H), 6.4 (m, 3 H), 6.0 (m, 1 H).

Dimethyloxosulfonium Methylide (1) in Dimethyl Sulfoxide. This reagent was prepared fresh by the method of Corey and Chaykovsky[1] and was used immediately.

Trimethyloxosulfonium-d_9 Iodide. This compound was prepared by the method of Corey and Chaykovsky.[1] A solution of 6.0 g (72 mmol) of dimethyl-d_6 sulfoxide and 10.0 g (69 mmol) of methyl-d_3 iodide was placed into a 15-mL one-necked, round-bottomed flask equipped with a reflux condenser, a magnetic stirrer, and a nitrogen inlet tube attached to the top of the condenser, with the other end of the nitrogen inlet tube connected to a mercury-sealed U-tube to which the system was opened. This mixture was refluxed under nitrogen for 2 days, during which time a yellowish solid precipitated. The solid was filtered and washed with 20 mL of cold chloroform and then air-dried to give fine white crystals of trimethyloxosulfonium-d_9 iodide: 6.96 g (30.8 mmol, 47%); mp 173–174 °C dec.

Dimethyloxosulfonium-d_6 Methylide-d_2 in Dimethyl-d_6 Sulfoxide. This reagent was prepared fresh by the method of Corey and Chaykovsky[1] and was used immediately.

Reaction of Dimethyloxosulfonium Methylide (1) with 2,3-Benzotropone (5). Preparation of 2,3-Benzo-6,7-monohomotropone (6) and 2,3-Benzo-4,5:6,7-bishomotropone (7). To a stirred solution of 6.6 mmol of **1** in 75 mL of dry dimethyl sulfoxide (Me_2SO) cooled in an ice bath to 0–5 °C was added dropwise a solution of 9.36 g (60 mmol) of 2,3-benzotropone (**5**) in 15 mL of dry Me_2SO. After the addition was completed, the solution was allowed to come to room temperature, stirred for 2 h, and then stirred for an additional 1 h at 50–60 °C (water bath). At this point the reaction mixture was poured into 200 mL of cold water and extracted thoroughly with several portions of ether, and the ether extracts were washed twice with water, dried over anhydrous magnesium sulfate, and then evaporated. This afforded 9.20 g of a red oil which was chromatographed on a 22 mm × 920 mm silica gel column, using carbon tetrachloride as eluent. Four bands were collected in the following order with the yields reported based upon the 9.20 g of red oil placed on the column.

(1) 0.93 g (10%) of uncharacterized polymer:[17] mp 65–66 °C; IR (KBr) 3010 (CH), 1670 (C=O) cm^{-1}; NMR (Me_2SO-d_6) δ 7.3 (m, 6 H), 3.5 (m, 1 H), 3.1 (m, 2 H), 2.5 (m. 3 H). Anal. Found: C, 70.06; H, 4.46.

(2) 2.85 g (28%) of 2,3-benzo-4,5:6,7-bishomotropone (**7**) as a light yellow oil: IR (neat) 3005 (CH), 1650 (C=O) cm^{-1}; mass spectrum *m/e* 184, 156, 155, 142, 129, 87; NMR (CCl_4) δ 7.4–7.1

(16) R. C. Gilmore and W. J. Horton, *J. Am. Chem. Soc.*, **73**, 1411 (1951).

(17) This material is referred to as a polymer because it was possible to cast a film of it in acetone.

(m, 4 H), 2.1 (m, 1 H), 1.9–1.6 (m, 3 H), 1.4–1.1 (m, 3 H), 0.6 (m, 1 H). Anal. Calcd for $C_{13}H_{12}O$: C, 84.66; H, 6.51. Found: C, 84.43; H, 6.24.

(3) 3.22 g (35%) of 2,3-benzo-6,7-monotropone (**6**) as a light yellow oil: IR (neat) 3010 (CH), 1660 (C=O) cm^{-1}; mass spectrum *m/e* 170, 142, 141, 128, 115, 89, 73; NMR (CCl_4) δ 7.6 (2 d, 1 H), 7.4–7.0 (m, 3 H), 6.2 (m, 2 H), 2.7 (2 q, 1 H), 2.1 (m, 1 H), 1.8–1.4 (m, 2 H). Anal. Calcd for $C_{12}H_{10}O$: C, 84.68; H, 5.92. Found: C, 84.49; H, 5.99.

(4) Also collected was 2.47 g (26.9%) of unreacted 2,3-benzotropone (**5**). The yields of products based upon the recovered unreacted **5** are therefore 38.3% of **7** and 47.9% of **6**.

Reaction of Dimethyloxosulfonium-d_6 Methylide-d_2 with 2,3-Benzotropone (5). Preparation of 2,3-Benzo-6,7-monohomotropone-d_2 (6-d_2) and 2,3-Benzo-*trans*-4,5:6,7-bishomotropone-d_4 (7-d_4). The method used for the preparation of these compounds was exactly the same as described above to the point of chromatography on a 22 mm × 920 mm silica gel column, using carbon tetrachloride as eluent. Four bands were collected in the following order and the respective yields are based upon 3.01 g of red oil placed on the column. (1) 0.30 g (10%) of uncharacterized polymer: mp 67 °C; IR (KBr) 3010 (CH), 1670 (C=O) cm^{-1}. (2) 0.75 g (4.0 mmol, 24.9%) of 2,3-benzo-*trans*-4,5:6,7-bishomotropone-d_4 (7-d_4) as a light yellow oil: NMR (CCl_4) δ 7.4–7.1 (m, 4 H), 2.2–1.8 (m, 2H), 1.7 (m, 2 H). (3) 1.05 g (6.1 mmol, 35%) of 2,3-benzo-6,7-monohomotropone-d_2 (6-d_2) as a light yellow oil: NMR (CCl_4) δ 7.6 (2 d, 1 H, 7.4–7.0 (m, 3 H), 6.2 (m, 2 H), 2.7 (d, 1 H), 2.1 (m, 1 H). (4) Also collected was 0.9 g (6.8 mmol, 29.9%) of unreacted 2.3-benzotropone (**5**). The yields of product based upon the original 3.01 g of red oil and recovered unreacted 2,3-benzotropone (**5**) are therefore 33.8% of 7-d_4, and 47.3% of 6-d_2.

2,4-Dinitrophenylhydrazone Derivative of 2,3-Benzo-6,7-monohomotropone. To a 1.0-g (5-mmol) sample of 2,4-dinitrophenylhydrazine dissolved in 25 mL of 85% orthophosphoric acid was added 25 mL of 95% ethanol, and the solution was cooled and clarified by suction filtration. To 10 mL of this 0.1 M hydrazine solution was added 0.17 g (1 mmol) of ketone **6** dissolved in 2 mL of 95% ethanol, and within 2 min the derivative began to precipitate from solution. The resulting orange solid was filtered, washed twice with 10-mL portions of cold 95% ethanol, and then allowed to air-dry. Recrystallization from a 1:1 mixture of 95% ethanol and methanol afforded 0.35 g (0.01 mmol, 100%) of 2,3-benzo-6,7-monohomotropone dinitrophenylhydrazone as an orange solid: mp 159–160 °C; IR (KBr) 3280 (NH), 1620 (C=N) cm^{-1}; NMR (Me_2SO-d_6) δ 9.1 (d, 1 H), 8.7 (2 d, 1 H), 8.4 (d, 1 H), 7.8 (m, 4 H), 6.7 (m, 2 H), 3.5 (m, 1 H), 2.4 (m, 1 H), 1.9 (m, 1 H), 1.6 (m, 1 H); mol wt calcd 350, mol wt found (mass spectrometry) 350. Anal. Calcd for $C_{18}H_{14}N_4O_4$: C, 61.71; H, 4.02; N, 15.99. Found: C, 61.97; H, 3.90; N, 16.06.

2,4-Dinitrophenylhydrazone Derivative of 2,3-Benzo-4,5:6,7-bishomotropone. To 7 mL of the 0.1 M solution prepared above was added 0.135 g (0.7 mmol) of ketone **7**. This mixture was warmed for 15 min and then cooled to room temperature at which point a precipitate formed. The resulting orange solid was filtered, washed twice with 5-mL portions of cold 95% ethanol, and allowed to air-dry. Two recrystallizations from 95% ethanol afforded 0.096 g (0.26 mmol, 38%) of 2,3-benzo-4,5:6,7-bishomotropone dinitrophenylhydrazone as an orange solid: mp 150–151 °C; IR (KBr) 3280 (NH), 1620 (C=N) cm^{-1}; NMR ($CDCl_3$) δ 9.0 (2 d, 1 H), 8.2 (2 d, 1 H), 8.0 (2 d, 1 H), 7.4–7.0 (m, 4 H), 2.0–1.6 (m, 3 H), 1.6–1.4 (m, 1 H), 1.4–1.0 (m, 3 H), 1.0–0.6 (m, 1 H); mol wt calcd 364, mol wt found (mass spectrometry) 364. Anal. Calcd for $C_{19}H_{16}N_4O_4$: C, 62.63; H, 4.43; N, 15.38. Found: C, 62.58; H, 4.57; N, 15.45.

Reaction of 2,3-Benzotropone (5) with Excess Dimethyloxosulfonium Methylide (1). A solution of ylide **1** was prepared under nitrogen from 1.63 g of sodium hydride (34 mmol, 50% mineral oil dispersion), 7.33 g (34 mmol) of trimethyloxosulfonium iodide, and 35 mL of dry Me_2SO. The ylide was cooled in an ice bath to 0–5 °C. To this solution was added dropwise a solution of 1.3 g (8.3 mmol) of 2,3-benzotropone (**5**) in 1.5 mL of dry Me_2SO. After the addition was completed the reaction was carried out as previously described. Evaporation of the ether extracts afforded 1.22 g of red oil which upon chromatography gave three bands collected in the following order (the respective yields reported are based upon the 1.22 g of red oil placed on the column): 0.647 g (53%) of **7**, 0.346 g (28%) of **6**, 0.227 g (19%) of the same uncharacterized polymer previously reported (mp 65–66 °C).

When this same reaction was run with 1:5 molar ratio of ketone **5** to ylide **1** there were obtained 0.412 g (34%) of **7**, 0.196 g (16%) of **6**, and 0.61 g (50%) of polymer.

Reaction of a Mixture Containing 2,3-Benzotropone (5), 2,3-Benzo-6,7-monohomotropone (6), and 2,3-Benzo-4,5:6,7-bishomotropone (7) with Dimethyloxosulfonium Methylide (1). To a 9.2-g sample of a red oil mixture obtained from reaction of **5** with **1** was added 15 mL of cyclohexane; within 1 min a solid began to precipitate from solution. The resulting solid was filtered and allowed to air-dry to yield 0.94 g of material whose melting point and spectroscopic data confirmed it to be the uncharacterized polymer isolated previously. The cyclohexane filtrate was evaporated to give 8.26 g of red oil containing 2.7 g (32%) of **7**, 3.3 g (40%) of **6**, and 2.3 g (28%) of **5**. This oil was treated with fresh Me_2SO solution containing 61 mmol of ylide **1**, and the reaction carried out as previously described. Workup afforded 7.93 g of red oil which upon chromatography gave 3.5 g (43.8%) of **7**, 4.1 g (52%) of **6**, and 0.33 g (4.2%) of the same uncharacterized polymer.

Reaction of Dimethyloxosulfonium Methylide (1) with 2,3-Benzo-6,7-monohomotropone (6). A solution of ylide **1** prepared under nitrogen from 0.2 g (4.4 mmol) of sodium hydride (50% mineral oil dispersion) and 0.97 g (4.2 mmol) of trimethyloxosulfonium iodide in 5 mL of Me_2SO was stirred and cooled in an ice bath at 0–5 °C. To this solution was added dropwise 0.34 g (2 mmol) of **6** dissolved in 1 mL of Me_2SO, and the solution was allowed to come to room temperature. Treatment and chromatographic workup as previously described afforded a 0.31-g (1.84-mmol, 92%) recovery of **6** and no other organic products.

Reaction of Dimethyloxosulfonium Methylide (1) with 2,3-Benzo-4,5:6,7-bishomotropone (7). When the same reaction as described above was performed with 0.37 g (2 mmol) of **7**, a 0.35-g (1.89-mmol, 95%) recovery of **7** with no other organic products was obtained.

Registry No. **1**, 5367-24-8; **5**, 485-46-1; **6**, 61578-05-0; **6** DNP, 70775-40-5; 6-d_2, 70775-41-6; **7**, 70812-14-5; **7** DNP, 70775-42-7; 7-d_4, 70775-43-8; 6,7,8,9-tetrahydrobenzocyclohepten-5-one, 826-73-3; 6,6-dibromo-6,7,8,9-tetrahydrobenzocycloheptan-5-one, 20848-05-9; trimethyloxosulfonium-d_9 iodide, 23726-00-3; dimethyloxosulfonium-d_6 methylide-d_2, 70775-44-9; trimethyloxosulfonium iodide, 1774-47-6.