86%) of (*Z*)- and (*E*)-**20** in a 4:1 ratio as determined by integration of the NMR peaks at δ 10.12 and 9.32. Short-path distillation afforded a fraction [bp 60–61 °C (0.08 mm)] of (*Z*)-**20** of greater than 95% purity.

The NMR spectrum shows a broad envelope from δ 0.67 to 1.67 and δ 2.3–2.8 (m, 3 H), 6.33 (t, 1 H), and 10.12 (s, 1 H). Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 78.81; H, 12.31.

4-*tert*-Butyl-6-*n*-butylcyclohexene-1-carboxaldehyde (22). By use of the procedure described above, 5.20 g (0.016 mol) of 4-*tert*-butylcyclohexanone tosylhydrazone in 30 mL of THF was treated at −78 °C with 22.0 mL (0.0321 mol) of *sec*-butyllithium and 2.4 mL (0.02 mol) of *n*-butyl iodide. After the mixture was stirred at −78 °C for 5 h, 50.0 mL (0.040 mol) of *sec*-butyllithium was added and the stirred mixture warmed to room temperature until nitrogen evolution ceased, at which time 1.5 mL of DMF was added. A standard workup and short-path distillation afforded 1.53 g (43%) of **22** [bp 104–106 °C (0.35 mm)], presumably the trans isomer as discussed in the text.

The NMR spectrum shows, in addition to a broad aliphatic envelope, peaks at δ 0.88 (s, 9 H), 6.67 (t, 1 H), and 9.34 (s, 1 H). Anal. Calcd for $C_{15}H_{26}O$: C, 81.02; H, 11.79. Found: C, 80.78; H, 11.88.

6-*n*-Butyl-2-methylcyclohexene-1-carboxaldehyde (26). A solution of 2.00 g (0.011 mol) of 2-methylcyclohexanone tosylhydrazone in 35 mL of dry THF was treated at −78 °C with 18.0 mL (0.026 mol) of *sec*-butyllithium and 1.2 mL (0.02 mol) of *n*-butyl iodide. After being stirred 24 h at −78 °C, the solution was treated with 35.0 mL (0.05 mol) of *sec*-butyllithium and allowed to warm to room temperature with stirring. Excess (1.5 mL) DMF was added, and the reaction mixture was stirred 0.5 h and worked up by the standard method. Preparative GLC afforded **26**. The NMR spectrum shows δ 0.87 (s, 3 H), 1.10–2.73 (m, 16 H including a singlet at 2.10), and 10.10 (s, 1 H). An aliquot of the crude reaction mixture showed the yield to be 47%. Both crude GLC and NMR spectroscopy suggested the presence of a small (<5%) amount of **27**.

When the alkylated tosylhydrazone dianion in a separate experiment was quenched with water and worked up as described above, 1.40 g of the alkylated tosylhydrazone (mp 96–102 °C) could be isolated. When this material was converted into the dianion, allowed to decompose, and then trapped with DMF in the usual manner, the crude GLC showed the presence of **26** and another product, **27**, in a 7:3 ratio. Preparative GLC afforded **27**, the NMR spectrum of which shows δ 0.78–1.08 (2 overlapping t, 6 H), 1.16–2.93 (m, 13 H), and 10.06 (s, 1 H).

Registry No. 5, 63883-67-0; **7**, 76421-17-5; **8**, 76421-18-6; **9**, 76421-19-7; **10**, 76421-20-0; **11**, 76421-21-1; **12**, 76421-22-2; **13**, 76421-23-3; **14**, 76421-24-4; **15**, 63883-82-9; (*E*)-**20**, 76421-25-5; (*Z*)-**20**, 76421-26-6; **21**, 41780-53-4; **22**, 76421-27-7; **23**, 52826-41-2; **26**, 76421-28-8; **27**, 76421-29-9; 3-methyl-2-borenecarboxaldehyde, 76421-30-2.

Cycloaddition Reactions of Indenes. 3. 1:1 Adduct from 1,1-Dimethyl-1*H*-indene and Dimethyl Acetylenedicarboxylate[1]

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In contrast to 1*H*-indene (**1a**) and 1-methyl-1*H*-indene (**1b**), which give stable 1:2 adducts (**3a**, 34%; **3b**, 30%) and with **1a** also a 1:3 adduct (**4a**; 40% from **1a**; 71% from **3a**) with dimethyl acetylenedicarboxylate (DMAD), 1,1-dimethyl-1*H*-indene (**1d**) and DMAD gave as the only crystalline product a cycloadduct of different structural type, dimethyl 1a,7b-*cis*-dihydro-1,1-dimethyl-1*H*-cyclopropa[*a*]naphthalene-2,3-dicarboxylate (**5a**, 14%), the structure of which has been confirmed by X-ray crystallography.

1*H*-Indene (**1a**) and 1-methyl-1*H*-indene (**1b**), but not the more sterically hindered 1-ethyl-1*H*-indene (**1c**) react with dimethyl acetylenedicarboxylate (DMAD) in refluxing benzene (with **1a**)[3] or toluene (with **1b**)[1b] via a Diels–Alder $[4_\pi + 2_\pi]$ cycloaddition across the 2- and 7a-positions to give 1:1 adducts **2** which undergo further, rapid, in situ $[2_\pi + 2_\pi]$ cycloaddition across the 4- and 4a-positions (of **2**) to give solid 1:2 adducts (**3a**, 34%; **3b**, 30%).[1b] In refluxing xylene the reaction of **1a** goes further to give a 1:3 adduct (**4a**; 40% from **1a** and 71% from **3a**), formed by a Diels–Alder addition of a third molecule of DMAD across the remaining diene system of **3a**.[1b] 1,1-Dimethyl-1*H*-indene (**1d**) and DMAD, however, in a 1:2 molar ratio in refluxing xylene for 22 h gave as the sole crystalline product only a 1:1 adduct (**5a**, 14%), different from **2** and having ultraviolet (UV), infrared (IR), and ^1H nuclear magnetic resonance (NMR) spectra consistent with the structure dimethyl 1a,7b-*cis*-dihydro-1,1-dimethyl-1*H*-cyclopropa[*a*]naphthalene-2,3-dicarboxylate (**5a**) (Scheme I).

The UV spectrum of **5a** [(95% C_2H_5OH) λ_{max} 240 nm (log ε 4.17), 296 (3.89), 308 (3.90), 325 (sh, 3.61)] is similar to that of 1,2-dihydronaphthalene-3,4-dicarboxylic acid derivatives **6a–c** [longest wavelength band at 290–292 nm (log ε 4.18–4.22)[4]] but has additional conjugation such as that which comes from the cyclopropane ring in the 1a,7b-dihydro-1*H*-cyclopropa[*a*]naphthalene derivatives **5b–l** [longest wavelength band or shoulder at 307–310 nm (log ε 3.0–3.35)], as shown in Table I. The ^1H NMR spectrum shows that the *gem*-dimethyl groups are retained in the adduct but are in widely different environments, as shown by the two methyl singlets (in $CDCl_3$) at δ 0.60 and 1.40. A similar difference in chemical shifts, averaging δ 1.65, has been noted for the 1-*endo* and 1-*exo* cyclopropyl protons in the methylene group at the corresponding position in the 2,3-benzonorcaradienes **5b–g** as shown in

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(1) (a) Paper 1: Noland, W. E.; Landucci, L. L.; Kameswaran, V. *J. Org. Chem.* **1980**, *45*, 3456–3461. (b) Paper 2: Noland, W. E.; Kameswaran, V.; Landucci, L. L. *Ibid.* **1980**, *45*, 4564–4572.

(2) Taken in part from the Ph.D. thesis of Venkataraman Kameswaran, University of Minnesota, Minneapolis, MN, June 1971; *Diss. Abstr. B* **1972**, *32*, 6918–6919; *Chem. Abstr.* **1972**, *77*, 151725.

(3) (a) Alder, K.; Pascher, F.; Vagt, H. *Ber. Dtsch. Chem. Ges. B* **1942**, *75*, 1501–1514. (b) Muir, K. W.; Sim, G. A.; Strachan, P.; Huebner, C. F. *Chem. Ind. (London)* **1964**, 1581–1582.

(4) (a) Lyssy, T. M. *J. Org. Chem.* **1962**, *27*, 5–13. (b) Schrecker, A. W.; Greenberg, G. Y.; Hartwell, J. L. *J. Am. Chem. Soc.* **1952**, *74*, 5669–5671. (c) Braude, E. A.; Evans, E. A. *J. Chem. Soc.* **1955**, 3337–3341.

0022-3263/81/1946-1318$01.25/0

Table I. UV Spectra of 5a and Related Model Compounds

compd (solv)	λ_{max} nm (log ϵ)					ref
5a (95% EtOH)		240 (4.17)		296 (3.89)	308 (3.90)	325 sh (3.61)	this work
5b (95% EtOH)	221 (4.32)		274 (3.81)		306 (3.02)		*a*
5b (hexane)	222 (4.19)	235 sh (3.95)	274 (3.82)		306 (3.02)		*a*
5d (EtOH)	220[b] (4.27)		275 (3.83)		308 sh (3.19)		*c*
5h (95% EtOH)	228 (4.2)		270 (3.7)		303 (3.0)		*d*
5i (EtOH)	225 (4.41)	235 sh (4.32)	271 (3.90)	290 sh (3.40)	310 (3.14)		*e*
5j (cyclohexane)	227 (4.40)	233 sh (4.32)	272 (3.90)				*f*
5k (EtOH)	225 (4.22)	231[g] (4.21)	278 (3.70)	307 sh (3.21)			*h*
5l (EtOH)	225 (4.29)	231[i] (4.28)	278 (3.77)	307 sh (3.35)			*h*

[a] Doering, W. v. E.; Goldstein, M. J. *Tetrahedron* **1959**, *5*, 53–69. [b] End absorption. [c] Reference 12g. [d] Badger, G. M.; Christie, B. J.; Rodda, H. J.; Pryke, J. M. *J. Chem. Soc.* **1958**, 1179–1184. [e] Huisgen, R.; Jupee, G. *Chem. Ber.* **1961**, *94*, 2332–2349. [f] Reference 12a. [g] Also 238 sh (4.08). [h] Reference 12j. [i] Also 238 sh (4.13).

Table II. NMR Spectra of 5a and Related Model Compounds

	shift,[s] δ				
compd (solv)	$H^{1\text{-endo}}$	$H^{1\text{-exo}}$	H^{1a}	H^{7b}	ref
5a ($CDCl_3$)[l]	0.61 (Me)	1.40 (Me)	2.27	2.31	this work
5b (CCl_4)[m]	−0.35	1.30	1.67	2.17	*a*
	−0.4	1.4	1.8	2.3	*b*
5c (CCl_4?)	−0.17	1.16	1.32 (Me)	2.15	*c*
5d (CCl_4)	−0.05	1.42	2.38, 3.60 (CH_2COOMe)	2.30	*d*
5e (CCl_4 or $CDCl_3$)	−0.02	1.62	1.75, 4.8 ($MeC{=}CH_2$)	2.37	*e*
5f ($CDCl_3$?)	0.2	2.1	3.7 (COOMe)	3.0	*f*, *g*
5g (CCl_4 or $CDCl_3$)	0.21	1.91	(CN)	2.92	*e*
5i ($CDCl_3$)[n]	0.85	(COOH)	2.67	3.12	*h*
5i (not given)[o]	0.86	(COOH)	2.72	3.16	*i*
5j ($CDCl_3$?)[p]	(CN)	(CN)	3.35	3.80	*j*
5k (CCl_4)[q]	(CH_2COOMe)	1.6–1.9	2.24	2.57	*k*
5l (CCl_4)[r]	0.26	(CH_2COOMe)	1.76	2.18	*k*

[a] Vogel, E.; Wendisch, D.; Roth, W. R. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 443. [b] Pomerantz, M.; Gruber, G. W. *J. Am. Chem. Soc.* **1967**, *89*, 6798–6799; **1971**, *93*, 6615–6622. [c] Reference 12h. [d] Reference 12g. [e] Swenton, J. S.; Burdett, K. A.; Madigan, D. M.; Rosso, P. D. *J. Org. Chem.* **1975**, *40*, 1280–1286. [f] Reference 12f. [g] Reference 12d. [h] Huisgen, R.; Juppe, G. *Chem. Ber.* **1961**, *94*, 2332–2349. [i] Günther, H.; Klose, H.; Cremer, D. *Ibid.* **1971**, *104*, 3884–3897. [j] Reference 12a. [k] Reference 12j. [l] $J_{1a,7b}$ = 8 Hz. [m] J(1-*exo*, 1a or 7b) = 8.5 Hz. [n] $J_{1a,7b}$ = 8.6 Hz. [o] $J_{1a,7b}$ = 8.39 Hz. [p] $J_{1a,7b}$ = 9 Hz. [q] $J_{1a,7b}$ = 7.5 Hz. [r] $J_{1a,7b}$ = 8.2 Hz. [s] Groups containing the designated atoms are given in parentheses.

Table II. The chemical shifts of the 1a- and 7b-methine protons are consistent, after allowance is made for neighboring electronegative substituents, with those previously observed for other 1a,7b-dihydro-1*H*-cyclopropa[*a*]naphthalene derivatives (**5b–l**), as shown in Table II. The cis vicinal coupling constants $J_{1a,7b}$ of 7.5–9 Hz reported in Table II for **5i–l** are in good agreement with our value of 8 Hz for **5a**. The proton-decoupled and off-resonance-decoupled ^{13}C NMR spectra (in $CDCl_3$) are also consistent with the presence of two upfield methine carbons, at δ 28.71 (1a-CH) and 33.64 (7b-CH), which must be attached to the two aliphatic protons which are coupled. Significantly, the quaternary 1-carbon appears farther upfield, at δ 10.74, than the *gem*-dimethyl carbons to which it is attached, which appear next at δ 13.56 (1-*endo*-CH_3) and 27.01 (1-*exo*-CH_3). The high-field chemical shifts of the methine protons and of these carbon atoms all are consistent with the presence of a cyclopropane ring, one side of which is poking into the shielding π electron clouds of the 2,3 double bond and the benzene ring. A good model for the high-field carbons in **5a** is the previously reported[5] ^{13}C NMR spectrum of **5i**, which shows three cyclopropyl methine carbons (one of which must be deshielded by the 1-carboxyl group) at the following chemical shifts (with the relative intensities in parentheses): δ 23.5 (27), 29.3 (40), 32.3 (47). In **5a**, the coupling constants $^1J_{CH}$ of 129 Hz for the 1a-CH and 119 Hz for the 7b-CH are well below the value of 160.5–162 Hz[6] for cyclopropane. While cyclopropane is an imperfect (but available) model for 1a,7b-dihydroxycyclopropa[*a*]naphthalene (2,3-benzonorcaradiene), this discrepancy brought into question the cyclopropane structure for **5a** and caused us to examine the structure by X-ray crystallography, which has confirmed structure **5a** for the 1:1 adduct.

The colorless crystals of $C_{17}H_{18}O_4$ belong to the monoclinic space group $P2_1/c$. The approximate size of the crystal used was 0.10 × 0.15 × 0.25 mm. The measured cell constants are a = 9.377 (5) Å, b = 10.451 (1) Å, c = 15.960 (5) Å, and β = 106.25 (3)° and gave a calculated density of 1.266 g/cm^3 for four molecules in the unit cell at ambient temperature. Data were collected on a fully automated Enraf-Nonius CAD-4 diffractometer by using a variable scan rate, ω–2θ scan technique and graphite-monochromatized Cu Kα radiation (λ = 1.54184 Å). After Lorentz and polarization corrections, 1739 of the 3077 total reflections (57%) with $0° < 2\theta \leq 15°$ were observed [$F_o \geq 2.5\delta(F_o)$]. A combination of direct methods and Fourier synthesis was used to locate all atoms.[7] Thermal anisotropic refinement was applied to all nonhydrogen atoms. In the final least-squares refinement, the hydrogen positions were refined with isotropic thermal parameters fixed at values one unit higher than those of the carbon atoms to which they are bonded. The R factor for the structure was 0.045. Figure 1 contains two ORTEP drawings of the

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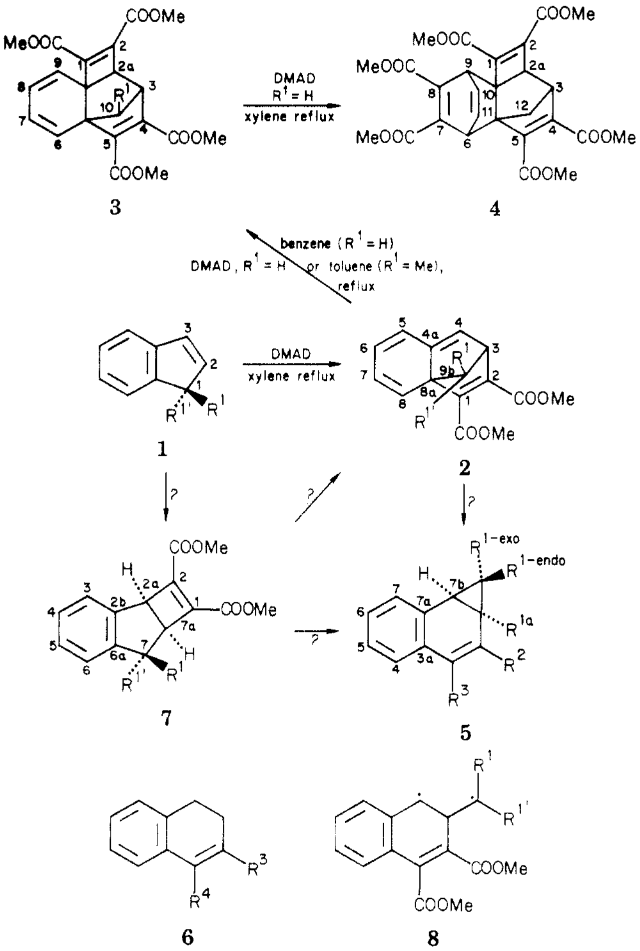
(5) Günther, H.; Keller, T. *Chem. Ber.* **1970**, *103*, 3231–3241.

(6) Stothers, J. B. "Carbon-13 NMR Spectroscopy"; Academic Press: New York, 1972; pp 333–336.

(7) All calculations were carried out on a PDP 11/34 computer using the Enraf-Nonius SDP programs. This crystallographic computing package is described by: Frentz, B. A. In "Computing in Crystallography"; Schenk, H., Olthof-Hazekamp, R., van Konigweld, H., Bassie, G. S., Eds.; Delft University Press: Delft, Holland, 1978; pp 64–71.

Scheme I



	R¹	R¹		R³	R⁴
1-4a	H	H	6a	COOMe	COOMe
1-3b	Me	H	b	COOH	COOH
1c	Et	H	c	COOH	H
1d, 2d	Me	Me			
7a, 8a	Me	Me			

	$R^{1\text{-endo}}$	$R^{1\text{-exo}}$	R^{1a}	R^2	R^3
5a	Me	Me	H	COOMe	COOMe
b	H	H	H	H	H
c	H	H	Me	H	H
d	H	H	CH_2COOMe	H	H
e	H	H	$MeC{=}CH_2$	H	H
f	H	H	COOMe	H	H
g	H	H	CN	H	H
h	H	COOEt	H	H	H
i	H	COOH	H	H	H
j	CN	CN	H	H	H
k	CH_2COOMe	H	H	H	$CHMe_2$
l	H	CH_2COOMe	H	H	$CHMe_2$

molecule shifted by 6° to facilitate three-dimensional viewing through a stereoviewer. Bond lengths, bond angles, and final coordinates are given in Tables 3-5, respectively, in the supplementary material. The numbering of the atoms can be deduced from that shown in structure **5a**. The data show that the cyclopropane ring is an equilateral triangle, with C–C bond distances of 1.516 Å. This value is slightly higher than the mean C–C (ring) bond length of 1.509 (2) Å for the cyclopropane ring in 115 variously substituted compounds and the value of 1.508 (3) Å for the 27 cyclopropanes having only C (sp^3) or H as substituents, as reported by Allen.[8] The C_1–$C_{1\text{-endo}}$ bond of **5a** is significantly shorter than the C_1–$C_{1\text{-exo}}$ bond to the other methyl group. The 1-*endo*-methyl group also appears to be relatively shielded in the NMR. Presumably, both these effects arise from the crowding of the methyl group by the nearby π-electron system. This crowding can be seen from the distances between $H_{1\text{-endo}}$ and C_2, C_3, C_{3a}, and C_{7a}, which are 2.752, 2.663, 2.612, and 2.677 Å, respectively. The benzene ring and the four carbon atoms of the six-membered ring fused to it are nearly coplanar; the mean distance of the atoms from the least-squares plane is 0.012 Å for the benzene ring and 0.014 Å for the six-membered ring, and the dihedral angle between the least-squares planes of these rings is 3.3°. The dihedral angle between the cyclopropane ring and the six-membered ring fused to it is 69.0°. The 2-ester group is conjugated with the double bond (the C_3–C_2–$C_{2'}$–$O_{2''}$ torsional angle is −6.2°), whereas the 3-ester group, which is subject to more crowding, is nearly orthogonal to the 2,3 double bond (the C_2–C_3–$C_{3'}$–$O_{3''}$ torsional angle is 97.9°). This indicates that conjugation of the benzene ring with the 2-ester group, aided by steric factors, dominates over potential conjugation of the cyclopropane ring with the 3-ester group.

If is is assumed that **1d** does not isomerize prior to addition by DMAD, then two addition pathways appear plausible. One would involve formation by a Diels–Alder reaction of an intermediate 1:1 adduct **2d**, a process which has ample analogy but which would be expected to be sterically hindered in this case and, therefore, relatively slow. This would then need to be followed by a rearrangement, possibly a [1,3]sigmatropic rearrangement of the suprafacial–antarafacial type in which the *gem*-dimethyl (9-position) carbon moves with inversion of its methyl groups from the 8a- to the 4-carbon of **2d**, which could give **5a** directly. This rearrangement would have to be faster than the formation of a 1:2 adduct of type **3**, which was not observed, even though the second addition of DMAD would not appear to be much more sterically hindered than in the monomethyl case (**2b**) where a 1:2 adduct (**3b**) was formed in 30% yield. Another possibility[9] is that **2d** undergoes homolytic fission at its C_{8a}–C_9 bond to an intermediate diradical (**8a**) which can then close to **5a**. This fission would be expected to proceed more readily with **2d** (Δ*H* is estimated to be 3–4 kcal/mol less[10]) than with **2b** (or the hypothetical **2c**), since, in addition to the benzylic radical at C_4 (of **2d**), **2d** would form a tertiary radical at C_9 whereas **2b**, which did not rearrange by this mechanism, would form only a secondary radical.

The other pathway would involve a $[2_\pi + 2_\pi]$ cycloaddition of DMAD across the 2,3 double bond of **1d** to give dimethyl 2a,7a-*cis*-dihydro-7,7-dimethyl-1*H*-cyclobuta[*a*]indene-1,2-dicarboxylate (**7a**). Formation of the 1:1 adduct **7a** would avoid destruction of the aromaticity of the benzene ring, making **7a** an energetically attractive alternative to the formation of **2d** in this sterically hindered environment. Furthermore, the mechanism of formation of **7a** would probably be analogous to the formation of **3** from **2**. In the formation of **7a**, a postulated diradical intermediate arising from an initial addition at the 2-position of **1d** would have a benzyl radical at the 3-position (of **1d**), whereas in the formation of **3** the diradical intermediate from initial addition at the 4-position of **2** would have a similarly resonance-stabilized allylic penta-

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[8] Allen, F. H. *Acta Crystallogr., Sect. B* **1980**, *B36*, 81-96.

[9] Suggested by referee II.

[10] Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976.

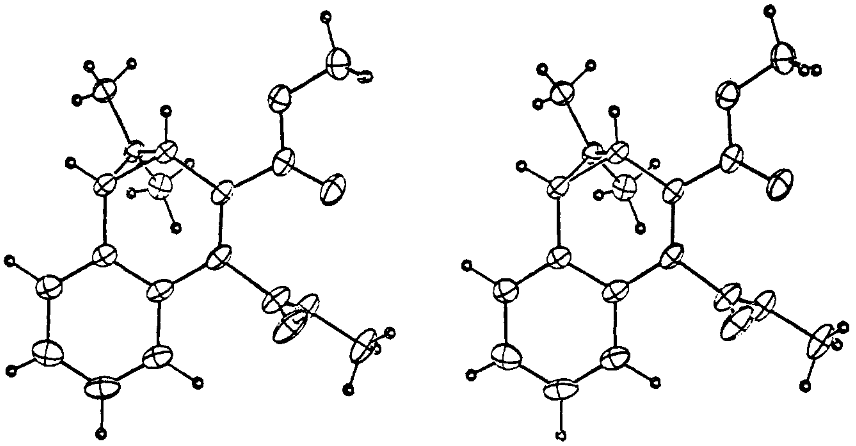

Figure 1.

dienyl radical[11] at the 4a-position (of **2**). Intermediate **7a** would then have to rearrange to the final product **5a**. One energetically unlikely pathway would be to rearrange to **2d**, possibly by a [1,3] sigmatropic rearrangement of the 2-carbon from the 2a- to the 6a-carbon of **7a**, which could give **2d**. Intermediate **2d** could then rearrange to **5a** as suggested above. Alternatively, **7a** could rearrange to **5a** by some other mechanism. The reverse of such a transformation, the rearrangement of derivatives of **5** to derivatives of **7**, has been observed numerous times under photochemical conditions[12] but would not place the 3-methoxycarbonyl group of **5a** in the proper position in **7** (it would be expected to go to the 2a-position) since, while the *gem*-1,1-substituents in **5** could be expected[12a,c,g] to remain intact as *gem*-7,7-substituents in **7**, the 1a-substituent in **5d** is known to become the 1-substituent in the corresponding derivative of **7**.[12e,f] Futhermore, the transformation may be energetically unfavorable in the reverse direction (**7** to **5**) and thermally forbidden.

Experimental Section

Melting points were determined on a calibrated Mel-Temp melting point apparatus. The ultraviolet spectrum (UV) was determined on a Beckman DK-2A recording spectrophotometer. Infrared spectra (IR) were determined on a Perkin-Elmer Model 257 spectrophotometer. Nuclear magnetic resonance spectra (NMR) were determined on a Varian Associates Model T-60 or XL-100A spectrometer, using tetramethylsilane as an internal standard. Those obtained on the latter instrument were done by Dr. Robert M. Riddle and Frank D. Blum. Mass spectra were determined at low resolution on a Hitachi Perkin-Elmer Model RMU-6D spectrometer by Adrian S. Swanson and his associates and at high resolution on an AEI MS-30 spectrometer and on a Finnigan 4000 spectrometer with chemical ionization detection, both by Dr. Roger A. Upham and Denise D. Beusen. Elemental microanalyses were performed by Fay M. Thompson under the supervision of Professor C. F. Koelsch at the University of Minnesota.

1,1-Dimethyl-1*H*-indene (1d). 2,3-Dihydro-3,3-dimethyl-1*H*-inden-1-one[13] was reduced with lithium aluminum hydride to 2,3-dihydro-3,3-dimethyl-1*H*-inden-1-ol[14] (96%), which was heated with potassium hydrogen sulfate at 150 °C for 1 h to give **1d**[14] (50%) having an NMR spectrum (in CCl_4) in good agreement with that reported[14] except that instead of the methyl singlet we observed a doublet at δ 1.29 ($J_{CH_3,2}$ = 1.2 Hz) attributed to U-coupling.

Reaction of 1,1-Dimethyl-1*H*-indene (1d) with DMAD: Dimethyl 1a,7b-*cis*-Dihydro-1,1-dimethyl-1*H*-cyclopropa[*a*]naphthalene-2,3-dicarboxylate (5a). A solution of **1d** (1.44 g, 10.0 mmol) and DMAD (2.84 g, 20.0 mmol) in xylene (5 mL) was refluxed for 22 h. The dark red solution was cooled and allowed to evaporate for 4 days, causing separation of a pale yellow crystalline solid: 0.60 g (14%); mp 112–115 °C. Recrystallization from benzene–petroleum ether (bp 60–68 °C) gave white crystals: mp 116–116.5 °C; IR (Nujol) 3440 (w), 3405 (w, C=O overtones), 1737 (s), 1718 (s, C=O), 1611 (ms), 1568 (m, C=C) cm^{-1}; ^1H NMR ($CDCl_3$, Varian XL-100A, 100.1 MHz) δ 0.61 (s, 3 H, 1-*endo*-CH_3), 1.40 (s, 3 H, 1-*exo*-CH_3), degenerate AB pattern (J_{AB} = 8 Hz) at 2.27 (1a-H) and 2.31 (7b-H, total 2 H), 3.82 (s, 3 H, 2-$COOCH_3$), 3.94 (s, 3 H, 3-$COOCH_3$), 7.13–7.35 (m, 4 H, 4–7-H);^{13}C NMR ($CDCl_3$, Varian XL-100A, 25.2 MHz, proton-decoupled, off-resonance decoupled with the decoupler set on the aromatic resonances, and fully coupled) δ (multiplicity, relative peak heights) 10.74 (s, 29, 1-C), 13.56 (q, $^1J_{CH_3}$ = 126 Hz, 24, 1-*endo*-CH_3), 27.01 (q, $^1J_{CH_3}$ = 126 Hz, 58, 1-*exo*-CH_3), 28.71 (d,[15] $^1J_{CH}$ = 129 Hz, 58, 1a-CH), 33.64 (dd,[15] $^1J_{CH}$ = 119 Hz, $^3J_{CH}$ = 6 Hz, 64, 7b-CH), 52.32 (q, $^1J_{CH_3}$ = 147.2 Hz, 100, 2- and 3-$COOCH_3$), 75.87, 77.14, 78.40 (t, 9, 11, 9, $CDCl_3$), 124.32 (s, 5, 2-C), 128.20 (s, 12, 3-C), four overlapping d (assignments are arbitrary, based on chemical shift) at 126.28 ($^1J_{CH}$ = 163 Hz, 57, 6-CH), 126.88 ($^1J_{CH}$ = 161 Hz, 54, 5-CH), 129.39 ($^1J_{CH}$ = 160 Hz, 33, 7-CH), 129.95 ($^1J_{CH}$ = 162 Hz, 58, 4-CH), 134.55 (s, 13, 7a-C), 137.90 (s, 8, 3a-C), 166.66 (s, 10, 2-$COOCH_3$), 169.17 (s, 9, 3-$COOCH_3$); mass spectrum (50 eV, 160 °C), *m*/*e* (relative intensity > 18, M* indicates ^{13}C peak) 286 (26, M), 271 (29, M – CH_3), 255 (59, M – OCH_3), 254 (28, M – CH_3OH), 239 (35, M – CH_3 – CH_3OH), 227 (81, M – $COOCH_3$), 213 (100, M – OCH_3 – $C(CH_3)_2$), 196 (28, M* – CH_3OH – $COOCH_3$), 195 (56, M – CH_3OH – $COOCH_3$), 168 (23, M* – $COOCH_3$ – $HCOOCH_3$), 167 (28, M – $COOCH_3$ – $HCOOCH_3$), 153 (25, M – CH_3OH – $COOCH_3$ – $C(CH_3)_2$), 152 (28, M – CH_3OH – $HCOOCH_3$ – $C(CH_3)_2$), 127 (20, M – 2 $COOCH_3$ – C_3H_5); high-resolution mass spectrum (70 eV, 200 °C), *m*/*e* (relative intensity > 20; calcd value) 286.1212 (29; $C_{17}H_{18}O_4$, 286.1203, M), 271.0969 (29; $C_{16}H_{15}O_4$, 271.0968, M – CH_3), 227.1196 (91; $C_{15}H_{15}O_2$?, 227.1072, M – $COOCH_3$), 226.1118 (25; $C_{15}H_{14}O_2$?, 226.0994, M – $HCOOCH_3$), 213.0557 (100; $C_{13}H_9O_3$, 213.0551, M – OCH_3 – $C(CH_3)_2$), 196.0843 (28; $^{13}C^{12}C_{13}H_{11}O$, 196.0841, M* – CH_3OH – $COOCH_3$), 195.0820 (74; $C_{14}H_{11}O$, 195.0808, M – CH_3OH – $COOCH_3$), 168.0878 (28; $^{13}C^{12}C_{12}H_{11}$, 168.0863, M* – $COOCH_3$ – $HCOOCH_3$), 167.0858 (41; $C_{13}H_{11}$, 167.0857, M – $COOCH_3$ –

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$HCOOCH_3$), 165.0729 (28; $C_{13}H_9$, 165.0703, M – 2 $HCOOCH_3$ – H?), 153.0348 (31; $C_{11}H_5O$, 153.0340, M – CH_3OH – $COOCH_3$ – $C(CH_3)_2$, 152.0210 (32; $C_{11}H_4O$?, 152.0262, M – CH_3OH – $HCOOCH_3$ – $C(CH_3)_2$), 127.0648 (31; $C_{10}H_7$?, 127.0548, M – 2 $COOCH_3$ – C_3H_5); CI mass spectrum (NH_3 at 0.15 torr, normalized against spectrum minus reagent gas ions, 230 °C), negative ion spectrum, *m/e* (relative intensity > 0.4) 286.2 (100, m), 271.2 (1.9, M – CH_3), 255.0 (1.3, M – OCH_3), 240.2 (2.4, M – CH_3 – OCH_3); positive ion spectrum, *m/e* (relative intensity > 0.9) 304.1 (100, M + NH_4), 303.0 (5.7, M – 1 + NH_4), 288.2 (15, M – CH_4 + NH_4), 255.2 (51, M – OCH_3), 254.4 (15, M – CH_3OH), 227.1 (3.2, M – $COOCH_3$), 212.8 (1.0, M – OCH_3 – $C(CH_3)_2$).

Anal. Calcd for $C_{17}H_{18}O_4$ (mol wt 286.33): C, 71.31; H, 6.33. Found: C, 71.41; H, 6.22.

In order to look for the possible presence of small amounts of a solid 1:2 adduct, the reaction was repeated and worked up by preparative TLC on silica gel PF-254, but the only solid product isolated was again **5**, as white crystals, mp 116–116.5 °C.

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Registry No. 1d, 18636-55-0; **5a**, 76402-82-9; DMAD, 762-42-5; 2,3-dihydro-3,3-dimethyl-1*H*-inden-1-one, 26465-81-6; 2,3-dihydro-3,3-dimethyl-1*H*-inden-1-ol, 38393-92-9.

Supplementary Material Available: Tables of bond distances (Table 3), bond angles (Table 4), final coordinates (Table 5), positional and thermal parameters and their estimated standard deviations, general temperature factor expressions, root-mean-square amplitudes of thermal vibration, weighted least-squares planes, and dihedral (torsional) angles (11 pages). Ordering information is given on any current masthead page.

Halogenated Ketenes. 34. Cycloaddition of Halogenated Ketenes and Conjugated Trimethylsilyl Enol Ethers

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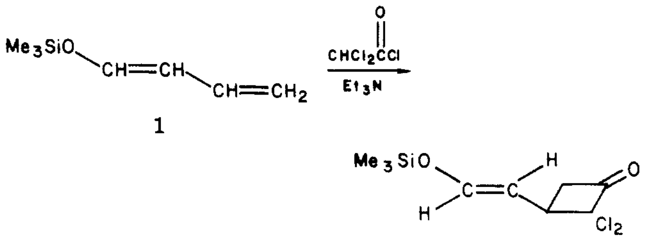
The generation of dichloroketene and methylchloroketene by the triethylamine dehydrohalogenation of the respective acid chlorides in the presence of conjugated trimethylsilyl enol ethers yields functionalized cyclobutanones with high regioselectivity. Both cross-conjugated and linear-conjugated trimethylsilyl enol ethers were found to yield [2 + 2] cycloaddition products in good yield.

The cycloaddition of dichloroketene and several mono- and disubstituted ketenes with a number of trimethylsilyl enol ethers to produce trimethylsiloxy- and hydroxy-functionalized cyclobutanones has recently been reported.[1-3] We now describe the reactions of dichloro- and methylchloroketene with several conjugated trimethylsilyl enol ethers. The conjugated trimethylsilyl enol ethers are readily prepared from α-enones by the procedure described by House.[4]

When dichloroacetyl chloride was slowly added to a dilute solution[5] of the trimethylsilyl enol ether from crotonaldehyde, **1**, and triethylamine, an exothermic reaction occured with the immediate precipitation of the triethylammonium salt. After the addition was complete, the reaction was stirred for several hours, and the salt was removed by filtration. The filtrate was concentrated and the residue vacuum distilled to yield a one to one adduct. A strong carbonyl absorption in the infrared at 1805 cm^{-1} as well as a strong vinyl absorption at 1655 cm^{-1} suggested that cyclobutanone **2** was the product of this cycloaddition.



1

2

The NMR spectrum of the product prior to distillation and after distillation supported **2** as the major product of this reaction. A coupling constant of J = 12.1 Hz for the vinyl protons confirms the trans geometry. Less than 5% hydrolysis of the parent compound **2** to yield the aldehyde was indicated by the infrared and NMR spectra. Although cycloaddition may have occurred at the 1,2 double bond of silyl enol ether **1**, we were unable to confirm the presence of this product in any of the spectra. When the reaction was repeated, using the zinc dehalogenation of trichloroacetyl chloride in ether to produce dichloroketene,[1] the same product was observed. Reaction of **2** with anhydrous

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