

temperature, 10 ml of 6 M NaOH was added, followed by 8 ml of 30% hydrogen peroxide. The reaction mixture was then heated at 60° for 45 min. The resulting mixture was diluted with water and extracted three times with pentane. The combined extracts were washed with water and dried with Na<sub>2</sub>SO<sub>4</sub>. Distillation of the solvent through a Vigreux column yielded 2.83 g of colorless oil. Ir analysis showed the presence of alcohol as well as exocyclic and endocyclic olefin. Without purification this material was oxidized with Jones reagent to yield 32% of crude acid **55**: ir 3725–2330, 3025, 2945, 1705, 1640, 1420, 1235, 1215, 690, and 650 cm<sup>-1</sup>.

A sample of **55** was treated with diazomethane to give 95% of crude ester **56**. Vpc analysis showed ca. 10% of a single impurity. An analytical sample of **56** was obtained from column A: ir 3020, 2980, 2950, 2840, 1740, 1640, 1450, 1430, 1360, 1345, 1325, 1230, 1185, 1100, 1075, 1045, 690, and 665 cm<sup>-1</sup>; nmr (220 MHz)  $\delta$  1.48–2.07 (m, 4 H), 2.15–2.28 (m, 2 H), 2.68 (br, 2 H), 3.14 (m, 1 H), 3.61 (s, 3 H), 5.60 (br d,  $J = 11$  Hz, 1 H), and 5.71–5.83 (m, 1 H).<sup>27</sup>

**endo-cis-Bicyclo[4.2.0]oct-2-en-7-yl Methyl Ketone (17)**. Reaction of acid **55** with methyl lithium yielded 89% of an 88:12 mixture (vpc) of endo and exo ketones, **17** and **18**, respectively. Preparative vpc on column A gave an analytical sample of endo ketone **17**: ir 3020, 2975, 2930, 2845, 1712, 1640, 1450, 1430, 1360, 1350, 1225, 1175, 1130, and 690 cm<sup>-1</sup>; nmr (220 MHz)  $\delta$  1.38–1.88 (m, 3 H), 1.91–2.09 (m, 2 H), 1.97 (s, 3 H), 2.23 (m, 1 H), 2.56–2.88 (m, 2 H), 3.21 (m, 1 H), 5.57 (ddd,  $J_1 \sim J_2 \sim 3$  Hz,  $J_3 = 10$  Hz, 1 H), and 5.67–5.78 (m, 1 H).<sup>27</sup>

**exo-cis-Bicyclo[4.2.0]oct-2-en-7-yl Methyl Ketone (18)**. Epimerization of the mixture of ketones **17** and **18** described above with KOH in aqueous methanol afforded an 86:14 mixture (vpc) of exo and endo ketones, **18** and **17**, respectively. An analytical sample of exo ketone **18** was obtained from column A: ir 3015, 2920, 2845,

1712, 1645, 1445, 1430, 1350, 1175, 710, and 675 cm<sup>-1</sup>; nmr (220 MHz)  $\delta$  1.43–1.78 (m, 3 H), 2.00 (s, 3 H), 2.06–2.12 (m, 2 H), 2.38 (m, 1 H), 2.49–2.61 (m, 1 H), 2.70–2.84 (m, 1 H), 2.97 (m, 1 H), 5.74 (d,  $J = 11$  Hz, 1 H), and 5.80 (d,  $J = 11$  Hz, 1 H).<sup>27</sup>

**3-Methylene-5-hexen-2-one (27)**. A mixture of 9.8 g (0.1 mol) of 5-hexen-2-one (**57**), 12.1 g (0.1 mol) of piperidine hydrochloride, and 7.5 ml (0.1 mol) of 37% formaldehyde was heated on a steam bath for 45 hr. Usual work-up<sup>1</sup> afforded 6.20 g (57%) of pale yellow lachrymatory liquid. Vpc analysis indicated the usual four-component mixture, and material for analysis and photolysis was obtained on column A: ir 3075, 3000, 2975, 2905, 1680, 1640, 1625, 1425, 1360, 1255, 1130, 1110, 985, 965, 925, and 910 cm<sup>-1</sup>; nmr (220 MHz)  $\delta$  2.27 (s, 3 H), 2.94 (br d,  $J = 7$  Hz, 2 H), 4.90–5.03 (m, 2 H), 5.59–5.80 (m, 1 H), 5.64 (br s, 1 H), and 5.92 (s, 1 H).<sup>27</sup>

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## The Synthesis, Stereochemistry, and Nuclear Magnetic Resonance Assignments of Polycyclic Cyclopentanones Obtained by Iron Carbonyl Induced Coupling of Olefins to Carbon Monoxide<sup>1,2</sup>

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**Abstract:** A thermally or photochemically initiated route from olefins to cyclopentanones using iron carbonyl reagents is described. Strained olefins proceed with greatest facility giving up to 77% yields of polycyclic ketones. Both symmetric and unsymmetric ketones are easily prepared by this method. An exo-trans-exo geometry was determined by considering the coupling constant between bridgehead and cyclopentanone ring protons on ketones containing norbornyl systems.

Transformations in which transition metals act to modify organic substrates have evoked considerable interest both because of their utility and the mechanistic information they supply. During the past few years many metal assisted reactions have received particular attention. These include the olefin metathesis reaction,<sup>3,4</sup> cyclodimerization,<sup>4,5</sup> oligomeriza-

tion,<sup>6</sup> and carbonyl insertion<sup>7,8</sup> reactions. Olefin coupling associated with carbonyl insertion has been briefly reported.<sup>1,9,10</sup> We wish to report observations and conclusions regarding metal-induced dimerization concurrent with carbonyl insertion. The procedure described represents a novel approach to synthesis of the cyclopentane skeleton. Particular attention is

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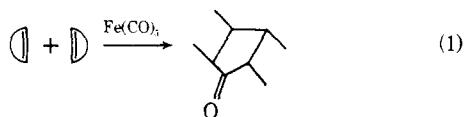
(9) (a) R. Pettit, *J. Amer. Chem. Soc.*, **81**, 1266 (1959); (b) S. G. Lewandus and R. Pettit, *ibid.*, **93**, 7087 (1971).

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paid to synthesis and product stereochemistry; mechanistic details are presented in the following paper.<sup>1b</sup>

## Results and Discussion

**Thermal Reactions.** The overall process (eq 1) being



considered is general with respect to cyclic olefins, but under the conditions employed, high yields are obtained only with strained olefins. These results are summarized in Table I. The carbonyls of molybdenum ( $\text{Mo}(\text{CO})_6$ ), chromium ( $\text{Cr}(\text{CO})_6$ ), and cobalt ( $\text{Co}_2(\text{CO})_8$ ) are active in effecting the carbonyl insertion-cyclization reaction but with reduced efficiency. Under normal conditions, the initially homogeneous solution changes to an inhomogeneous mixture with separation of a mildly pyrophoric iron-rich deposit.<sup>11</sup>

Coupled products are all high-melting crystalline solids with a characteristic carbonyl stretching frequency at  $1722\text{ cm}^{-1}$  ( $\text{CCl}_4$ ), consistent with that reported for related cyclopentanones<sup>12</sup> and semiempirical<sup>13,14</sup> considerations.

The carbonyl chemistry exhibited by ketonic products appears normal for hindered carbonyl functions. Reduction of compounds **1a** and **2a** with  $\text{LiAlH}_4$  in THF afforded the corresponding alcohols in high yield; however, reflux times of up to 6 hr were necessary to bring about complete reduction. Reduction by the Meerwein-Ponndorf method and bromination in acetic acid were unsuccessful. Hydrocarbon reduction was efficiently accomplished by the Huang-Minlon modification of the Wolff-Kishner procedure. Hydrogenation of the double bonds in **1a** proceeds smoothly with Pt/C in a Brown<sup>2</sup> apparatus.

The fact that diene **1** possesses two dissimilar regions of unsaturation raises a question regarding the reactivities of different types of double bonds in the formation of the coupled products. That the unhindered bond is reactive while the hindered bond is totally unreactive was shown<sup>1a</sup> unequivocally by considering the results obtained from reactions carried out with compounds **7** and **8** and comparison of the nmr spectra of olefins **1**, **7**, and **8** with that of coupled product **1a**.

The cyclization reaction generates highest yields with strained olefins as a consequence of increased metal to olefin binding with increasing ring strain.<sup>1b,15</sup> Differences in strain energy may also be responsible for the relatively low yields of ketones derived from compounds **3** and **4**. The decreased yield in these cases is apparently a consequence of reduced reaction rates; glc analysis of the reacting solution shows that no detectable side products are being formed.

Several methods have proved efficacious in the dimeri-

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**Table I.** Product Distribution from Reaction of Cyclic Olefins with Iron Carbonyls

Reagents	Products	% yield
1		74 <sup>a</sup> , 70 <sup>b</sup> , 67 <sup>c</sup> , 26 <sup>d</sup>
		<sup>f</sup>
2		57 <sup>a</sup> , 77 <sup>b</sup> , 67 <sup>c</sup> , 50 <sup>d</sup>
		27 <sup>a,c</sup> , 2-5 <sup>b</sup> , 2-5 <sup>c</sup> , 17 <sup>d,e</sup>
3		10 <sup>a</sup>
		12 <sup>a</sup>
4		12 <sup>a</sup>
		42 <sup>a</sup>
5		42 <sup>a</sup>
	Ketone	0 <sup>a-c</sup> , 1 <sup>d</sup>
6		62 <sup>a</sup>
		62 <sup>a</sup>
7		62 <sup>a</sup>
		0 <sup>a-d</sup>
8		0 <sup>a-d</sup>
		0 <sup>a-d</sup>

<sup>a</sup> Thermal,  $\text{Fe}(\text{CO})_5$ . <sup>b</sup> Thermal,  $\text{Fe}_2(\text{CO})_9$ . <sup>c</sup> Thermal,  $\text{Fe}_3(\text{CO})_{12}$ . <sup>d</sup> Photochemical,  $\text{Fe}(\text{CO})_5$ , see Experimental Section for details of a-d. <sup>e</sup> Yields are variable. <sup>f</sup> Relative yields of **1a**, **2a**, and **2ab** depend upon the ratio of **1**:**2**.

zation of norbornyl systems.<sup>5,16</sup> For example, benzonorbornadiene gives high yields of exo-trans-exo dimer **2b** when treated with Rh/C.<sup>17</sup> Under our reaction conditions, simple hydrocarbon dimerization does not occur in high yields as a general rule. Benzonorbornadiene **2** is the only olefin from which hydrocarbon dimer has been isolated and characterized as a product under

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conditions where the carbonyl insertion-cyclization reaction also takes place. Formation of a small amount of hydrocarbon dimer from compound **1** was shown by high-resolution mass spectroscopy.<sup>18</sup> Moreover, thermal dimer formation from **2** is not reproducible and yields are variable (0–27%) under seemingly identical reaction conditions. The variable results observed for the dimerization of **2** suggest that a heterogeneous reaction involving the iron-rich deposit may be operative. Further evidence<sup>1b</sup> garnered from photochemically induced couplings shows that no hydrocarbon dimer is formed during ketone formation so long as the reaction solution remains homogeneous.

The cyclobutane derivative may be regarded as an intermediate in the olefin metathesis reaction with full isomerization being blocked. Pettit<sup>9b</sup> has reported that  $W(CO)_6$  and  $Mo(CO)_6$  act as catalysts for olefin metathesis although their effectiveness was notably less than that of the metal complex-Lewis base combinations usually employed. Osborn<sup>4</sup> has discussed norbornadiene coupling on iridium in terms of the metathesis reaction. Nevertheless, presently available evidence does not demonstrate the conclusion that the coupling insertion and dimerization reactions brought about by iron carbonyls are related to the metathesis reaction.

**Photochemical Reactions.** Carbonyl insertion to form dimer ketone (eq 1) occurs at room temperature during photolysis of  $Fe(CO)_5$  in the presence of olefins as listed in Table I. The products produced photochemically were found to be identical with those generated thermally. Although quantum yields have not been determined, comparative yields are listed to indicate the relative ease with which photochemical transformations occur. As the mechanism of the photochemical process is discussed separately,<sup>1b</sup> only salient features regarding synthetic aspects are described here.

Photolytic experiments were performed in a variety of solvents. Solvents containing basic functions, e.g., acetonitrile, hexamethylphosphoramide, and tetrahydrofuran, although suitable for ketone formation, react with  $Fe(CO)_5$  to give complexes and/or carbonyl anionic species.<sup>19</sup> No detectable products indicative of competing reactions were obtained in hydrocarbon solvents such as benzene, hexane, and *n*-octane.

Photolysis of a reaction mixture in *n*-octane or benzene saturated with nitrogen causes the solution to turn slowly heterogeneous. This is due in part to the precipitation of ketone product and in part to iron products. When a mixture of **2** saturated with carbon monoxide at 1 atm was photolyzed, the solution remained homogeneous and the ketone yield was decreased approximately threefold with respect to that obtained when photolysis was carried out under nitrogen. Thus while beneficial in maintaining homogeneity, carbon monoxide drastically reduces the rate of product formation.

Though quantum yield data have not yet been obtained, the synthetic utility of photolysis appears to be quite good. Yields of up to 50% were realized in 75 min using a photochemical reactor equipped with 3500-Å lamps. During this time interval, solutions

became heterogeneous. Starting material may be easily separated by column chromatography and recycled. Although  $Fe_2(CO)_9$  is readily formed during photolysis of  $Fe(CO)_5$  in the absence of olefin under either nitrogen or carbon monoxide, no detectable  $Fe_2(CO)_9$  was observed when olefin was present. Irradiation of olefin- $Fe_2(CO)_9$  solutions in *n*-octane showed that  $Fe_2(CO)_9$  is not responsible for photolytic coupling.

Unsymmetric ketones are readily prepared by sequential addition of olefins to the iron system. A reactive intermediate<sup>1b</sup> may be prepared by photolyzing a mixture of  $Fe(CO)_5$  and olefin under an atmosphere of carbon monoxide. Once a considerable quantity of this intermediate has been prepared, photolysis is ended, a second olefin added and excess carbon monoxide removed by purging with  $N_2$ . The yield of ketone **2ab** depends upon the relative concentrations of olefins **1** and **2**. Yields of the unsymmetric ketone **2ab** are higher in glacial acetic acid than in hydrocarbon solvents. This route to unsymmetric cyclopentanones should prove of great synthetic utility. Unsymmetric ketone **2ab** may also be prepared thermally from a mixture of **1** and **2**.

**Stereochemistry.** In all cases investigated, the olefin moieties fused trans to one another. Assignment of product stereochemistry is based upon assignment of nmr spectra in conjunction with the Karplus<sup>20</sup> relationship. Without exception we have found the spectra of products from norbornyl systems to be in agreement with the exo-trans-exo geometry. Green and Luken,<sup>21</sup> and others<sup>22</sup> showed that the Karplus relationship can be used to distinguish between isomers having endo geometry and forms having exo geometry. The product obtained upon coupling norbornadiene was first correctly assigned by Green<sup>21</sup> and later confirmed by Cookson.<sup>23</sup> Consideration of steric interactions based on Dreiding models has been discussed.<sup>1a</sup>

Differentiation between those structures having a  $C_2$  symmetry axis (exo-trans-exo and endo-trans-endo) from that belonging to the  $C_1$  point group (exo-trans-endo) is based on the relatively simple spectra expected for the former. The spectra of structurally related compounds **1a**, **2a**, **2ab**, **3a**, **4a**, and **5a** have been analyzed and the indicated stereochemistry has been confirmed. Spin-decoupling studies<sup>24</sup> and chemical shift sensitivity<sup>25</sup> to  $Eu(fod)_3$  have facilitated the assignments and have shown the presence of long range nuclear spin-spin coupling. Proton assignments based upon relative downfield motion of the absorption peaks with addition of the shift reagent agree with those made on the basis of spin decoupling and published<sup>26</sup> spectra of related compounds.

In a recently reported example,<sup>27</sup> exo-cis-exo stereochemistry was depicted although stereochemical details

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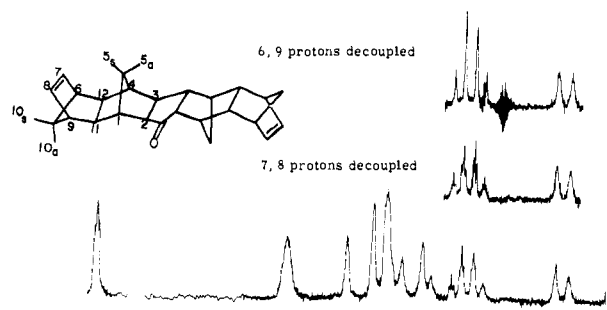


Figure 1. The 90-MHz spectrum of ketone **1a**.

were not implied. Without direct contrary evidence, we suspect that this material also has exo-trans-exo stereochemistry. Laszlo<sup>28</sup> has heated 7,7-dimethoxybenzonornbornadiene with  $\text{Fe}(\text{CO})_5$  in di-*n*-butyl ether and reported exclusive formation of an exo-trans-endo ketone. To date, this is the only confirmed case of a non-exo-trans-exo product using the method under discussion. Spiropentane derivative **6** is thermally unreactive due to steric hindrance leading us to conclude that the methoxy groups are playing a direct role in the synthesis.

The 90-MHz spectra of **1a** are shown in Figure 1 and assignments tabulated in Table II. The cyclopentanone

Table II. Chemical Shift and Coupling Constant Assignments for Ketone **1a**

Proton	Assignment ( $\delta$ , ppm)	$J$ (Hz)
1	2.30	$J_{2,3}$ (7.8)
2	1.84	$J_{5a,5}$ (10.8)
3	1.59	$J_{6,7}$ (3.0)
4	2.07	$J_{6,10a(10s)}$ (1.5)
5a	0.39	$J_{7,10a}$ (1.0)
5s	2.00	$J_{7,8}$ (5.5)
6, 9	2.82	$J_{10a,10s}$ (8.0)
7, 8	5.91	
10a	1.13	
10s	1.32	
11, 12	1.94	

ring protons (2, 3) are assigned to the AB pattern of two sets of doublets centered at  $\delta$  1.59 and 1.84, respectively. The low-field portion of this doublet is partially buried under the broad singlet at  $\delta$  1.94; however, addition of shift reagent resolves this doublet. The relative shift of the 2 and 3 protons (2.5/1) upon addition of  $\text{Eu}(\text{fod})_3$  from their initial positions permits the assignment of proton 2 to the low-field doublet. This is in agreement with the expectation that proton 2 will be deshielded relative to proton 3 by its proximity to the carbonyl function. Spin-decoupling studies show that the 2, 3 protons are strongly coupled and are thus *cis* to one another.

The 10s, 10a protons appear as two sets of a doublet of triplets (AB pattern) centered at  $\delta$  1.13 and 1.32, respectively. Triplet character is due to spin coupling between the equivalent, adjacent bridgehead (6, 9) protons and 10s, 10a protons. Irradiation at  $\delta$  2.82 (bridgehead (6, 9) protons decoupled) reduces the 10s, 10a resonances to a doublet of singlets. The assign-

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ment of the relative positions of the 10s, 10a proton absorptions is based on the observation that decoupling the olefinic protons causes the higher field proton of the (10s, 10a) AB pattern to become more sharply defined. This sharpness arises with loss of stereospecific coupling between the 10a and 7, 8 protons leading to the conclusion that the antibrIDGE proton (10a) absorbs at higher field than does the corresponding *syn* proton. Marchand and Rose<sup>26</sup> have presented a similar interpretation for compound **1**.

The one-proton doublet centered at  $\delta$  0.39 is assigned to proton 5a in agreement with assignments of **1** made by Wege.<sup>29</sup> Irradiation at  $\delta$  2.00 collapses this doublet to a singlet; hence the doublet is assigned to 5a coupled to sterically compressed<sup>30</sup> 5s at  $\delta$  2.00. The unusually large separation (1.61 ppm) observed between the 5s and 5a protons has also been noted by Marchand and Rose<sup>26</sup> for compound **1** ( $\Delta\delta = 1.49$  ppm). We have confirmed<sup>31</sup> the assignments made by Marchand, with switching of the 5s, 5a assignments, by assigning the spectrum of the Diels-Alder adduct derived from 2 mol of cyclopentadiene and 1 mol of norbornadiene. Further confirmation of the assignment of the high-field resonance observed from **1a** to proton 5a derives from the nmr spectrum of hydrogenated ketone **7a**. Saturation of the olefinic bonds of ketone **1a** would eliminate an anisotropic effect from the  $\Delta^7$  bond causing shielded protons to move well downfield. However, the nmr spectrum of **7a** (not shown) does display a one-proton doublet at  $\delta$  0.77, only 0.38 ppm downfield from that observed from ketone **1a**.

Irradiation of ketone **1a** at  $\delta$  0.39 (5a decoupled) converts the broad singlet at  $\delta$  1.94 (5s, 11, 12 protons) into three discernible but poorly resolved absorptions. These additional peaks represent a portion of the coupling between the 11 and 12 protons in addition to the 5s proton. On the basis of available data, however, it is difficult to assign absolutely the couplings responsible for these absorptions. Bridgehead (1, 4) protons are assigned to the two singlet absorptions at  $\delta$  2.30 and 2.07, respectively. These assignments are substantiated by the relative shifts of 3.5/1/2 for protons 1/4/11, 12 upon addition of shift reagent. One would expect the 11, 12 proton chemical shifts to be similar because of their similar environments, both being far removed from the carbonyl function. Also, proton 1, being in a region where the deshielding effect of the carbonyl group is operative, should resonate at a lower field than the 4 proton, as observed.

The olefinic (7, 8) protons appear as a triplet centered at  $\delta$  5.91; decoupling shows that these are coupled to the bridgehead (6, 9) protons located at  $\delta$  2.82. While in principle olefinic protons 7 and 8 of ketone **1a** have different chemical and magnetic environments, they are unresolved at 90 MHz. However, with addition of  $\text{Eu}(\text{fod})_3$  the "back-front" differences of the ketone are enhanced and the two olefinic protons develop a distinct AB pattern with a coupling constant of 5.5 Hz, a reasonable coupling for adjacent, parallel protons.<sup>32</sup>

(29) R. McCulloch, A. R. Rye, and D. Wege, *Tetrahedron Lett.*, **59**, 5163 (1969).

(30) (a) S. Winstein, P. Carter, F. A. L. Anet, and A. J. R. Bourn, *J. Amer. Chem. Soc.*, **87**, 5247 (1965); (b) F. A. L. Anet, A. J. R. Bourn, P. Carter, and S. Winstein, *J. Amer. Chem. Soc.*, **87**, 5249 (1965).

(31) J. Mantzaris and E. Weissberger, *J. Org. Chem.*, **39**, 726 (1974).

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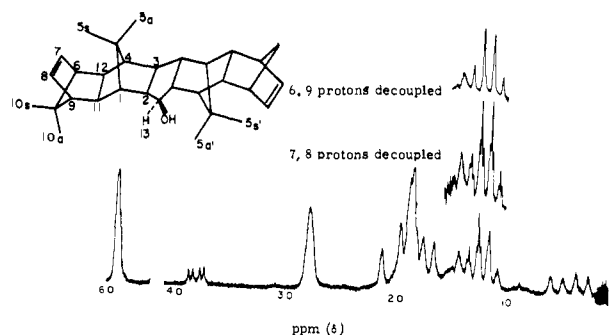


Figure 2. The 90-MHz spectrum of the alcohol.

The coupling between the 1, 2 protons is small; irradiation at  $\delta$  2.30 (proton 1 decoupled) produced no discernible changes in the absorption assigned to proton 2 at  $\delta$  1.84. Therefore, the 1,2 coupling is less than 1.0 Hz. These data imply that the 2, 3 protons are endo with respect to the norbornyl ring and that the molecule has exo carbon-carbon linkages. Thus the exo-trans-exo isomer is assigned as the correct stereochemistry.

In order to obtain further evidence for the symmetric nature of the coupled products, the alcohol of **1a** was prepared and its nmr spectrum analyzed. Ketones having  $C_2$  axes may form but one alcohol, while that belonging to the  $C_1$  point group may form two isomeric alcohols. The nmr spectrum of the ketone reduction product of **1a** is best interpreted as arising from a single, homogeneous product. Moreover, the spectrum of this product differs markedly in only two respects from that of ketone **1a** (Figure 1). Resonances due to the carbinol methine and hydroxy protons appear. The antibridge protons (5a, 5a') no longer have the same chemical shift indicating loss of  $C_2$  symmetry axis.

The 90-MHz spectrum of the alcohol derived from **1a** is shown in Figure 2 and assignments are tabulated in Table III. The two sets of doublets centered at

Table III. Chemical Shift and Coupling Constant Assignments for Alcohol of **1a**

Proton	Chemical shift ( $\delta$ , ppm)	$J$ (Hz)
1	2.10	$J_{2,12}(\text{cis})$ (9.2)
2	1.56	$J_{2',12}(\text{trans})$ (3.5)
3	1.38	$J_{2,3}$ (7.0)
4	1.94	$J_{5a,5a'}$ (10.7)
5a	0.54	$J_{5a',5a'}$ (10.5)
5a'	0.30	$J_{6,10a}$ (1.5)
6, 9	2.88	$J_{7(8),10a}$ (1.0)
7, 8	5.91	$J_{6(9),10a(10a)}$ (1.5)
10a	1.10	
10s	1.29	
13	3.80	
11, 12, 11', 12', 5s, 5s'	1.85	
OH	1.61	

$\delta$  0.30 and 0.54 are assigned to the magnetically non-equivalent 5a and 5a' protons. These two doublets were shown to be independent of one another by their relative behavior upon addition of  $\text{Eu}(\text{fod})_3$ . The underlying cause responsible for the difference in chemical shift of the 5a, 5a' protons must be related to deshielding of proton 5a and shielding of 5a' relative to

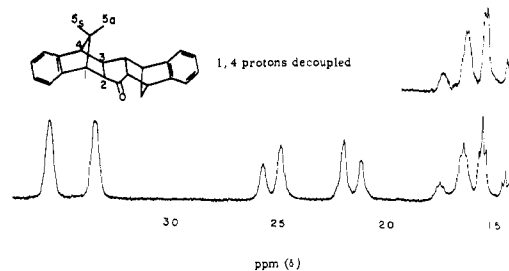


Figure 3. The 90-MHz spectrum of ketone **2a**. Aromatic region not shown.

the corresponding protons of ketone **1a** by the change in location of the oxygen atom. Deshielding effects by near-by oxygen functions have been reported.<sup>30, 33</sup>

The carbinol methine proton appears as a doublet of doublets centered at  $\delta$  3.80 and moves as a single unit upon the addition of  $\text{Eu}(\text{fod})_3$  implying the presence of one compound. Unlike many other systems,<sup>34</sup> cis coupling is greater than trans coupling in five-membered rings. The appearance of the methine proton as a doublet of doublets supports our conclusion that the two norbornyl systems are fused trans to one another. If the rings were cis to one another, a triplet pattern would be observed.

The hydroxyl proton appears at  $\delta$  1.61 and exchanges rapidly with  $\text{D}_2\text{O}$ . Spin-decoupling studies show that the remaining features of the nmr spectrum of the alcohol are substantially similar to those found for ketone **1a**. The large multiplet centered at  $\delta$  1.85 integrates for six protons and is assigned to the 11, 12, 11', 12', and 5s, 5s' protons.

Benzonorbornadiene ketone (**2a**) has been previously discussed<sup>1a, 28</sup> and provides additional conformation for the assignments of **1a**. Our interpretation of exo-trans-exo geometry is identical with that reported<sup>28</sup> by Laszlo; however, we observe resonance for the antibridge proton at  $\delta$  1.51. The data and assignments for **2a** are shown in Figure 3, and Table IV.

Table IV. Chemical Shift and Coupling Constant Assignments for Ketone **2a**

Proton	Chemical shift ( $\delta$ ppm)	$J$ (Hz)
1	3.58	$J_{1(4),5}$ (1.5)
2	2.54	$J_{2,3}$ (7.5)
3	2.17	
4	3.37	
5a	1.51	
5s	1.70	
Ar	7.19	

Spin decoupling shows that the 2, 3 protons at  $\delta$  2.54 and 2.17, respectively, are strongly coupled. The two singlet absorptions at  $\delta$  3.58 and 3.37 are assigned to the bridgehead 1, 4 protons, respectively, and confirmed by studies in the presence of  $\text{Eu}(\text{fod})_3$ . Irradiating either the 1 or the 4 proton reduces the low field AB triplet centered at  $\delta$  1.60, and assigned to the 5a, 5s protons, to an AB pattern of doublets. Thus the pattern of triplets arises from coupling of the 5 protons to the 1, 4 protons.

(33) M. P. Cava and F. M. Scheel, *J. Org. Chem.*, **32**, 1304 (1967).

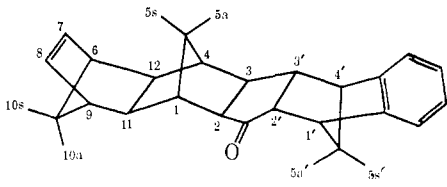
(34) P. Laszlo and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **86**, 1171 (1964).

Inspection of the AB pattern assigned to the 5s, 5a protons shows the low-field portion to be less well defined. The proton resonating at the lower field strength is subject to an additional coupling compared to that of the proton resonating at the higher field strength. The exo-trans-exo stereochemistry is correct for long range coupling between the 5s proton and protons 2 and 3, a coupling which would not be present if the geometry were endo-trans-endo. The 5s proton is therefore assigned to the lower field doublet, an assignment in agreement with Tori's<sup>35</sup> assignments of benzonorborene. The long range coupling assignment is confirmed by decoupling proton 2 or 3. This relationship has been reported for norbornene.<sup>35</sup> In compound **2a** the possibility exists that the carbonyl group may exert a (+)-shielding effect on the 5a proton thereby causing it to absorb at a higher field than the 5s proton, as observed. Models show that the extent of this shielding depends upon the geometry of the cyclopentanone ring. If the ring is twisted slightly from a planar configuration, the possibility of strong shielding becomes plausible.

The nmr spectra of the coupled ketone products from endo- and exo-3,4-benzotricyclo[4.2.1.0<sup>2,5</sup>]nona-3,7-diene, **3a** and **4a**, respectively, indicate the exo-trans-exo geometry, once again. These data will be reported separately.

Assignments of the spectra obtained from the mixed ketone **2ab** are shown in Table V. These assignments

Table V



Proton	Chemical shift ( $\delta$ ppm) <sup>a</sup>	<i>J</i> (Hz)
1, 2, 2', 3', 4, 5s, 11, 12	1.80–2.38	<i>J</i> <sub>5s,5a</sub> (11.0)
1'	3.48	<i>J</i> <sub>10s,10a</sub> (8.0)
4'	3.29	<i>J</i> <sub>5s',5a'</sub> (8.0)
5a	0.40	
3, 5a'	1.50–1.60	
5s'	1.70	
6, 9	2.86	
7, 8	5.91	
10a	1.16	
10s	1.36	
Ar	7.10	

<sup>a</sup> 90 MHz without decoupling.

are in agreement with those for **1a** and **2a**. Once again, exo-trans-exo geometry is observed.

### Experimental Section

All melting points were taken in open capillaries and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 437 spectrophotometer in carbon tetrachloride. Nmr spectra were obtained in CHCl<sub>3</sub> on either a Varian A-60A instrument or a Bruker 90-MHz spectrometer and chemical shifts are reported in parts per million ( $\delta$ ) downfield from an internal tetramethylsilane (TMS) standard. Mass spectra were recorded on a Hitachi-Perkin-

Elmer Model RMU-6L spectrometer. Gas-liquid chromatography (glc) was carried out on a Varian Aerograph Series 1200 flame ionization chromatograph with a 0.125  $\times$  2 ft, 20% SE-30 on 60-80 Chromosorb W column. Analyses were performed by the Eastman Kodak Co., Rochester, N. Y. Solvents were distilled and dried by standard methods prior to use.

**General Procedure for Thermal Coupling of Olefins to Carbon Monoxide.** The general procedure consisted of heating a mixture of the olefin and Fe(CO)<sub>5</sub> (2:1 mol ratio) in a deaerated pressure flask at 85° for 42 hr. The solution was cooled, unreacted Fe(CO)<sub>5</sub> was removed under vacuum, and the crude product was dissolved in chloroform, filtered, chromatographed, and recrystallized. With other carbonyls, *viz.*, Fe<sub>2</sub>(CO)<sub>9</sub> and Fe<sub>3</sub>(CO)<sub>12</sub>, a 5-ml solution of the metal carbonyl and olefin in *n*-octane was used.

**Preparation of Ketone 1a.** Two grams (0.13 mmol) of 1,4,4a-,5,8,8a-hexahydro-1,4,5,8-exo,endo-dimethanonaphthalene<sup>36</sup> (**1**) was placed in a 30-ml annealed Pyrex pressure bottle equipped with a stirring bar. After deaerating with oil-pumped nitrogen for 25 min, 1.37 g (0.007 mol) of Fe(CO)<sub>5</sub> was added.<sup>37</sup> The bottle was sealed and placed in an oil bath, and the solution was stirred for 42 hr at 85°. During this time the appearance of the solution changed from a homogeneous yellow to a heterogeneous black solid mass. After the vessel had been cooled to room temperature and unreacted Fe(CO)<sub>5</sub> removed under vacuum, the crude product was slurried with CHCl<sub>3</sub> and filtered.<sup>11</sup> The filtrate was reduced under vacuum, the residue was redissolved in a minimum volume of chloroform (1 ml), and the solution was chromatographed on a 2  $\times$  20 cm silica gel column (100–200 mesh). Elution with chloroform gave unreacted starting material and **1a**. Recrystallization from benzene gave 1.5 g (70%) of pure **1a**: mp 217–218.5; ir (CCl<sub>4</sub>) 1722 cm<sup>-1</sup> ( $\nu_{C=O}$ ); mass spectrum *m/e*<sup>+</sup> (parent) 344 (calcd 344). *Anal.* Calcd for C<sub>25</sub>H<sub>28</sub>O: C, 87.16; H, 8.19; O, 4.64. Found: C, 87.2; H, 8.5.

**Preparation of 1a Using Fe<sub>2</sub>(CO)<sub>9</sub> and Fe<sub>3</sub>(CO)<sub>12</sub>.** Diene **1** (300 mg, 1.9 mmol) was placed in a 30-ml pressure bottle and deaerated with nitrogen. To the deaerated vessel was added 0.69 g (1.9 mmol) of Fe<sub>2</sub>(CO)<sub>9</sub>; the vessel was sealed and placed in an oil bath, and the mixture was stirred for 42 hr at 85°. The work-up procedure described for the thermal reaction of **1** with Fe(CO)<sub>5</sub> was followed; a 70% yield was obtained. Similarly, Fe<sub>3</sub>(CO)<sub>12</sub> (0.48 g, 0.95 mmol) produced **1a** in 67% yield.

**Hydrogenation of 1a.** A solution of 500 mg (1.5 mmol) of **1a** in 15 ml of THF was hydrogenated in a Brown<sup>2</sup> apparatus using 0.1 *M* sodium borohydride in ethanol. Uptake of sodium borohydride was 2.92 mequiv (5.84 mg). The mixture was filtered, water added, and the product multiply extracted with pentane. The combined pentane extract was dried (MgSO<sub>4</sub>), filtered, and evaporated. Recrystallization from benzene gave 434 mg (86%) of pure saturated ketone **7a**: mp 201.0–202.5°; mass spectrum *m/e*<sup>+</sup> (parent) 349 (calcd 349); nmr (CDCl<sub>3</sub>)  $\delta$  0.77 (d, 2, antibridge, *J* = 10.8 Hz), 2.16–2.40 (m, 4), 2.0–1.0 (m, 26). *Anal.* Calcd for C<sub>25</sub>H<sub>32</sub>O: C, 86.15; H, 9.25; O, 4.59. Found: C, 86.6; H, 8.9.

**Preparation of the Alcohol of 1a.** A solution of 400 mg (1.2 mmol) of **1a** in 25 ml of THF was added to a fivefold excess of LiAlH<sub>4</sub> in 10 ml of THF and the solution refluxed for 6 hr. Excess LiAlH<sub>4</sub> was destroyed; the crude material was filtered and the filtrate reduced under vacuum. Chromatography of the residue on a 2  $\times$  20 cm silica gel column (100–200 mesh) with benzene-dichloromethane (50:50) followed by recrystallization from benzene gave 263 mg (65%) of pure alcohol: mp 195–196.5°; ir (CCl<sub>4</sub>) 3620 cm<sup>-1</sup> (OH); mass spectrum *m/e*<sup>+</sup> (parent) 347 (calcd 347). *Anal.* Calcd for C<sub>25</sub>H<sub>30</sub>: C, 86.66; H, 8.73; O, 4.62. Found: C, 86.9; H, 8.7.

**Reaction of Benzonorborene<sup>38</sup> (2) with the Carbonyls of Iron.** A solution of 2.0 g (14.1 mmol) of **2** was used according to the general procedure. In a typical experiment the products eluted from the silica gel column were benzonorborene hydrocarbon dimer<sup>39</sup> (**2b**), 0.54 g (27%), and benzonorborene ketone dimer (**2a**), 1.25 g (57%). Alternatively, with Fe<sub>2</sub>(CO)<sub>9</sub> the yield of **2b** was less than 1% and that of **2a** was 67%. Dimer **2b**: mp 250–251.5° dec; mass spectrum *m/e*<sup>+</sup> (parent) 284 (calcd 284); nmr (CDCl<sub>3</sub>)  $\delta$  1.61 and 2.03 (AB, 4, *J* = 10 Hz, bridge), 1.71 (s, 4, cyclobutyl), 3.17 (t, 4, *J* = 1.5 Hz, bridgehead), 7.16 (m, 8, aro-

(36) J. K. Stille and D. A. Frey, *J. Amer. Chem. Soc.*, **81**, 4273 (1959).

(37) A 2:1 mole ratio of olefin to Fe(CO)<sub>5</sub> gave best results.

(38) G. Wittig and E. Knauss, *Chem. Ber.*, **91**, 895 (1958).

(39) We have found that the yield of hydrocarbon dimer is not reproducible. Some evidence indicates that the yield of **2b** is dependent upon the method of work-up.

(35) K. Tori, K. Aono, Y. Hata, R. Muneyuki, T. Tsuji, and H. Tanida, *Tetrahedron Lett.*, **9** (1966).

matic). *Anal.* Calcd for  $C_{22}H_{20}$ : C, 92.91; H, 7.09. Found: C, 93.0; H, 6.9. Ketone dimer **2a**: mp 223–224°; ir (CCl<sub>4</sub>) 1722 cm<sup>-1</sup> ( $\nu_{CO}$ ); mass spectrum  $m/e^+$  (parent) 312 (calcd 312). *Anal.* Calcd for  $C_{22}H_{20}O$ : C, 88.43; H, 6.45; O, 5.12. Found: C, 88.5; H, 6.3.

**Preparation of the Alcohol of 2a.** The procedure used was identical with that for the preparation of the alcohol of **1a**. The reduction of 400 mg (1.3 mmol) of **2a** gave 0.27 g (68%) of alcohol: mp 168–169°, ir (CCl<sub>4</sub>) 3350 cm<sup>-1</sup> (broad, OH), 3630 cm<sup>-1</sup> (S, OH); mass spectrum  $m/e^+$  (parent) 314 (calcd 314); nmr (CDCl<sub>3</sub>)  $\delta$  7.1 (m, 8, aromatic), 4.15 (d of d, 1, carbinol methine,  $J_{cis} = 9.0$  Hz,  $J_{trans} = 3.5$  Hz), 1.90 (s, 1, OH). *Anal.* Calcd for  $C_{23}H_{22}O$ : C, 87.86; H, 7.05; O, 5.09. Found: C, 88.3; H, 6.8.

**Reaction of Spiro[2,3-benzonorbornadiene-7,1'-cyclopropane] (5)<sup>40</sup> with Fe(CO)<sub>5</sub>.** A solution of 1.5 g (8.9 mmol) of **5** was treated in the usual manner. The sole product was the ketone dimer **5a**, 0.69 g (42%): mp 234–235.5°; ir (CCl<sub>4</sub>) 1722 cm<sup>-1</sup> ( $\nu_{CO}$ ); mass spectrum  $m/e^+$  (parent) 364 (calcd 364); nmr (CDCl<sub>3</sub>)  $\delta$  0.48 (m, 8, bridge cyclopropyl), 2.86 and 3.03 (s, 2, bridgehead), 2.43 and 2.83 (AB, 4, cyclopentanone,  $J = 8.0$  Hz), 7.06 (m, 8, aromatic). *Anal.* Calcd for  $C_{27}H_{24}O$ : C, 88.97; H, 6.64; O, 4.39. Found: C, 89.2; H, 6.5.

**Reaction of Spiro[2,3-benzonorbornadiene-7,1'-cyclopentane] (6)<sup>41</sup> with Fe(CO)<sub>5</sub>.** A solution of 1.5 g (7.6 mmol) of **6** was reacted in the usual way. After 42 hr no reaction products were found. The infrared spectrum showed the absence of any organic ketonic product and starting material was quantitatively recovered. On the assumption that carbon monoxide pressure might inhibit the formation of ketone, the reaction was run in an open system under an atmosphere of nitrogen. After 42 hr the infrared spectrum did show a band at 1722 cm<sup>-1</sup>; however, the yield was less than 1%.

**Reaction of endo-3,4-Benzotricyclo[4,2,1,0<sup>2,5</sup>]nona-3,7-diene (3)<sup>42</sup> with Fe(CO)<sub>5</sub>.** A solution of 1.5 g (8.9 mmol) of **3** was reacted according to the general procedure. The sole product isolated was the ketone dimer **3a**, 0.19 g (12%): mp 248–249.5°; ir (CCl<sub>4</sub>) 1722 cm<sup>-1</sup> ( $\nu_{CO}$ ); mass spectrum  $m/e^+$  (parent) 364 (calcd 364); nmr (CDCl<sub>3</sub>)  $\delta$  1.47 and 1.73 (AB, 4,  $J = 8.0$  Hz, cyclopentyl). *Anal.* Calcd for  $C_{27}H_{24}O$ : C, 88.97; H, 6.64; O, 4.39. Found: C, 89.0; H, 6.6.

**Reaction of exo-3,4-Benzotricyclo[4,2,1,0<sup>2,5</sup>]nona-3,7-diene (4)<sup>43</sup> with Fe(CO)<sub>5</sub>.** A solution of 1.5 g (8.9 mmol) of **4** was reacted as above with continuous nitrogen degassing. The sole product isolated was ketone dimer **4a**, 0.16 g (10%): mp 275–277°; ir (CCl<sub>4</sub>) 1722 cm<sup>-1</sup> ( $\nu_{CO}$ ); mass spectrum  $m/e^+$  (parent) 364 (calcd 364); nmr (CDCl<sub>3</sub>)  $\delta$  1.89 and 2.13 (AB, 4,  $J = 7.5$  Hz, cyclopentyl). *Anal.* Calcd for  $C_{27}H_{24}O$ : C, 88.97; H, 6.64; O, 4.39. Found: C, 89.0; H, 6.4.

**Reaction of Cyclohexene with Fe(CO)<sub>5</sub>.** A solution of 0.5 g (6.1 mmol) of cyclohexene was reacted in the usual way. After 42 hr an infrared spectrum (CCl<sub>4</sub>) showed the presence of a band at 1720 cm<sup>-1</sup>. No ketonic product was isolated, however. Reaction of cyclohexene with Fe<sub>2</sub>(CO)<sub>9</sub> or Fe<sub>3</sub>(CO)<sub>12</sub> produced the same results. No change was observed upon heating in an open system under an atmosphere of nitrogen. Glc analysis of the reaction mixture showed no well-defined peaks which could be attributed to cyclohexene dimer ketone.

**Reaction of Monoene<sup>44</sup> 7 with Fe(CO)<sub>5</sub>.** A solution of 0.8 g (5.0 mmol) of **7** was reacted in the usual way. The sole product was ketone dimer **7a**, 0.54 g (62%), mp 201–202.5°; the infrared, mass, and nmr spectra were identical with that of ketone derived by hydrogenation of **1a**. *Anal.* Calcd for  $C_{25}H_{32}O$ : C, 86.15; H, 9.25; O, 4.59. Found: C, 86.6; H, 8.9.

**Reaction of Monoene 8<sup>40</sup> with Fe(CO)<sub>5</sub>.** The reaction of a solu-

tion of 0.8 g (5.0 mmol) of **8** was carried out according to the general procedure. Infrared and glc analysis showed the absence of products. Starting material was recovered.

**Reaction of Norbornene with Fe(CO)<sub>5</sub>.** Norbornene (0.5 g, 5.3 mmol) was reacted in the usual manner. Thin-layer chromatography (silica gel–CHCl<sub>3</sub>) showed the presence of four separate products and separation was accomplished by column chromatography on a 2 × 40 cm silica gel column (100–200 mesh). Elution with chloroform gave four products. Mass spectra of the separate fractions gave the following parent peaks in order of elution: 188, 282, 216, and 310. These parent peaks correspond to the hydrocarbon dimer (2%) and trimer (1%) of norbornene, and the ketone dimer (5%) and trimer of (1%) of norbornene, respectively.

**Preparation of Mixed Ketone 2ab.** A solution containing 0.2 g (1.20 mmol) of **1** and 0.18 g (1.20 mmol) of **2** was treated in the usual fashion. After 42 hr glc analysis showed the presence of compounds **1a**, **2a** and a new compound **2ab** in relative amounts of 0.01:2:1. A mass spectrum of the mixture showed the following parent peaks: 344; 312, and 328. The latter parent peak corresponds to mixed dimer ketone **2ab**. The relative yield of **2ab** was increased by increasing the molar ratio of **1**:**2**; A ratio of 5:1 gave relative yields of **1a**:**2a**:**2ab** of 0.1:1:2. Separation by column chromatography proved unsuccessful. Subsequently it was found that fractional crystallization from chloroform gave **2ab** as the first fraction: mp 196–198°; ir (CCl<sub>4</sub>) 1722 cm<sup>-1</sup> ( $\nu_{CO}$ ); mass spectrum  $m/e^+$  (parent) 328 (calcd 328). *Anal.* Calcd for  $C_{24}H_{24}O$ : C, 87.6; H, 7.37; O, 4.69. Found: C, 87.2; H, 7.6.

**General Procedure for Photolysis Reactions of Pentacarbonyliron(0) with Olefins.** Photolysis was performed in a Rayonet Photochemical Reactor (Southern New England Ultraviolet Co., Middletown, Conn.) using R. P. R. -16-8, 3500-Å Rayonet photochemical reactor lamps. The reaction vessel consisted of a Pyrex tube equipped with a bubbler and an outlet so as to maintain either a carbon monoxide or nitrogen atmosphere during the reaction. A cooling fan maintained the temperature within  $\pm 5^\circ$  of room temperature.

Olefin concentrations were 0.1 M in *n*-octane and were deaerated with either nitrogen or carbon monoxide, *vide infra*, prior to the addition of Fe(CO)<sub>5</sub> (0.5 mol) and photolysis. No dark reactions were observed.

Product formation was monitored by glc on a 0.125 in. × 2 ft SE-30 (68–80 Chromosorb W) column using ballistic temperature programming. Peak areas of the products were measured against peak areas of standard solutions of pure compounds. Reproducibility within  $\pm 5\%$  was maintained using an absolute injection technique. Product work-up paralleled the procedure outlined for thermal reactions.

**Photolysis of Fe(CO)<sub>5</sub> with Diene 1.** A 0.13 M solution of **1** (nitrogen atmosphere) was photolyzed according to the general procedure. The solution became heterogeneous in 1 hr. Glc analysis showed the presence of ketone **1a** only; 0.51 g (24%).

**Photolysis of Fe(CO)<sub>5</sub> with Benzonorbornadiene (2).** A 0.12 M solution of **2** (nitrogen atmosphere) containing Fe(CO)<sub>5</sub> was photolyzed in the usual way. After 1 hr of photolysis the solution became heterogeneous. Glc analysis showed the presence of ketone **2a**. Evaporation of the solution produced a brown chloroform soluble residue. Glc analysis of the chloroform solution produced peaks corresponding to ketone **2a** and dimer **2b** in approximately equal amounts. Elution of the residue from a 2 × 20 cm silica gel column (100–200 mesh) yielded 0.37 g of **2a** (17%) and 0.34 g of **2b** (17%).

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(40) J. Ipaktschi, *Chem. Ber.*, **105**, 1989 (1972).

(41) Prepared by the method of Wittig and Knauss;<sup>36</sup> characterized by nmr and mass spectroscopy.

(42) M. D. Cava and M. J. Mitchell, *J. Amer. Chem. Soc.*, **81**, 5409 (1959).

(43) H. E. Simmons, *J. Amer. Chem. Soc.*, **83**, 1657 (1961).

(44) S. B. Soloway, *J. Amer. Chem. Soc.*, **72**, 5612 (1950).