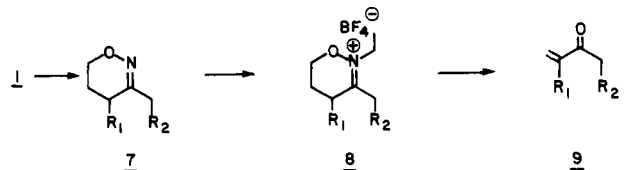
Scheme I



	R_1	R_2
a	$C_6H_5CH_2-$	H
b	H	$C_6H_5CH_2-$
c	$C_6H_5CH_2-$	CH_3-
d	CH_3-	$C_6H_5CH_2-$

We may state the following on the basis of many experiments:[11] At low temperatures, hindered bases remove a proton from **1** more rapidly from the less hindered position, the methyl group; unhindered bases deprotonate at the methylene group. The higher the temperature, the less important steric hindrance is. The removal of a proton from the methyl group is a result of easier approach of the hindered base. Both kinetic and thermodynamic acidity are greater at the 4-methylene position as judged by results of deprotonation with unhindered bases and under conditions in which lithium aggregates are completely dissociated.[10]

In order to illustrate the synthetic usefulness of these findings, we elaborated **1** to the four enones **9a–d** as follows (Scheme I): Deprotonation of **1** with 1 equiv of lithium dimethylamide at −65 °C over 30 s in 1:1 THF–hexane followed by reaction with benzyl bromide over 1 min gave **7a** after workup in 85% yield. Deprotonation of **1** with lithium *tert*-butylisopropylamide for 2 min followed by reaction with benzyl bromide for 1 min yielded 80% **7b**. The monobenzylated products were then subjected to methylation. Compound **7a** was deprotonated with lithium *tert*-butylisopropylamide and **7b** with lithium dimethylamide for 2 min and 30 s, respectively. Compounds **7c** and **7d** were isolated in 80 and 85% yield, respectively, after reaction with methyl iodide.

The procedure for converting **7a–d** to the enones **9a–d** is as follows: Reaction of the oxime ethers with 1 equiv of $Et_3O^+BF_4^-$ in CH_2Cl_2 at room temperature over 30 min gave, after evaporation of solvent and crystallization from Et_2O/CH_2Cl_2, 98% of the oxoiminium salts **8a–d**. Solutions (10% by weight) of the salts in $CHCl_3$ were subjected to reaction with 1 equiv of a 2 M solution of Me_3N in CCl_4 at −65 °C; after 1 min, the $Me_3NH^+BF_4^-$ was filtered off. The solution was allowed to warm up to room temperature and the resulting α,β-unsaturated imines hydrolyzed by passing them through SiO_2 containing 10% water at 0 °C, eluting with a $CHCl_3$/hexane (1:1) solution. The enones were isolated in over 80% yield starting from the oxoiminium salts **8a–d**.

The extremely fast and regioselective lithiation–alkylation reactions here reported and subsequent rapid and simple conversion to enones suggest that **1** may be a generally useful precursor to α-methylene ketones.[12] The selectively formed isomeric lithiated derivatives of **1** can be viewed as synthons for essentially unknown α anions of methyl vinyl ketone.

Acknowledgment. This work was carried out in part at the Pharmazeutisch Chemisches Institute der Universitat Heidelberg (West Germany). We thank Professor R. Neidlein of this institute for his hospitality. We thank also Professor E. M. Kosower for helpful discussions.

(11) More than 200 experiments were carried out in which base solvent and temperatures were systematically varied. The pattern of products variation is quite interesting. Details will be presented in a full publication.

(12) The lithiation–alkylation procedure was applied also to many other alkyl halides, among which are allyl bromide, *n*-propyl iodide, isopropyl iodide, propargyl bromide, and 1,4-diiodobutane. In all these cases, including the isolation, the corresponding enones were obtained. Details will be presented in subsequent publications.

Transition-Metal-Catalyzed Rearrangements of Oxocyclopropanes to Vinyl Ethers. Activation by Vicinal Carboalkoxy Substituents

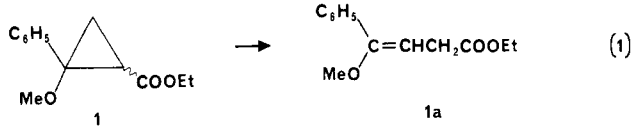
Michael P. Doyle* and Daan Van Leusen

Department of Chemistry, Hope College
Holland, Michigan 49423

Received February 23, 1981

Transition-metal-assisted rearrangements of strained ring organic compounds continue to receive intense examination.[1,2] The underlying basis for these structural transformations, particularly those involving the conversion of cyclopropanes to olefins, is metal insertion into the strained ring. A number of metallocycles formed by metal insertion into a three-membered ring have been isolated,[3] and several derivative η^3-allyl metal complexes have been reported.[4] Ring strain facilitates these reactions,[5] and both electronic and steric factors govern their outcome.[1,6] However, there are few reports of catalytic activity by transition-metal complexes for these structural rearrangements,[7] and although numerous transition-metal-assisted methodologies that would convert cyclopropanes to olefins under mild conditions are available, thermal reactions remain the preferred method[8] for this synthetically useful transformation. Rhodium(I) complexes have thus far exhibited the greatest potential for catalytic cyclopropane to olefin conversions,[7,9] but prior investigations have been limited to ring-opening transformations of vinylcyclopropanes. We have examined catalytic methodologies for the structural rearrangements of a broad selection of readily accessible functionalized cyclopropanes[8,10,11] to their corresponding ring-opened olefinic counterparts, and we now wish to report convenient catalytic methods for the strikingly selective transformation of β-alkoxycyclopropanecarboxylate esters to vinyl ethers.

From an examination of the catalytic effectiveness of a series of transition-metal compounds, $PtCl_2 \cdot 2PhCN$, $[Rh(CO)_2Cl]_2$, and $[Ru(CO)_3Cl_2]_2$ were determined to be of comparable activity. Nearly quantitative conversion of **1** to **1a** (eq 1) occurred within



(1)

1 h at 70 °C with 2.5 mol % of these catalysts, whereas there was

(1) (a) Bishop, K. C., III. *Chem. Rev.* **1976**, *76*, 461–486. (b) Halpern, J. In "Organic Syntheses via Metal Carbonyls"; Wender, I.; Pino, P., Eds.; Wiley: New York, 1977; Vol. II, pp 705–730. (c) Tolman, C. A. In "Transition Metal Hydrides"; Muetterties, E. L., Ed.; Marcel Dekker: New York, 1971; pp 271–312.

(2) Sarel, S. *Acc. Chem. Res.* **1978**, *11*, 204–211.

(3) (a) Casey, C. P.; Scheck, D. M.; Shusterman, A. J. *J. Am. Chem. Soc.* **1979**, *101*, 4233–4236. (b) Rajaram, J.; Ibers, J. A. *Ibid.* **1978**, *100*, 829–838. (c) Cushman, B. M.; Brown, D. B. *J. Organomet. Chem.* **1978**, *152*, C42–C44. (d) Al-Essa, R. J.; Puddephatt, R. J.; Quyser, M. A.; Tipper, C. F. H. *Ibid.* **1978**, *150*, 295–307. (e) Brown, D. B.; Viens, V. A. *Ibid.* **1977**, *142*, 117–121. (f) Johnson, B. F. G.; Lewis, J.; Tam, S. W. *Ibid.* **1976**, *105*, 271–279.

(4) (a) Tulip, T. H.; Ibers, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 4201–4211. (b) *Ibid.* **1978**, *100*, 3252–3254.

(5) (a) Sohn, M.; Blum, J.; Halpern, J. *J. Am. Chem. Soc.* **1979**, *101*, 2694–2698. (b) Hogeveen, H.; Nusse, B. J. *Tetrahedron Lett.* **1973**, 3667–3670. (c) Roth, R. J.; Katz, T. J. *J. Am. Chem. Soc.* **1972**, *94*, 4770–4771. (d) Gassman, P. G.; Armour, E. A. *Tetrahedron Lett.* **1971**, 1431–1431. (e) Hogeveen, H.; Volger, H. C. *Chem. Commun.* **1967**, 1133–1134.

(6) Kozikowski, A. P.; Wetter, H. F. *Synthesis* **1976**, 561–590.

(7) Salomon, R. G.; Salomon, M. F.; Kachinski, J. L. C. *J. Am. Chem. Soc.* **1977**, *99*, 1043–1054.

(8) Wenkert, E. *Acc. Chem. Res.* **1980**, *13*, 27–31.

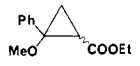
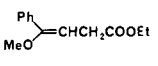
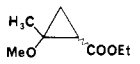
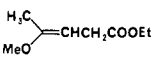
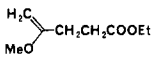
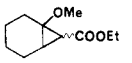
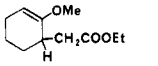
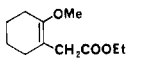
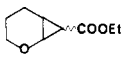
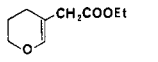
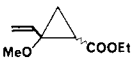
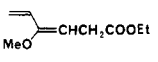
(9) (a) Voigt, H. W.; Roth, J. A. *J. Catal.* **1974**, *33*, 91–97. (b) Russell, R. K.; Wingard, R. E.; Paquette, L. A. *J. Am. Chem. Soc.* **1974**, *96*, 7483–7491. (c) Barnett, K. W.; Beach, D. L.; Garin, D. L.; Kaempfe, L. A. *Ibid.* **1974**, *96*, 7129–7128. (d) Grigg, R.; Hayes, R.; Sweeney, A. *J. Chem. Soc., Chem. Commun.* **1971**, 1248–1249.

(10) Doyle, M. P.; van Leusen, D.; Tamblyn, W. H. *Synthesis* **1981**, in press.

(11) Danishefsky, S. *Acc. Chem. Res.* **1979**, *12*, 66–72.

0002-7863/81/1503-5917$01.25/0

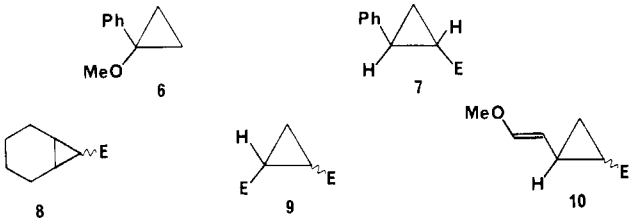
Table I. Product Yields from Transition-Metal-Catalyzed Rearrangements of β-Alkoxycyclopropanecarboxylate Esters[a]

	reactant	product	$PtCl_2 \cdot 2PhCN$[b] yield, % (a/b)	$PtCl_2 \cdot 2PhCN$[b] rxn time, min	$[Rh(CO)_2Cl]_2$[c] yield, % (a/b)	$[Rh(CO)_2Cl]_2$[c] rxn time, min	Cu bronze[d] yield, % (a/b)	Cu bronze[d] rxn time, min
1		1a 	98	10	98	60	97	5
2		2a 	70 (1.0)	30	92 (1.0)	60	83 (1.0)	150
		2b 						
3		3a 	98 (2.0)	20	98 (1.7)	60	94 (1.7)	10
		3b 						
4		4a 	86	60			80	240
5		5a 	30[g]	30	46[h]	60	(40)[i]	120

[a] Reactions performed on neat reactant. Yields were determined for products isolated by distillation. [b] 100 °C; 0.5–1.0 mol % catalyst. [c] 110 °C; 0.5 mol % catalyst. [d] Reflux temperature; 10–20 mol % catalyst. [e] Z/E ratio = 1.0. [f] Z/E ratio = 1.4. [g] Contains less than 2% ethyl 4-methoxy-2,4-hexadienoate. [h] Contains 6% ethyl 4-methoxy-2,4-hexadienoate; reaction performed in toluene. [i] Compounds 5b and 5c; contains less than 10% 5a.

no identifiable conversion of **1** to **1a** with 5 mol % of $Rh_2(OAc)_4$, CuCl, $MoBr_2$, $PdCl_2 \cdot C_7H_8$, or $(Ph_3P)_2Ir(CO)Cl$ under identical conditions. These reactions were performed with undiluted reactant without noticeable loss of reactant and products as a result of competing reactions, and **1a** did not exhibit a tendency for carbon–carbon double-bond migration. The addition of 2 equiv of triphenylphosphine, based on catalyst, quenched any further reaction and facilitated the isolation of the ring-opened products. Compounds **2–5** (Table I) were also specifically converted to their corresponding vinyl ethers, but structural rearrangement of these compounds generally required higher temperatures.[12] The use of a reaction solvent, typically toluene, did not generally improve product yields and did not affect product ratios (a/b).

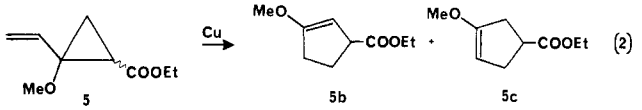
Cyclopropane derivatives analogous to compounds **1–5**, but lacking either the alkoxy group or the carboethoxy group (**6–10**, E = COOEt), were inert to ring opening under reaction conditions



identical with those reported in Table I, even after prolonged reaction times. These results were surprising since electronic influences from cyclopropane substituents on metal insertion into the carbon–carbon σ bond have been generally regarded to be unidirectional: electron-donating cyclopropane substituents such as phenyl promote metal insertion whereas electron-withdrawing substituents inhibit this process.[13,14] However, although phenyl activates the cyclopropane ring for catalytic ring opening relative to methyl (**1** vs. **2**), it is the combination of vicinal alkoxy and carboalkoxy cyclopropane substituents that is essential for this catalyzed rearrangement. In the ring-opening process alkoxy and carboalkoxy substituents exhibit opposing electron-donor capacities that can be expected to facilitate rearrangement. Similar activation by vicinal electron-donor and -acceptor substituents should find applications in a variety of bond reorganization processes.[15]

Copper compounds have generally been considered to be relatively ineffective in structural rearrangements of strained ring compounds.[1] We were therefore surprised to discover that copper bronze effectively catalyzed the conversions of β-alkoxycyclopropanecarboxylate esters to vinyl ethers, albeit at relatively high temperatures (Table I). In the absence of a catalyst these cyclopropane compounds were generally inert to ring opening at their boiling points. In the presence of 15 mol % of copper bronze, **1** was converted to **1a** in nearly quantitative yield after 6 h at 160 °C, whereas no ring opening of **1** occurred without a catalyst under these same conditions. Copper(I) chloride was even more active than copper bronze as complete conversion of **1** to **1a** (70% yield) was realized within 2 h at 160 °C (10 mol % CuCl). In contrast, rhodium(II) acetate catalysis of this same transformation occurred at 135 °C and was complete within 2 h. Thus a broad spectrum of transition-metal compounds are effective catalysts for structural rearrangements of these cyclopropane compounds, and the copper catalysts are both convenient and economical for synthetic applications of these transformations.

The action of copper catalysts on **5** results in products that either are not observed or are produced as only minor constituents in the platinum(II), rhodium(I), or rhodium(II) catalyzed reactions. With either copper bronze or copper(I) chloride, **5** undergoes predominant ring expansion at 160 °C to the isomeric 3-methoxy-2-cyclopentenecarboxylate and 3-methoxy-3-cyclopentenecarboxylate esters[16] (eq 2, **5b**/**5c** = 2), whereas the platinum and



(2)

rhodium compounds catalyze the conversion of **5** to **5a**.[17] This

(12) With prolonged reaction times **5a** isomerized to the conjugated ester, ethyl 4-methoxy-2,4-hexadienoate. Similar rearrangements of **1a**, **2a**, **3b**, and **4a** were not observed.

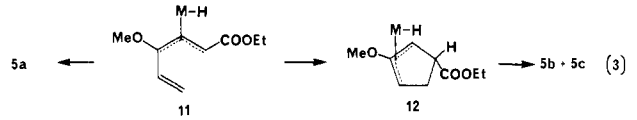
(13) McQuillan, F. J.; Powell, K. G. *J. Chem. Soc., Dalton Trans.* **1972**, 2123–2129; *Tetrahedron Lett.* **1971**, 3313–3316.

(14) Benson, D. B. *J. Organomet. Chem.* **1970**, *24*, 787–790.

(15) The apparent allylic C–H insertion of a carbenoid species generated by metal catalyzed decomposition of diazo compounds is consistent with this consideration. For reviews and prior interpretations of this insertion process, see: (a) Alonso, M. E.; Gomez, M. *Tetrahedron Lett.* **1979**, 2763–2766. (b) Wulfman, D. S.; Linstrumelle, G.; Cooper, C. F. In "The Chemistry of Diazonium and Diazo Groups"; Patai, S., Ed.; Wiley: New York, 1978; Chapter 18.

(16) Acid catalyzed hydrolysis converted these vinyl ethers to 3-(carboethoxy)cyclopentanone exclusively.

dichotomy and the production of both **5b** and **5c**, rather than only the vinylcyclopropane–cyclopentene[18] rearrangement product **5c**, is consistent with the generation of **12** from the initially formed[4] η^3-allyl metal hydride complex **11** (eq 3). The formation of **12**



and subsequent production of **5b** and **5c** are presumed to be competitive with the generation of **5a** from **11** in the copper catalyzed reactions. Further extensions of these and related transformations are currently being investigated in our laboratory.

Acknowledgment. The support of this research by the National Science Foundation is gratefully acknowledged.

Supplementary Material Available: Experimental details for the preparation of vinyl ethers from oxocyclopropanes as well as pertinent physical properties and NMR data for **1a–5a** (3 pages). Ordering information is given on any current masthead page.

(17) **5b,c** are not formed from **5a**, and **5c** is not converted to **5b** under the reaction conditions employed.

(18) (a) Hudlicky, T.; Koszyk, F. F.; Kutchan, T. M.; Sheth, J. P. *J. Org. Chem.* **1980**, *45*, 5020–5027. (b) Muralkami, M.; Nishida, S. *Chem. Lett.* **1979**, 927–930. (c) Alcock, N. W.; Brown, J. M.; Conneely, J. A.; Williamson, D. H. *J. Chem. Soc., Perkin Trans. 2* **1979**, 962–971.

syn- and *anti*-Norcaradieneiron Tricarbonyl

Wolfram Grimme* and Hans Günter Köser

Institut für Organische Chemie der Universität Köln
D-5000 Köln, Federal Republic of Germany

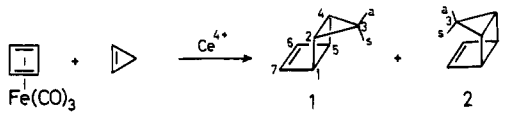
Received March 30, 1981

The bicyclo[4.1.0]hepta-2,4-diene structure, commonly known as norcaradiene, does not possess a particularly high strain or electronic energy but still lacks molecular reality. Its illusiveness is attributed to the easy valence isomerization to cycloheptatriene, which is well documented for some of its derivatives.[1] Although the energy difference between the two valence isomers seems to have been overestimated,[2] there is no clear evidence for an equilibrium concentration of norcaradiene in cycloheptatriene.

Several unstable structures have been isolated as ligands in transition-metal complexes, and in the case of norcaradiene the iron tricarbonyl group seems an especially fitting partner. From a number of cycloocta-1,3,5-triene–bicyclo[4.2.0]octa-2,4-diene equilibria the less stable bicyclic component is complexed by this group either selectively[3] or via isomerization of the monocyclic ligand.[4] Cycloheptatriene, however, only yields the monocyclic iron tricarbonyl complex[5] and so does a 7,7-disubstituted derivative[6] with a high equilibrium concentration of the norcaradiene isomer. It has been postulated[6] that *anti*-norcaradieneiron tricarbonyl is less stable than the cycloheptatriene complex and is an intermediate in the rapid 1,3-metal shift of the latter.

Cyclooctatetraene, whose equilibrium concentration of bicyclo[4.2.0]octa-2,4,7-triene is well established,[7] also gives only the monocyclic iron tricarbonyl complex,[8] but the syn and anti complex of its bicyclic valence isomer have been obtained via ring opening of *anti*- and *syn*-tricyclo[4.2.0.$0^{2,5}$]octa-3,7-dieneiron tetracarbonyl.[9] The bicyclooctatriene complexes do not rearrange to the more stable cyclooctatetraene complex even at 60 °C; evidently the iron tricarbonyl group effectively blocks the ring opening of the ligand that in the free form occurs at −20 °C.[10]

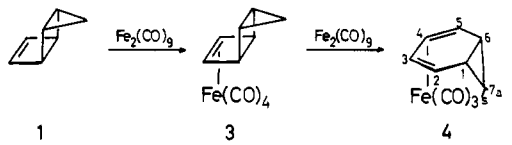
We patterned our synthesis of the norcaradieneiron tricarbonyls upon these results. The required valence isomer of norcaradiene with a contracted cyclohexadiene ring, i.e., tricyclo[3.2.0.$0^{2,4}$]-hept-6-ene, was built up as mixture of the anti and syn stereoisomer **1** and **2** in a straightforward way by Diels–Alder reaction of cyclopropene with cyclobutadiene: Cyclobutadieneiron tri-



carbonyl[11] (0.66 equiv) is added to an ice cold 0.3 M solution of cyclopropene[12] in 95% aqueous acetone, and 2.5 equiv of ceric ammonium nitrate are added over a period of 10 min. After the usual workup, using butane as extractant, the cycloadducts are obtained in a 47% yield with a syn–anti ratio of 1.3:1 and are isolated by VPC (20% bis(β-cyanoethyl) ether on kieselguhr, 2.5 m × 0.64 cm, 62 °C, 30 mL of He/min). **1**:[13] 6.6 min; ^{1}H NMR (CCl_4) δ 6.40 (narrow m, H-6, -7), 2.87 (narrow m, H-1, -5), 1.80 (m, H-2, -4), 1.13 (q, J = 4.8 Hz, H-3a), 0.88 (narrow m, H-3s); ^{13}C NMR ($CDCl_3$) δ 143.0 (C-6, -7), 48.2 (C-1, -5), 23.7 (C-2, -4), 20.0 (C-3). **2**:[13] 12.8 min; ^{1}H NMR (CCl_4) δ 5.70 (s, H-6, -7), 3.07 (d, J = 5 Hz, H-1, -5), 1.45 (t, J = 5 Hz, H-2, -4), 1.08 (d, J = 5 Hz, H-3s), 0.28 (q, J = 5 Hz, H-3a); ^{13}C (C_6D_6) δ 134.6 (C-6, -7), 38.8 (C-1, -5), 6.8 (C-2, -4), 4.6 (C-3).

The anti configuration of the adduct **1** is derived from the shielding of the allylic protons H-1, -5 as well as from their small coupling constant (<1 Hz) with the tertiary cyclopropane protons H-2, -4.[14] In the syn stereoisomer **2** the allylic protons adsorb at a 0.2 ppm lower field and couple strongly with the tertiary cyclopropane protons. The deshielding of the *syn*-cyclopropane proton is unexpected and may arise from steric compression that overcompensates the shielding by the double bond.

Stirring a 0.1 M pentane solution of **1** at room temperature successively with two 1.5 equiv portions of diiron nonacarbonyl gives after chromatographic workup on alumina with hexane a 14% yield of *anti*-tricyclo[3.2.0.$0^{2,4}$]hept-6-eneiron tetracarbonyl (**3**):[13] ^{1}H NMR (C_6D_6) δ 3.75 (s, H-6, -7), 2.49 (narrow m, H-1,



-5), 1.75 (m, H-2, -4), 0.90 (q, J = 5 Hz, H-3a), 0.69 (m, H-3s) followed by a 50% yield of *syn*-norcaradieneiron tricarbonyl (**4**):[13] mp −5 °C; ^{1}H NMR (C_6D_6) δ 4.48 (AA′ part of AA′XX′ system, J(2,3) = 5.99 Hz, J(2,4) = 1.11 Hz, J(2,5) = 0 Hz, J(3,4) = 3.74 Hz, H-3, -4), 3.15 (XX′ part, H-2, -5), 0.19 (m, H-1, -6, -7a), −0.10 (m, H-7s); ^{13}C NMR (C_6D_6) δ 212.4 (CO), 84.9 (^1J = 173.3

(1) (a) Görlitz, M.; Günther, H. *Tetrahedron* **1969**, *25*, 4467. (b) Ciganek, E. *J. Am. Chem. Soc.* **1971**, *93*, 2207.

(2) Warner, P. M.; Lu, S.-L. *J. Am. Chem. Soc.* **1980**, *102*, 331.

(3) (a) Cotton, F. A.; Deganello, G. *J. Am. Chem. Soc.* **1973**, *95*, 396. (b) Graham, C. R.; Scholes, G.; Brookhart, M. *Ibid.* **1977**, *99*, 1180.

(4) (a) Manuel, T. A.; Stone, F. G. A. *J. Am. Chem. Soc.* **1960**, *82*, 6240. (b) McFarlane, W.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1963**, 2162. (c) Brookhart, M · Lippman, N. M.; Reardon, E. J. *J. Organomet. Chem.* **1973**, *54*, 247.

(5) (a) Burdon, R.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1961**, 594. (b) Dauben, H. J.; Bertelli, D. J. *J. Am. Chem. Soc.* **1961**, *83*, 497.

(6) Karel, K. J.; Brookhart, M. *J. Am. Chem. Soc.* **1978**, *100*, 1619.

(7) Huisgen, R.; Boche, G.; Dahmen, A.; Hechtl, W. *Tetrahedron Lett.* **1968**, 5215.

(8) (a) Rausch, M. D.; Schrauzer, G. N. *Chem. Ind. (London)* **1959**, 957. (b) Manuel, T. A.; Stone, F. G. A. *J. Am. Chem. Soc.* **1960**, *82*, 366. (c) Dickens, B.; Lipscomb, W. N. *J. Chem. Phys.* **1962**, *37*, 2084.

(9) Slegeir, W.; Case, R.; McKennis, J. S.; Pettit, R. *J. Am. Chem. Soc.* **1974**, *96*, 287.

(10) Vogel, E.; Kiefer, H.; Roth, W. R. *Angew. Chem.* **1964**, *76*, 432; *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 442.

(11) Pettit, R.; Henery, J. *Org. Synth.* **1970**, *50*, 21.

(12) Closs, G. L.; Krantz, K. D. *J. Org. Chem.* **1966**, *31*, 638.

(13) Satisfactory elemental analyses and/or exact mass molecular weights were obtained on all new compounds.

(14) Cf. the small coupling of the allylic protons in *anti*-tricyclo-[4.3.0.$0^{7,9}$]nona-2,4-diene.[4c]

0002-7863/81/1503-5919$01.25/0