238. The Photoisomerization of 1,2,3,4,5-Pentamethyl-5-vinyl-1,3-cyclopentadiene

by **Ulrich Burger*** and **Robert Etienne**

Department of Organic Chemistry, University of Geneva, CH-1211 Geneva 4

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Summary

The title compound **1** is shown to give, both upon direct irradiation at 254 nm and upon acetophenone-sensitized photolysis at 300 nm, the *syn*-vinyl-pentamethylhousene **5**, which spontaneously rearranges in a [3,3]-sigmatropic process to give the bicyclo[3.2.0]heptadiene skeleton **2**. Based on the photochemical behaviour of selectively deuterated starting material, the suggestion is made that the direct photolysis produces the vinylhousene skeleton by a classic electrocyclization, whereas the sensitized reaction reaches the same target *via* a di-π-methane rearrangement. The bicyclo[3.2.0]heptadiene derivative **2** gives pentamethylhomoprismane **3** upon prolonged irradiation at 254 nm.

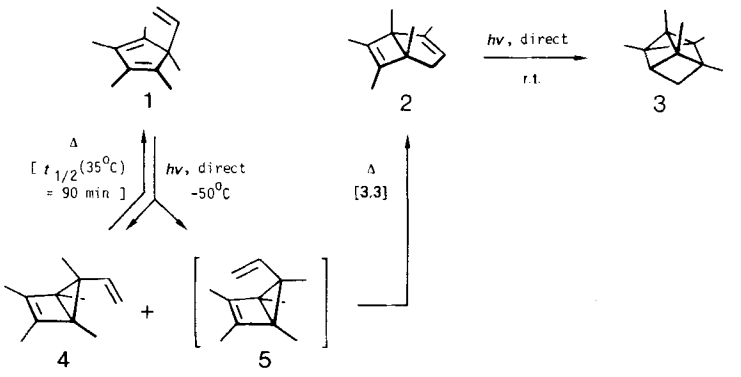
Exploiting the particular geometry of symmetrical cyclopentadiene derivatives, we recently have been able to uncover unusual pathways and details of intramolecular reactions [1]. Continuing our studies in this area, we have examined the photochemical behaviour of the cross-hyperconjugate π-system of symmetrical vinylcyclopentadiene and wish to report here on our findings.

Results and Discussion of Photochemical Processes. – Irradiation of the title compound **1** [2] in hexane with light of 254 nm gives, at room temperature, 1,2,5,6,7-pentamethylbicyclo[3.2.0]hepta-2,6-diene (**2**) and the homoprismane derivative **3**. The ratio of these isomers **2** and **3** decreases with increasing irradiation time. Independent examination proved that compound **2** gives **3** under the reaction conditions by means of intramolecular photoaddition [3]. The isomerization **1**→**2** + **3** can be brought nearly to completion at room temperature. At −50°C, however, it becomes extremely slow after some 50% conversion. ^{1}H-NMR analysis of the photoproducts obtained at −50°C after 30% conversion of **1** to **2** revealed the presence of still another isomeric hydrocarbon, namely *anti*-1,2,3,4,5-pentamethyl-5-vinylbicyclo[2.1.0]pent-2-ene (**4**)[1]). This *anti*-vinylhousene[1]) decays in a dark reaction with a half-life of 90 min at +35°C to give the

[1]) The descriptors *syn* and *anti* indicate that the substituent with highest priority at C(5) is oriented towards and off the C(2),C(3) branch, respectively.

starting cyclopentadiene derivative **1**[2]). The corresponding *syn*-vinylhousene[1]) **5**, the key intermediate, is not seen in the ^{1}H-NMR spectra at room temperature. It obviously is intercepted *in situ* by a *Cope* rearrangement[3]) and clearly is the precursor of the bicyclo[3.2.0]heptadiene **2** *(Scheme 1)*.

Scheme 1



Irradiation of a hexane solution of **1** in a *Pyrex* vessel with light of 300 nm and in presence of acetophenone as triplet sensitizer (E_T = 73.7 kcal/mol) again gave compound **2**, accompanied, however, by large amounts of polymeric material. Long irradiation times (*ca.* 15 h) were required to obtain compound **2** in some 35% yield, which amounts to the maximum that could be achieved. A control experiment (*Pyrex*, 300 nm) run without sensitizer gave unchanged **1** and some polymer, but virtually no compound **2**.

These findings suggest that both, the direct irradiation and the sensitized reaction produce *syn*-vinylhousene **5** (and subsequently compound **2**), but by entirely different pathways. Indeed, a classic electrocyclization (**1**→**5**) [6] and a di-π-methane rearrangement implicating the vinyl group (**1**→**5**) can be invoked [7].

In order to get further insight into the reaction mechanism, we have prepared the pentamethyl-5-vinylcyclopenta-1,3-diene **6** deuterated to some 75–80% at all allylic positions, but virtually undeuterated at CH_3–C(5) *(vide infra)*. This latter group thus serves as a label for our purposes. Direct irradiation of **6** gave bicyclo[3.2.0]heptadiene **8**, which was fully protonated at CH_3–C(2) *(Scheme 2)*. This result is in agreement with the electrocyclization mechanism. During the valence isomerization **6**→**7**, the proton label remains in the C_s-plane, which happens to be the permanent symmetry element of both this reaction and the corresponding recycling process of the *anti*-vinylhousene (*i.e.* **1**→**4**→**1**). For geometric reasons, the label is insensitive to a superimposed walk-rearrangement [8].

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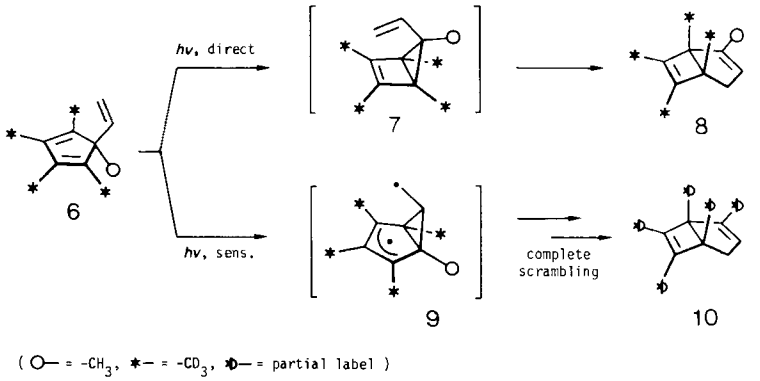
[2]) *Note added in proof.* Careful ^{1}H-NMR integration reveals that compound **4** does not quantitatively return to **1**. Some 6% is converted into **2**.

[3]) A closely related *Claisen* rearrangement of *syn*-5-acetylhousene is known [4]. A corresponding photocycloreversion has also been observed [5].

Scheme 2

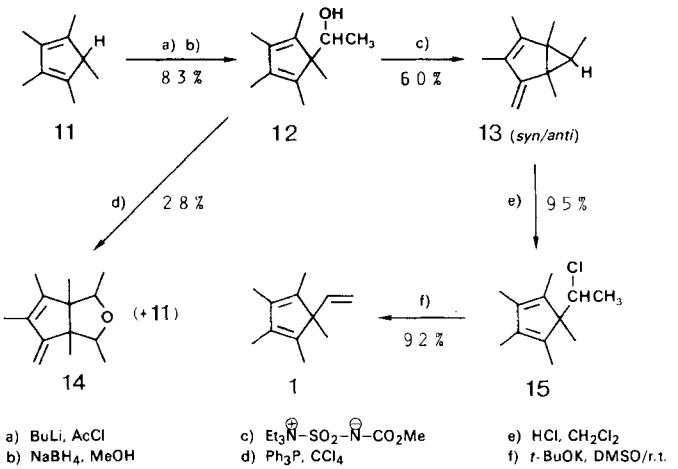


The sensitized reaction of **6**, however, gave bicyclo[3.2.0]hepta-2,6-diene **10** in which the label was completely scrambled over all methyl positions. Scrambling was also observed in the starting material recovered (20%) from this experiment. Precise information about the mechanism of the sensitized reaction, thus, is over-shadowed by a fast superimposed rearrangement. Since triplet sensitization does not normally bring about [1,3]- or [1,5]-sigmatropic shifts [9] (*i.e.* independent scrambling in the starting material), the suggestion is made, that the scrambling observed is directly connected with the di-π-methane rearrangement itself. Indeed, in the diradical **9** resulting from initial diene-vinyl bonding the CH_3 group becomes equivalent with a CD_3 group (for the direct observation of diradicals in the di-π-methane rearrangement, see [10]). Efficient return from this or any later stage to the starting material can account for our observations. Moreover, the intermediate **9**, in contrast to **7**, is not insensitive to a walk-rearrangement [11]. Finally it should be mentioned that compound **1** has an exocyclic free rotor, notorious for efficient triplet-energy dissipation [7a]. This accounts for the low chemical yield of the sensitized process.

Synthesis of 1,2,3,4,5-Pentamethyl-5-vinyl-1,3-cyclopentadiene (1) and Its Selective Deuteration. Compound **1** has previously been obtained in a reaction sequence starting from hexamethyl-*Dewar*-benzene [2]. For economic reasons, we attempted and accomplished its preparation starting from pentamethylcyclopentadiene (**11**) [12] *(Scheme 3)*. The two-carbon side chain was introduced by standard methods [13] to give the neopentyl-type alcohol **12** [14]. Dehydration of **12**, however, met with difficulties. It gave, under various conditions, the epimeric homofulvenes **13** (*syn*/*anti*) [15]. This is exemplified in *Scheme 3* for the use of *Burgess'* method [16]. Conversion of alcohol **12** into its chloride **15** [2b] turned out also to be difficult. Reaction with PPh_3 and CCl_4, for instance, which normally allows the transformation of neopentyl-type alcohols into their chlorides [1], gave a 1:1 mixture of the bicyclic ether **14** and pentamethylcyclopentadiene (**11**). Clearly, the two-carbon side chain was cleaved off in this reaction and transferred to a second molecule of the starting alcohol.

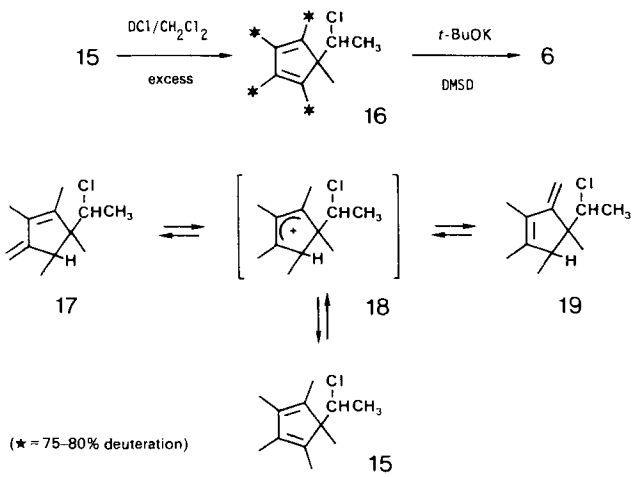
Addition of HCl to the homofulvenes **13** (*syn*/*anti*), on the other hand, was known [17a] to give the 5-(1-chloroethyl)-1,2,3,4,5-methyl-1,3-cyclopentadiene (**15**). The final β-elimination to **1** was achieved at room temperature by use of *t*-BuOK in dimethyl sulfoxide.

Scheme 3



When we added a twofold excess of DCl in CH_2Cl_2 to the homofulvenes **13** (*syn*/*anti*), we became aware of an unexpectedly large deuterium incorporation in the resulting chloride. The MS showed unambiguously that up to 12 D-atoms per molecule had been incorported. Detailed studies revealed that all allylic H-atoms of **15** undergo rapid isotopic exchange at room temperature upon repetitive treatment with 0.5M DCl in CH_2Cl_2. Exchange at CH_3–C(5) of **15** becomes detectable only after a long reaction time and at high acid concentrations. Based on this large kinetic exchange effect, we prepared the chloride **16** labelled to 75–80% at the allylic positions, but virtually unlabelled (< 5%) at CH_3–C(5). The final β-elimination under the thermally mild conditions mentioned above proceeded smoothly without [1,5]-sigmatropic scrambling [18] and gave the selectively deuterated vinyl compound **6** *(Scheme 4)*.

Scheme 4



The excessive deuterium exchange can most conveniently be rationalized in terms of a fast equilibration between the three tautomers **15**, **17**, and **19**. The mechanism proposed in *Scheme 4* finds corroboration in the work of *Hogeveen & Kwant* [17a] who observed the intermediate allylic cation **18** directly by low-temperature ^{1}H-NMR spectroscopy. Moreover, the chloride **17** was found to give **15** upon treatment with HCl. From the low exchange rate at CH_3–C(5), we can safely conclude that the principal exchange mechanism does not imply bridged carbocations.

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Experimental Part

General Remarks. Direct photolyses in quartz vessels with internal cooling were carried out in a *Srinivasan-Griffin* photochemical reactor *(Rayonet RPR-100)* equipped with *RPR* lamps 2537 Å. Sensitized reactions were run in *Pyrex* vessels with internal cooling in the same photoreactor equipped, however, with *RPR* lamps 3000 Å. Sensitizers were applied in 5 mol-% concentration. Prior to irradiation, the solutions were deoxygenated by flushing with N_2 for 20 min. A positive pressure of N_2 was maintained throughout the irradiations. Gas chromatography: anal. and semiprep. GC on *Carlo-Erba Fractovap F-2150* on glass columns. UV spectra: *Beckmann-Acta-III* spectrometer; in hexane; λ_{max} [nm] (log ε), sh = shoulder. MS [*m*/*z*]: *Varian-MAT-CH4* spectrometer, electron impact (70 eV). ^{1}H-NMR spectra: δ[ppm] relative to internal TMS; *J*[Hz] apparent scalar coupling constant; *Varian-XL-100*-FT-NMR spectrometer operating at 100.1 MHz or *Bruker-WM-360* pulse spectrometer operating at 360.1 MHz. ^{13}C-NMR spectra: δ[ppm] relative to internal TMS; *Bruker-WM-360* pulse spectrometer operating at 90.56 MHz.

1,2,5,6,7-Pentamethylbicyclo[3.2.0]hepta-2,6-diene (**2**) *and 1,2,3,4,6-Pentamethyltetracyclo[3.1.1.0^{2,4}.0^{3,6}]-heptane* (**3**) *by Direct Photolysis of* **1**. A solution of **1** [2] (195 mg, 1.2 mmol, UV (hexane): 241 (4.70), 259 (sh)) in 150 ml of hexane was irradiated at 25° in a quartz vessel with light of wavelength 254 nm. The reaction was monitored by GC (*SE-30*, 5% on *Chromosorb*, 2-m glass column, oven temp. (max.) 120°). After 3 h, **1** had nearly disappeared. The solvent was removed *i.v.* at r.t. Flash distillation of the crude products at 10^{-4} Torr gave 168 mg (86% yield) of a 3.2:1 mixture of **2**/**3**. Their separation was achieved by prep. GC (*SE-30*, 5% on *Chromosorb*, 6-m glass column, oven temp. 120°); relative retention time: **3** (0.47), **2** (0.77), and **1** (1.00). Compound **2**: colourless oil. ^{1}H-NMR (360 MHz, $CDCl_3$): 1.00 (*s*, CH_3–C(5)); 1.08 (*s*, CH_3–C(1)); 1.51 (*q*, ^5J(homoallyl) = 1.2, CH_3–C(6) or CH_3–C(7)); 1.58 (*q*, ^5J(homoallyl) = 1.2, CH_3–C(7) or CH_3–C(6)); 1.69 (*m*, CH_3–C(2)); 1.89, 2.27 (*m*(*AB*), ^2J = 16.5, CH_2); 5.15 (narrow *m*, H–C(3)). ^{13}C-NMR (90.56 MHz, $CDCl_3$): 7.7, 10.1, 13.6, 14.7, 19.1 (5*q*, CH_3); 37.8 (*t*, C(4)); 52.2, 61.6 (*s* and *s* (uncertain), C(1) and/or C(5)); 121.9 (*d*, C(3)); 140.6, 146.2, 146.6 (3*s*, C(2), C(6), C(7)).

Compound **3**: colourless oil, acid sensitive. ^{1}H-NMR (360 MHz, $CDCl_3$): 0.79, 1.01, 1.07, 1.09, 1.13 (5*s*, 5 CH_3); 1.35 (*dd*, ^2J = 8.6, ^3J = 2.8, H_{eq}–C(7)); 1.70 (*d*, ^2J = 8.6 H_{ax}–C(7)); 2.45 (*d*, ^3J = 2.8, H–C(5)).

The procedure described above was also applied for the synthesis of *1,2,5,6,7-[1,5,6,7-D_3]Pentamethylbicyclo[3.2.0]heptadiene* (**8**) from *1,2,3,4,5-[1,2,3,4-D_3]Pentamethyl-5-vinyl-1,3-cyclopentadiene* (**6**). Irradiation time, however, was reduced to 1 h. The isotopic distribution both in recovered **6** and in **8** prepurified by flash distillation at 10^{-4} Torr, was determined before and after GC separation by ^{1}H-NMR spectroscopy at 360 MHz. GC did not bring about further rearrangement (the bicyclo[3.2.0]hepta-2,6-diene skeleton can, in principle, undergo a degenerate *Cope* rearrangement [19]).

anti-*1,2,3,4,5-Pentamethyl-5-vinylbicyclo[2.1.0]pent-2-ene*[1]) (**4**). A solution of **1** (194 mg, 1.2 mmol) in 150 ml of hexane was irradiated at −50° (quartz vessel, 254 nm). After 1 h, the solvent was rapidly removed under high vacuum at 0° and replaced by $CDCl_3$. ^{1}H-NMR analysis (100.1 MHz at 35°) showed, after a set-up time of *ca.* 5 min, the following product composition: **1** (37.5%), **2** (30.5%), **3** (< 3%), and **4** (29.0%). The disappearance of **4** and the concomitant increase of the resonances of **1** was monitored in the NMR spectrometer. **4**: ^{1}H-NMR (100.1 MHz, $CDCl_3$): 1.21 (*s*, CH_3–C(1), CH_3–C(4)); 1.26 (*s*, CH_3–C(5)); 1.51 (*s*, CH_3–C(2), CH_3–C(3)); 5.01, 5.03, 5.72 (*ABM*, $^3J_{cis}$ = 10.2, $^3J_{trans}$ = 17.5, ^2J = 2.5, CH_2=CH).

syn- *and* anti-*1,2,3,5,6-Pentamethyl-4-methylidenebicyclo[3.1.0]hex-2-ene*[4]) (**13**) *from* **12**. A solution of **12** (1.0 g, 5.6 mmol) [14] in 25 ml of THF was added slowly at r.t. to a solution of *Burgess'* reagent ($Et_3NSO_2NCO_2CH_3$; 1.4 g, 5.9 mmol) [16] in 25 ml of THF and brought to reflux for 45 min. After addition of

[4]) The descriptors *syn* and *anti* refer to the orientation of CH_3–C(6) with respect to the main branch.

Et_2O (150 ml), the mixture was washed (3 × H_2O, 1 × sat. aq. NaCl) and dried ($MgSO_4$). Solvent removal *i.v.* followed by flash distillation gave 544 mg (60% yield) of **13** (*syn*/*anti* 0.35) identical by ^{1}H-NMR with an authentic sample [15].

1,2,4,5,6,7-Hexamethyl-8-methylidene-3-oxabicyclo[3.3.0]oct-6-ene (**14**; configuration at C(2) and C(4) unknown). A solution of **12** (1.0 g, 5.6 mmol) and Ph_3P (1.5 g, 5.8 mmol) in 8 ml of CCl_4 was brought to reflux for 20 min, diluted with Et_2O (10 ml) and filtered. The solvents were removed *i.v.* Distillative prepurification (120–150°/12 Torr) followed by column chromatography (silica gel, hexane/Et_2O 6:1) gave **11** (129 mg, 34%), identical by ^{1}H-NMR with authentic material [12], and **14** (162 mg, 28% yield). **14**: colourless liquid. UV (pentane): 243 (3.83). ^{1}H-NMR (100.1 MHz, $CDCl_3$): 1.00 (*s*, CH_3–C(1), CH_3–C(5)); 1.16 (*d*, ^3J = 6.5, CH_3–C(2) or CH_3–C(4)); 1.20 (*d*, ^3J = 6.5, 3H, CH_3–C(4) or CH_3–C(2)); 1.69, 1.73 (2 narrow *m*, CH_3–C(6), CH_3–C(7)); 3.43 (2 superimposed *q*, ^3J = 6.5 each, H–C(2), H–C(4)); 4.42, 4.48 (2 br. *s*, CH_2=C). MS: 206, 162, 147. Anal. calc. for $C_{14}H_{22}O$ (206.33): C 81.55, H 10.68, O 7.77; found: C 81.77, H 10.70, O 7.53.

Conversion of 5-(1-Chloroethyl)-1,2,3,4,5-pentamethyl-1,3-cyclopentadiene (**15**) *to* **1** (same procedure for conversion of **16** to **6**). A solution of **15** (4.0 g, 20 mmol) [2b] in 75 ml of DMSO and 10 ml of Et_2O was added slowly under Ar to *t*-BuOK (2.96 g, 26.4 mmol) in 75 ml of DMSO and stirred for 12 h at 25°. After addition of Et_2O (200 ml), the mixture was washed to neutrality and the org. layer dried over $MgSO_4$. Removal of the solvent *i.v.* followed by flash distillation at 10^{-4} Torr gave **1** (2.98 g, 92% yield), identical by ^{1}H-NMR with an authentic sample [2].

Selective Deuterium Exchange, 5-(1-Chloroethyl)-1,2,3,4,5-[1,2,3,4-D_3]pentamethyl-1,3-cyclopentadiene (**16**) *from* **15**. A solution of **15** (300 mg, 1.5 mmol) [2b] in 10 ml of CH_2Cl_2 was combined at 0° with 0.5M DCl in CH_2Cl_2 (40 ml, 20 mmol) and stirred at r.t. for 5 h. The mixture was washed rapidly with 2M aq. NH_3 at 0°, H_2O, and a sat. aq. NaCl sol. and then dried over $MgSO_4$. After removal of the solvent *i.v.*, this exchange procedure was repeated twice again. Finally, the crude **16** was purified by flash distillation at 10^{-3} Torr (yield 278 mg, 91%). ^{1}H-NMR integration at 360 MHz ($DCCl_3$) showed, in agreement with the isotope-shift effects, an average of 75–80% deuteration in the four allylic positions at 1.65, 1.70, 1.76, and 1.85 ppm. The *s* of CH_3–C(5) at 1.10 ppm had lost less than 5% of its intensity compared with the intact CH_3CH_2Cl–C(5) (1.04 (*d*) and 4.12 (*q*, ^3J = 6.7)).

REFERENCES

[1] *U. Burger, G. Gandillon & J. Mareda,* Helv. Chim. Acta *64,* 844 (1981).

[2] a) *W. Schäfer & H. Hellmann,* Angew. Chem. *79,* 566 (1967); b) *M. Kunz & W. Lüttke,* Chem. Ber. *103,* 315 (1970).

[3] *Cf. A.R. Brember, A.A. Gorman & J.B. Sheridan,* Tetrahedron Lett. *1973,* 481.

[4] *B.C. Baumann, M. Rey, J. Markert, H. Prinzbach & A.S. Dreiding,* Helv. Chim. Acta *54,* 1589 (1971).

[5] *H. Hart, S.M. Chen & M. Nitta,* Tetrahedron *37,* 3323 (1981).

[6] *J.I. Brauman, L.E. Ellis & E.E. van Tamelen,* J. Am. Chem. Soc. *88,* 846 (1966); ibid. *93,* 6145 (1971).

[7] a) *H.E. Zimmerman,* in 'Rearrangements in Ground and Excited States', Vol.3, ed. P. de Mayo, Academic Press, New York, 1980, p.131; b) *H. Hart & M. Nitta,* Tetrahedron Lett. *1974,* 2113.

[8] *G.D. Andrews & J.E. Baldwin,* J. Am. Chem. Soc. *99,* 4851, 4853 (1977); *R.F. Childs,* Tetrahedron *38,* 567 (1982); *F.G. Klärner & F. Adamsky,* Chem. Ber. *116,* 299 (1983); *F.G. Klärner,* Topics in Stereochemistry *15,* 1 (1984).

[9] *N.J. Turro,* 'Modern Molecular Photochemistry', Chap.12, Benjamin-Cummings Publishing Co., Inc., Menlo Park, 1978.

[10] *M. Demuth, W. Amrein, C.O. Bender, S.E. Braslavsky, U. Burger, M.V. George, D. Lemmer & K. Schaffner,* Tetrahedron *19,* 3245 (1981).

[11] *R. Sustmann & F. Lübbe,* Chem. Ber. *112,* 42 (1979).

[12] *R.S. Threlkel & J.E. Bercaw,* J. Organomet. Chem. *136,* 1 (1977).

[13] *R.F. Childs & M. Zeya,* J. Am. Chem. Soc. *96,* 6418 (1974).

[14] *U. Burger, A. Delay & F. Mazenod,* Helv. Chim. Acta *57,* 2106 (1974).

[15] *R. Criegee, H. Grüner, D. Schönleber & R. Huber,* Chem. Ber. *103,* 3696 (1970).

[16] *E.M. Burgess, H.R. Penton, Jr., & E.A. Taylor,* J. Org. Chem. *38,* 26 (1973); Org. Synth. *56,* 40 (1976).

[17] a) *H. Hogeveen & P.W. Kwant,* J. Org. Chem. *39,* 2624 (1974); ibid. *39,* 2626 (1974); b) *H. Hogeveen & E.M.G.A. van Kruchten,* Topics Curr. Chem. *80,* 89 (1979).

[18] *G.W. Spangler,* Chem. Rev. *76,* 187 (1976); *R.J. Bushby & D.W. Jones,* J. Chem. Soc., Chem. Commun. *1979,* 688.

[19] *E.W. Otterbacher & J.J. Gajewski,* J. Am. Chem. Soc. *103,* 5862 (1981).