Table I

time, h	CN-DMANO[a]	CN-DMA[a]	CN-NMA[a]	BZALD[a]	oxidative balance[b]
3.0	−0.8	0.72	0.01	0.60	−0.19
17.3	−1.7	1.64	0.04	1.24	−0.42
45.0	−10.8	10.63	0.13	9.00	−1.63

[a] Nanomoles consumed (−) or produced (+) per nanomole of Cr(TPP)Cl. [b] Until the reaction is complete, as much as 1 equiv of oxygen may be sequestered on the porphyrin.

cholesterol by cytochrome P-450$_{SCC}$.[10] Cleavage of the cholesterol side chain is the first step in the biosynthesis of steroid hormones and the primary regulatory site in steroidogenesis[11] during which cytochrome P-450$_{SCC}$ carries out three successive oxidations of cholesterol, with 22(R)- and 20-α-hydroxylations producing a vicinal diol oxidatively cleaved in the third step[10,12] at the expense of atmospheric dioxyygen and two reducing equivalents.

The title reaction was initiated by the addition of CN-DMANO to a CH_3CN solution of Cr(TPP)Cl and PED[13] and was monitored by HPLC and quatitated by integration of the UV chromatogram. The results of a typical experiment are presented in Table I. Glycol cleavage was stoichiometric at all time points. The endpoint oxidation balance showed 10.8 equiv of CN-DMANO consumed and 9.0 equiv of benzaldehyde (BZALD) produced. The competing N-demethylation reaction is minor (0.1 equiv of 4-cyano-N-methylaniline, CN-NMA) with 1.7 equiv of oxidation potential unaccounted for. All of the N-oxide consumed can be accounted for as 4-cyano-N,N-dimethylaniline (CN-DMA, 10.6 equiv) and CN-NMA. In contrast to the complete reaction mixture, omission of either CN-DMANO or CrTPPCl resulted in no detectable cleavage of PED.

Cr(TPP)Cl was chosen as a model metalloporphyrin for this study because it forms a spectrally defined, stable complex with an oxygen atom, oxo(5,10,15,20-tetraphenylporphinato)chromium (oxo-(TPP)Cr).[2,14] That this oxometalloporphyrin complex is the active species in diol cleavage was suggested by separation of the overall process into two sequential steps: transfer of an oxygen atom from CN-DMANO to Cr(TPP)Cl and the subsequent reaction of the oxo-(TPP)Cr with PED to cleave the diol and regenerate Cr(TPP)Cl. Addition of CN-DMANO to a solution of Cr(TPP)Cl in CH_2Cl_2[13] resulted in the rapid spectral transition shown in Figure 1, which is consistent with the spectrum of the compound generated from Cr(TPP)Cl and iodosobenzene and identified as oxo(5,10,15,20-tetraphenylporphinato)chromium(IV).[14] HPLC analysis of an aliquot of the mixture after addition of oxidant showed that N-demethylation occurred at a slow but significant rate during formation of oxo-(TPP)Cr, explaining the residual Cr(TPP)Cl seen in the optical spectrum. When decay of the spectrum indicated that the velocity of N-demethylation now exceeded the velocity of oxygen transfer, diol clevage was initiated by addition of PED. Concomitant with formation of benzaldehyde, the spectrum of Cr(TPP)Cl was regenerated. In our hands the rate of cleavage of PED by Cr(TPP)Cl is slightly higher than the rate of the corresponding alkene epoxidation reaction in which styrene oxide is produced from styrene.

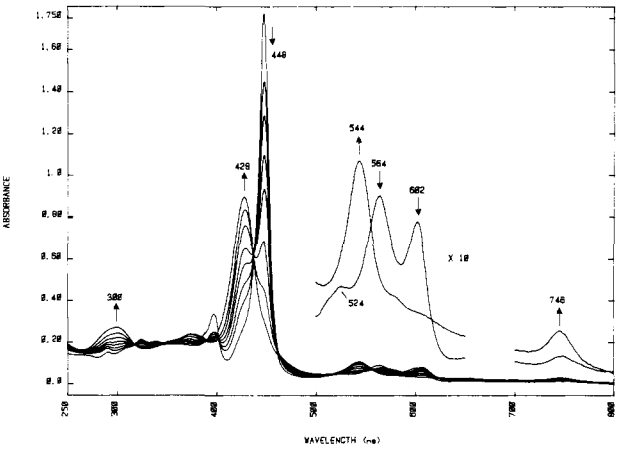

Figure 1. Formation of oxo(5,10,15,20-tetraphenylporphinato)chromium. One equivalent of CN-DMANO was added to Cr(TPP)Cl (8 μM) in CH_2Cl_2. Initial spectrum is prior to addition of CN-DMANO; arrows indicate direction of change with time following addition of CN-DMANO. The expanded sensitivity (500–650, 700–800 nm) shows the initial and final (60 min) spectra.

The exogenous oxidant supported cleavage of the vicinal diol PED by Cr(TPP)Cl is an example of a previously unrecognized reactivity of metalloporphyrins. That the oxene complex, oxo-(TPP)Cr, is the probable reactive species for glycol cleavage in this model system extends the role of these metalloporphyrins as models for cytochrome P-450 monoxygenases to include those enzyme systems that catalyze the oxidative cleavage of vicinal diols. These studies are currently being expanded to include Fe^{III}- and Mn^{III}(TPP)Cl and a variety of aryl and alkyl diol substrates. Together with Cr(TPP)Cl, these porphyrins may well provide a simplified model system for studying the mechanism of cytochrome P-450$_{SCC}$ catalyzed conversion of cholesterol to pregnenolone.

(10) Shimizu, K.; Gut, H.; Dorfman, R. I. *J. Biol. Chem.* **1962**, *237*, 699–702.
(11) Stone, D.; Hechter, O. *Arch. Biochem. Biophys.* **1954**, *51*, 457–469.
(12) Burstein, S.; Gut, M. *Steroids* **1976**, *28*, 115–131.
(13) Experimental section: (i) The reaction mixture for multiple turnover reactions consisted of Cr(TPP)Cl (100 μM), PED (30mM), and CN-DMANO (1.2 mM) in 300 μL of CH_3CN. Reactions were carried out at 23 °C under a nitrogen atmosphere. HPLC analyses were on a 30 cm × 4 mm MCH-10 (octadecylsilane, Varian) column eluted with a CH_3CN/H_2O gradient (10% initially, 15-min ramp to 45%, 10-min ramp to 100%; elution times, PED, 11.4 min; CN-DMANO, 17.4 min; Bzald, 22.6 min; CN-NMA, 23.6 min; CN-DMA, 25.4 min). Elution was monitored at 258 nm, and peak areas were calibrated with multiple runs of standards. No secondary oxidants (cyanoaniline, benzoic acid) were detected. (ii) The reaction mixture for spectral analysis of the oxo-(TPP)Cr intermediate consisted of Cr(TPP)Cl (8 μM) and CN-DMANO (8 μM) in 3 mL of CH_2Cl_2. The spectrum of the Cr(TPP)Cl solution was recorded after which reaction was initiated by addition of CN-DMANO in a minimum volume (2.4 μL). The solution was mixed by rapid inversion nd the spectrum was recorded at intervals (10 s for the first 10 min, 1 min thereafter) on a Hewlett-Packard Model 8450A diode-array spectrophotometer. When the oxo-(TPP)Cr concentration reached a maximum, the cleavage reaction was initiated by addition of PED (2.4 mM). Reaction progress was monitored spectrally during the 48 h required to complete the reaction. HPLC analyses were performed on aliquots of the reaction mixtures concentrated 30-fold under nitrogen.
(14) Groves, J. T.; Kruper, W. J., Jr.; Haushalter, R. C.; Bulter, W. A. *Inorg. Chem.* **1982**, *21*, 1363–1368.

Cumulene Photochemistry: Evidence for *cis*- and *trans*-Cyclopropylidene Intermediates in Triplet Photoreactions of 1,2-Cyclodecadiene

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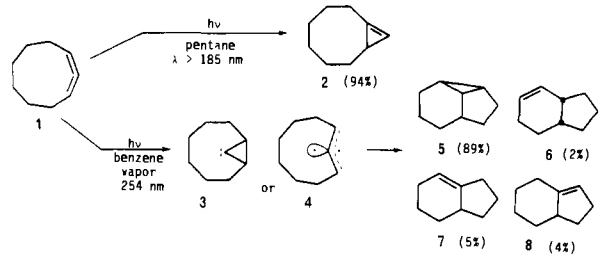
We have previously reported that direct irradiation of 1,2-cyclononadiene (**1**) affords predominantly cyclopropene **2**.[1] Independent generation of potential vinylcarbene intermediates led to arguments for a concerted [$_\sigma 2_a + {}_\pi 2_a$] mechanism.[1] Vapor-phase triplet rearrangement of **1** to **5** was suggested by Ward and



(1) (a) Stierman, T. J.; Johnson, R. P. *J. Am. Chem. Soc.* **1983**, *105*, 2492. (b) Small amounts (ca. 3% each) of cyclononyne and **5** also are observed at low conversion.[3]

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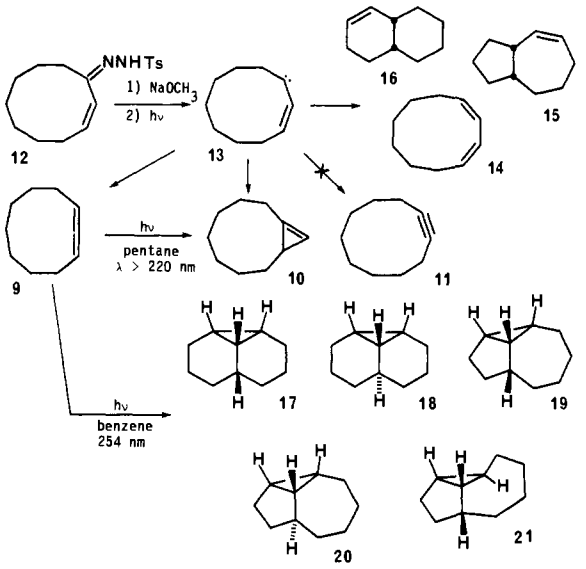
Scheme I



Karafiath[2] to require triplet cyclopropylidene **3**. However, minor triplet products **6–8** implicate competitive 1,3-biradical pathways.[3] Planar triplet allene **4** also must be considered a potential progenitor of **5–8**.

We report here on photoreactions of homologue 1,2-cyclodecadiene (**9**). Results for **9** suggest that ring strain in **1**[4] does not strongly affect its singlet rearrangement mechanism. Triplet reactions of allene **9** afford a remarkable collection of new C_{10} tricyclic hydrocarbons, which apparently result from two stereoisomeric cyclopropylidenes.

Direct irradiation of dilute pentane solutions of **9**[5] (Scheme I) yielded, at low conversion (<1%), cyclopropene **10** and cyclodecyne (ratio 5:1) as primary photoproducts.[6,7] At higher conversions, a complex product mixture resulted from secondary reactions of **10**. As in our earlier study,[1] independent generation[8] of **13**, the likely result of 1,2-hydrogen shift, yielded (70%) a number of isomeric products (**9**, **10**, **14**, **15**, **16**, ratios 11:21:9:46:9), but no alkyne **11**. Significantly, both transannular insertion products **15** and **16** have cis stereochemistry, which implies concerted insertion by a singlet vinylcarbene. Singlet photoreactions of **9** thus differ little from those of more highly strained homologue **1**.[1,3] Vinylcarbene **13** is an unlikely intermediate, and we favor a concerted mechanism.[1]

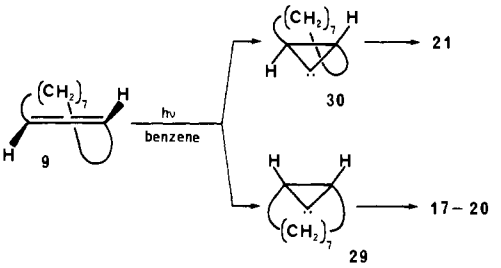
Benzene-sensitized irradiation of **9** in the vapor phase (ca. 0.15 torr) reproducibly yielded a complex product mixture (Scheme I).[9,10] Capillary GLC–MS showed all products to be isomeric (*m/e* 136) with **9**; structures **17–21** were assigned to the five major products (ratios 23:14:27:18:14 by GLC), based upon spectral[11] and chemical data.

Two of the major triplet photoproducts displayed six ^{13}C NMR resonances, consistent with assignment as symmetrical structures **17** or **18**. Hydrogenation of **18** afforded[12a] *trans*-decalin (**25**). Cis isomer **17** was reduced under more vigorous conditions[12b] to a mixture of **25** and *cis*-decalin (**26**). Under these conditions, **26** is converted to **25**.[12c] The reluctant, yet regioselective, hydrogenation of **17** is attributed to minimal strain and to steric inaccessibility of the C_1–C_9 bond.[13] The remaining three major products displayed 10 ^{13}C resonances; all were hydrogenated to *trans*- or *cis*-decahydroazulenes (**27** or **28**, respectively). Trans isomer **20** led cleanly[12a] to **27**, while **19** was slowly reduced[12b] to **28**. The similar hydrogenation behavior of **17** and **19** argues for like (cis) stereochemistry.

Unexpectedly, a second photoproduct, **21**, also was reduced[12a] to *cis*-decahydroazulene (**28**). Assignment as structure **21** was further supported by the ^1H NMR spectrum, which displays a resonance (1 H) at −0.9 ppm. From molecular models, this is assigned as H_1, which should be bent into the cyclopropane ring anisotropic shielding region. This compound contains a *trans*-bicyclo[5.1.0]octane fragment.[14]

Irradiation of **9** in benzene solution yielded the same products but in different ratios (26:6:14:10:41 for **17–21**). Remarkably, the major product was highly strained trans isomer **21**. No evidence was observed by NMR or GLC for significant cycloadduct formation. Under identical conditions, allene **1** yielded only ca. 1% of **5** and >30% of cycloadducts.[3,15] The absence of cycloadducts of **9** with benzene is at present inexplicable.[16]

Triplet solution and vapor-phase reactions of **9** thus afford stereoisomeric pairs of tricyclics, whose likely progenitors are *cis*- and *trans*-cyclopropylidenes **29** and **30**. In principle, nonvertical



energy transfer from triplet benzene ($E_T \sim 3.7$ eV) could result in triplet cyclopropylidene (ca. 3.4 eV above allene) or planar triplet allene (ca. 2.2 eV).[3] Present results favor the higher energy cyclopropylidene pathway. Preference for closure to trans structure **30** in solution is tentatively attributed to minimization of hydrogen motion and deformation of the methylene skeleton in three-membered ring formation, during triplet energy transfer from

(2) Ward, H. R.; Karafiath, E. *J. Am. Chem. Soc.* **1969**, *91*, 7475.

(3) Stierman, T. J.; Johnson, R. P. *J. Am. Chem. Soc.*, in press.

(4) Angus, R. O., Jr.; Schmidt, M. W.; Johnson, R. P. *J. Am. Chem. Soc.* **1985**, *107*, 532–537. The allenic moiety in **1** is predicted to be bent ca. 10° due to ring constraints. Models show that **9** should be unstrained.

(5) Moore, W. R.; Bertelson, R. C. *J. Org. Chem.* **1962**, *27*, 4182.

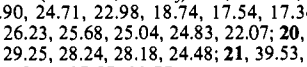
(6) (a) Isomers **10** and **11** were isolated by preparative GLC.[7] Spectral data for **10** were similar to those for **2**.[1] Cyclodecyne was prepared as previously reported: Brandsma, L.; Verkruijsse, H. D. *Synthesis* **1978**, 290. (b) Satisfactory combustion analyses or high-resolution mass spectra were obtained for new compounds.

(7) Preparative separations were performed with a glass 15% Carbowax on Chromosorb W column (10 ft × 0.25 in.) at 90 °C. Analytical separations employed a 25-m Carbowax capillary column at 60 °C.

(8) Tosylhydrazone **12** (mp 116–119 °C) was prepared (45% yield) from cyclodecenone in standard fashion. Isomers **15** and **16** were identified by their spectral data and by hydrogenation to the known cis bicyclic skeletons. An authentic sample of **14** was prepared by base isomerization of **10**.

(9) In a typical experiment, a mixture of allene **9** (500 mg) and benzene (200 mg) in an evacuated (0.15 torr) Vycor tube was irradiated for 3 days in a Rayonet reactor (254 nm). Capillary GLC analyses[7] of the isolated product mixture (445 mg) indicated 77% conversion, with **17–21** accounting for >95% of products.[10] In other runs, product ratios proved invariant to conversion. In preparative separations, isomers **17**, **18** and **20** were resolved, while **19** and **21** were collected as a mixture. A pure sample of **19** was obtained by selective hydrogenation of **21**.

(10) (a) Minor products (ca. 5% total) in triplet reactions are believed to be alkenes **22–24**. Spectral data were in agreement with a previous report.[10b]



(b) Becker, K. B. *Helv. Chim. Acta* **1977**, *60*, 68.

(11) ^{13}C NMR data (74 mHz, $CDCl_3$): **17**, δ 26.95, 21.76, 19.42, 17.12, 11.33, 8.01; **18**, 33.90, 24.71, 22.98, 18.74, 17.54, 17.34; **19**, 39.66, 30.96, 30.11, 27.98, 26.59, 26.23, 25.68, 25.04, 24.83, 22.07; **20**, 44.96, 41.48, 33.39, 32.60, 29.73, 29.44, 29.25, 28.24, 28.18, 24.48; **21**, 39.53, 36.60, 34.90, 33.50, 32.74, 32.08, 30.52, 28.11, 27.57, 22.77.

(12) (a) H_2 (1 atm), Pd/C, 25 °C, 0.5 h. (b) H_2 (3 atm), Pd/C, 50 °C, 0.5–2 days. (c) Allinger, N. L.; Coke, J. L. *J. Am. Chem. Soc.* **1959**, *81*, 4080.

(13) Regioselective hydrogenolysis has ample precedent: Osawa, E.; Musso, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 1 and references therein.

(14) (a) Kirmse, W.; Hase, Ch. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 891. (b) Wiberg, K. B.; DeMeijere, A. *Tetrahedron Lett.* **1969**, 519. (c) Gassman, P. G.; Williams, F. J.; Seter, J. *J. Am. Chem. Soc.* **1968**, *90*, 6893.

(15) Berridge, J. C.; Forrester, J.; Foulger, B. E.; Gilbert, A. *J. Chem. Soc., Perkin Trans. 1* **1980**, 2425.

(16) Precedent for ring size disparity exists in other benzene cycloadditions. Cyclohexene does not cycloadd to benzene, whereas cyclopentene, -heptene, etc. do cycloadd: Bryce-Smith, D.; Foulger, B.; Forrester, J.; Gilbert, A.; Orger, B. H.; Tyrrell, H. M. *J. Chem. Soc., Perkin Trans. 1* **1980**, 55.

benzene. Although cyclopropylidene is predicted to have a singlet ground state,[3] the cis and trans tricyclic pairs **17**,**18** and **19**,**20** which are observed here provide argument for a stepwise triplet process, indicating that spin inversion must be slow relative to hydrogen abstraction.

We are continuing to study the mechanism of this reaction, as well as its potential for the synthesis of other novel polycyclic hydrocarbons.

Acknowledgment. We are grateful to the National Science Foundation for support of this research.

Evidence for the Hydride Abstraction Mechanism in the C–H Insertion Reaction as Illustrated in the Reaction of Secondary Alkoxide with Alkylidenemethylene Carbenoid

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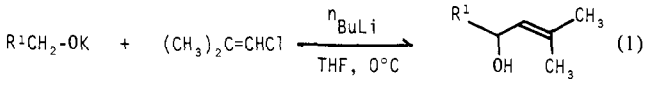
We report here the evidence for hydride abstraction–recombination mechanism in the carbenic C–H insertion reaction of alkoxides obtained by the stereochemical investigation[1] of alkylidenemethylene carbenoid ($R^1R^2C{=}C{:}\cdots MX$)[2] insertion into α-C–H bond of secondary alkoxides.

In an examination of the oxy anionic effect on the selective C–H insertion,[3] alkylidenemethylene carbenoid was inserted into the α-C–H bond of alkoxides regioselectively, as illustrated by the exclusive formation of insertion product **3** in the reaction of potassium primary alkoxide (**1**) with 1-chloro-2-methylpropene (**2**) (2.0 equiv) by the action of *n*-BuLi (2.0 equiv) in THF at 0 °C for 10 min (eq 1).

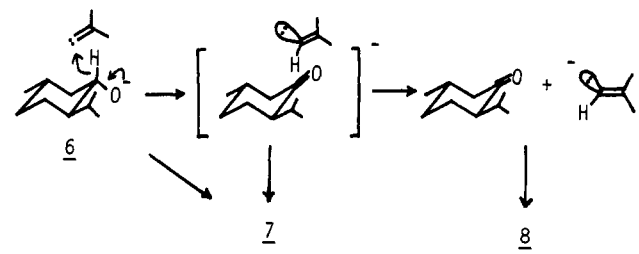


1a-d 2 3a-d

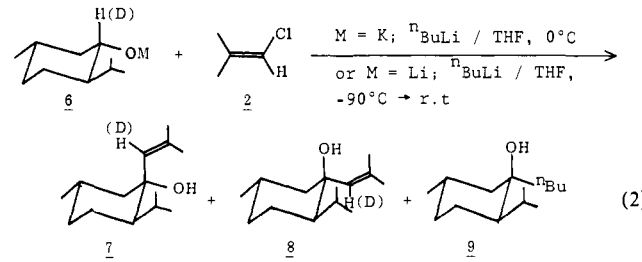
a, $R^1 = C_6H_5CH_2$, Y; 67% (42% conversion); b, $R^1 = C_6H_5$, Y; 61% (62% conversion); c, $R^1 = n\text{-}C_7H_{15}$, Y; 50% (50% conversion); d, $R^1 = 2,4,6\text{-}Me_3C_6H_2$, Y; 64% (34% conversion)

On the other hand, secondary alkoxides behaved differently and rendered important evidence for the insertion mechanism. Thus, when potassium cyclohexyl oxide was treated with **2** under similar conditions, 1-butylcyclohexanol (**5**, 17%) was obtained together with the insertion product **4** (41% yield, 43% conversion). The formation of **5** strongly suggests the intermediacy of cyclohexanone, which is most likely produced from the alkoxide by the hydride abstraction by isopropylidenemethylene carbenoid.[4] The formation of **4** is also explainable in terms of the same hydride abstraction mechanism in which the insertion may proceed nonstereospecifically. To examine this, we chose menthyl oxide (**6**) as a suitable substrate, since we found in separate experiments that menthone undergoes an exclusive equatorial attack by (2-methylpropenyl)lithium or *n*-BuLi.[5]

Scheme I



The reaction of potassium menthyl oxide (**6**, M = K) proceeded distinctively without stereospecificity to give a mixture of axial insertion product **7**, equatorial insertion product **8**, and butyl adduct **9** in the ratio of 24:4:72 (total yield 56%, 37% conversion) (eq 2). When a THF solution of lithium menthyl oxide (2.0 equiv) and **2** was treated with *n*-BuLi at −90 °C and then warmed up to a room temperature, the relative yield of **8** increased in comparison to those of **7** and **9** (7:8:9 = 47:12:41, total yield 30%). Moreover, the reaction of lithium menthyl-*1*-d_1 oxide (**6**-*d* *d* content >95%) gave **8**-*d* which contained 84% deuterium at the vinylic position.[6] Thus, it is evident that **8** was produced via the hydride abstraction–recombination mechanism. Also highly probable is that in-cage recombination between intermediates menthone and 2-methylpropenyl anion is responsible, at least partly, for the formation of axial insertion product **7** (Scheme I).



6 2 7 8 9

The reaction conditions employed here for the generation of the carbenic species suggest that the reactions proceed not through a free carbene but through a carbenoid. This can be further verified by the comparison of above reaction with that of a free (or an unencumbered) carbene[2b] generated from 2-methylpropenyl triflate (**10**); the reaction of **6** with the carbene generated from **10** and *t*-BuOK in THF gave 4-(menthyloxy)butyl 2-methylpropenyl ether (**11**) as a major product (17%),[7,8] whereas **11** was absent in the reaction of **2** with *n*-BuLi.

Primary alkoxides can also be inserted either through the concerted mechanism (path a) or through the hydride abstraction followed by a rapid recombination (path b) because no H–D scrambling was observed in the reaction of **2** with a mixture of benzyl-α,α-d_2 oxide and *p*-chlorobenzyl oxide by the action of *n*-BuLi and because butyl adduct was not formed in the reaction of primary alkoxides. However, we excluded path b for the following reason: In contrast to other primary alkoxides, the reaction of **2** with sterically hindered potassium 2,4,6-trimethylbenzyl oxide (**1d**) gave the butyl adduct (17% yield) together with insertion product **3d**. If path b were the case, the above anomaly can only be understood in terms of the steric effect of trimethylphenyl group which retards the recombination. But a competition reaction of (2-methylpropenyl)lithium with 2,4,6-

(1) (a) Kirmse, W. "Carbene Chemistry", 2nd ed.; Academic Press: New York, 1971; Chapter, 7. (b) Gasper, P. P.; Hammond, G. S. "Carbenes"; Moss, R. A., Jones, M. Jr., Eds.; Wiley: New York, 1975; Vol. II, Chapter 6.

(2) For reviews, see: (a) Stang, P. J. *Acc. Chem. Res.* **1982**, *15*, 348. (b) Stang, P. J. *Chem. Rev.* **1978**, *78*, 383. (c) Hartzler, H. D. "Carbenes"; Moss, R. A., Jones, M., Jr., Eds.; Wiley: New York, 1975; Vol. II, Chapter 2.

(3) (a) Harada, T.; Oku, A. *J. Am. Chem. Soc.* **1981**, *103*, 5965. (b) Harada, T.; Akiba, E.; Oku, A. *Ibid.* **1983**, *105*, 2771. (c) Harada, T.; Nozaki, Y.; Oku, A. *Tetrahedron Lett.* **1983**, *24*, 5665.

(4) The possibility of the fragmentation of C–H insertion product into a ketone and a vinylic anion was excluded by the following experiment: Potassium alkoxide **7** was treated with *n*-BuLi in THF at 0 °C for 30 min. Formation of neither stereoisomer **8** nor butyl adduct **9** was detected by the VPC analysis (for the structure of **7**, **8**, and **9**, refer to eq 2).

(5) Ashby, E. C.; Laemmele, J. T. *Chem. Rev.* **1975**, *75*, 521.

(6) **7**-*d* was obtained with more than 95% deuterium incorporation. A slight decrease in the deuterium content in **8**-*d* might suggest the generation of (2-methylpropenyl)lithium by the reaction of **2** with *n*-BuLi.

(7) **10** reacts with THF in the presence of alkoxides to give a ring-cleaved product. (a) Gilbert, J. C.; Weerasooriya, U. *Tetrahedron Lett.* **1980**, *21*, 2041; (b) *J. Org. Chem.* **1982**, *47*, 1837.

(8) Besides **11**, menthyl 2-methylpropenyl ether (27%) was formed together with a small amount of **7** (3%) and menthone (2%).

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