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Chrysanthemylcarbenes. An Isobutenyl Substituent Effect and Conformational Control in Cyclopropylcarbene Rearrangements[1a]

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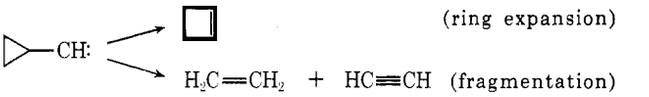
Thermal and photodecompositions of sodium and lithium salts of *cis*- and *trans*-chrysanthemyl-(2,2-dimethyl-3-isobutenylcyclopropyl-) aldehyde *p*-tosylhydrazones (*cis*- and *trans*-**5**) and *cis*- and *trans*-chrysanthemyl methyl ketone tosylhydrazones (*cis*- and *trans*-**6**) were carried out under various conditions. The products from *cis*- and *trans*-**5** under aprotic conditions were 2,5-dimethyl-2,4-hexadiene (**8**), a fragmentation product, and 3,3-dimethyl-4-isobutenylcyclobutene (**9**), a ring-expansion product, in 62–68:38–32 ratio, respectively. Thermal decomposition of lithium salts of *cis*- and *trans*-**6** under aprotic conditions afforded predominantly a ring-expanded product, 1,3,3-trimethyl-4-isobutenylcyclobutene (**12**) rather than the fragmentation product **8** with 70:30 and 92:8 ratios, respectively, indicating an exclusively selective C_1–C_3 bond migration. Under protic conditions, both *cis*- and *trans*-**5** gave 2,5,5-trimethyl-1,3,6-heptatriene (**10**) and 2,5-dimethyl-3-vinyl-1,4-hexadiene (**11**). A notable isobutenyl substituent effect as well as a conformational effect of divalent carbon is advanced to rationalize the intramolecular cyclopropylcarbene rearrangements.

The nature and extent of carbene interactions with neighboring heteroatoms like oxygen or chemical bonds of unsaturated character involving phenyl, carbonyl, and cyclopropyl functions has recently become a fascinating problem, on which the reorganization of highly reactive intermediates is particularly focused.[2,3] Cyclopropylcarbene is well known to undergo a ring-expansion reaction to give cyclobutene accompanied with a fragmentation to acetylene and ethylene.[4]



However, the diversity of mechanistic pathways for this very reactive intermediate seems not to be well clarified compared with that for cyclopropylcarbinyl cation rearrangements.[5] In the previous papers[6] we have described carbonium ion promoted cyclopropane ring opening reactions of *cis*- and *trans*-chrysanthemyl (2,2-dimethyl-3-isobutenylcyclopropyl) systems, where a notable substituent effect of an isobutenyl group is realized in the facile and selective ring-opening reactions.[7] This paper deals with chemical behaviors of chrysanthemyl- and chrysanthemylmethylcarbenes generated *via* the Bamford–Stevens reaction[8] in order to obtain information on steric and electronic substituent effects on cyclopropylcarbene reactivity, and thus to effect synthetic application of such a highly reactive intermediate.[2]

(1) (a) Studies on Chrysanthemic Acid. XI. Part X of this series: T. Sasaki, S. Eguchi, M. Ohno, and T. Umemura, *Chem. Lett.*, 503 (1972). (b) Toyoda Physical and Chemical Research Institute Postdoctoral Research Fellow, 1972 to present.

(2) For recent reviews on carbene chemistry, see (a) R. A. Moss, *Chem. Eng. (N. Y.)*, June 16, 60 (1969); June 30, 50 (1969); (b) G. L. Closs, "Topics in Stereochemistry," Vol. 3, Interscience, New York, N. Y., 1968, p 193; (c) W. Kirmse, "Carbene Chemistry," 2nd ed, Academic Press, New York, N. Y., 1971.

(3) For oxacarbene–1-oxo-1,4-diradical rearrangement, see (a) A. M. Foster and W. C. Agosta, *J. Amer. Chem. Soc.*, **94**, 5777 (1972); (b) D. R. Morton, E. Lee-Ruff, R. M. Southam, and N. J. Turro, *ibid.*, **92**, 4349 (1970). For carbonylcarbene–oxirene rearrangement, see (c) S. A. Matlin and P. G. Sammes, *Chem. Commun.*, 11 (1972); (d) J. Ciabattoni, R. A. Campbell, C. A. Renner, and P. W. Concannon, *J. Amer. Chem. Soc.*, **92**, 3826 (1970). For arylcarbene rearrangement, see (e) W. D. Crow and M. N. Paddon-Row, *ibid.*, **94**, 4746 (1972), and references cited therein. For β-cyclopropylcarbene, see (f) P. K. Freeman, R. S. Raghavan, and D. G. Kuper, *ibid.*, **93**, 5288 (1971).

(4) For cyclopropylcarbenes, see (a) L. Friedman and H. Shechter, *J. Amer. Chem. Soc.*, **82**, 1002 (1960); (b) H. M. Frey and I. D. R. Stevens, *Proc. Chem., Soc., London*, 144 (1964); (c) J. A. Smith, H. Shechter, J. Bayless, and L. Friedman, *J. Amer. Chem. Soc.*, **87**, 659 (1965); (d) J. Bayless, L. Friedman, J. A. Smith, F. B. Cook, and H. Shechter, *ibid.*, **87**, 661 (1965); (e) K. B. Wiberg and J. M. Lavanish, *ibid.*, **88**, 365 (1966); (f) F. Cook, H. Shechter, J. Bayless, L. Friedman, and R. L. Flots, *ibid.*, **88**, 3870 (1966); (g) P. B. Shevlin and A. P. Wolf, *ibid.*, **88**, 4735 (1966); (h) A. Guarino and A. P. Wolf, *Tetrahedron Lett.*, 655 (1969); (i) C. L. Bird, H. M. Frey, and I. D. R. Stevens, *Chem. Commun.*, 707 (1967); (j) S. Nishida, I. Moritani, E. Tsuda, and T. Teraji, *ibid.*, 781 (1969); (k) R. R. Sauers, S. B. Schlosberg, and P. E. Pfeffer, *J. Org. Chem.*, **33**, 2175 (1968); (l) W. Kirmse and K. H. Pook, *Angew, Chem., Int. Ed. Engl.*, **6**, 594 (1966); (m) M. A. Battiste and M. E. Burns, *Tetrahedron Lett.*, 523 (1966); (n) J. W. Wilt, Jr., J. M. Kosturik, and R. C. Orlowski, *J. Org. Chem.*, **30**, 1052 (1965); (o) L. A. Paquette and G. H. Birnberg, *J. Amer. Chem., Soc.*, **94**, 164 (1972); (p) H. E. Zimmerman and L. R. Sousa, *ibid.*, **94**, 834 (1972); (q) P. K. Freeman and D. G. Kuper, *J. Org. Chem.*, **30**, 1047 (1965); (r) J. W. Wheeler, R. H. Chung, Y. N. Vaishnav, and C. C. Shroff, *ibid.*, **34**, 545 (1969).

(5) For cyclopropylcarbinyl cation rearrangements, see (a) R. Breslow in "Molecular Rearrangements," Part I, P. de Mayo, Ed., Interscience, New York, N. Y., 1963; (b) references in F. Majerski and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **93**, 665 (1971).

(6) T. Sasaki, S. Eguchi, M. Ohno, and T. Umemura, *J. Org. Chem.*, **63**, 1968 (1971), and ref 1a.

(7) For ring openings in the Cope rearrangement, see (a) T. Sasaki, S. Eguchi, and M. Ohno, *J. Amer. Chem. Soc.*, **92**, 3192 (1970); (b) T. Sasaki, S. Eguchi, and M. Ohno, *J. Org. Chem.*, **37**, 466 (1972).

(8) W. R. Bamford and T. S. Stevens, *J. Chem. Soc.*, 4735 (1952).

TABLE I

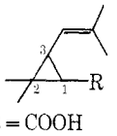
PRODUCT COMPOSITION OF THERMAL AND PHOTODECOMPOSITIONS OF TOSYLHYDRAZONES 5 AND 6 ALKALI SALTS

Tosylhydrazone	Alkali metal	Medium	Conditions, temp, °C (mm)	Product composition,[a] % 8	9	12	10	11
trans-5	Li	None	90–110 (2)	68	32			
cis-5	Li	None	90–110 (2)	73	27			
trans-5	Na	None	90–110 (2)	46	24		8	22
	Na	Celite	90–110 (2)	52	32		4	12
	Na	DEG[b]	80–120 (21)	8	4		19	69
cis-5	Na	None	90–110 (2)	54	29		4	13
	Na	Celite	90–110 (2)	55	26		4	15
	Na	DEG[b]	80–120 (21)	16	9		19	56
trans-5	Na	Ether	$h\nu$[c]	54	25		5	16
cis-5	Na	Ether	$h\nu$[c]	45	22		7	26
trans-6	Li	None	110–120 (2)	8		92		
cis-6	Li	None	105–120 (2)	30		70		
21[d]	Na	DEC[b]	180	Ethylene, 13–18 Cyclobutene, 82–87				

[a] Based on relative peak areas on glpc. [b] DEG, diethylene glycol; DEC, diethylcarbitol. [c] Irradiated with a 100-W high-pressure mercury lamp (quartz filter). [d] Taken from ref 4a.

Results

cis- and *trans*-chrysanthemylaldehydes (*cis*- and *trans*-**3**) and -chrysanthemyl methyl ketones (*cis*- and *trans*-**4**) were obtained by oxidation of chrysanthemol (*cis*- and *trans*-**2**) with the Sarett reagent, and by reaction of chrysanthemic acid (*cis*- and *trans*-**1**) with methyllithium, respectively. The corresponding *p*-tosylhydrazones (*cis*- and *trans*-**5** and -**6**) were prepared by the standard procedure.



1, R = COOH
2, R = CH_2OH
3, R = CHO
4, R = $COCH_3$
5, R = CH=NNHTs
6, R = $C(CH_3)$=NNHTs

Thermal decomposition of the lithium salt of *trans*-**5** under reduced pressure of nitrogen at 90–110° afforded an extremely volatile oil in a 60% yield, which was a 68:32 mixture of two hydrocarbons **8** and **9** (Scheme I). Compound **8** was identified as 2,5-dimethyl-2,4-hexadiene, a fragmentation product,[9] by spectral and glpc comparisons with an authentic specimen. Compound **9** was not thermostable enough to be isolated by preparative glpc at 80°. The structure was assigned as 3,3-dimethyl-4-isobutenylcyclobutene, a ring-expansion product, on the basis of spectral and glpc comparisons with a specimen synthesized by photocycloaddition of maleic anhydride to **8**, followed by alkaline hydrolysis and oxidative decarboxylation (Scheme II). Thermal decomposition of *cis*-**5** afforded also **8** and **9** in 73:27 ratio. The decomposition products of *cis*- and *trans*-**5** and -**6** under various conditions are summarized in Table I and Scheme I.

Thermal decompositions of *cis*- and *trans*-**5** in diethylene glycol with a high protonicity[10] resulted in the formation of 2,5,5-trimethyl-1,3,6-heptatriene (artemisia triene)[11] (**10**) and 2,5-dimethyl-3-vinyl-1,4-hexadiene (santorina triene)[12] (**11**) as the major products and **8** and **9** as the minor products (Scheme I and Table I). Both **10** and **11** might be produced *via* a cationic precursor, since the deamination of chrysanthemylamine gives similar ring-opened products.[6,13] Photolytic decompositions[14] of *cis*- and *trans*-**5** gave results similar to those of thermal ones, though the use of sodium methoxide as a base in the photolytic and thermal decompositions resulted in contamination with the products *via* cationic intermediate because of the very strong hygroscopicity of the sodium salt of **5**. It is notable that no appreciable difference in the product distributions was observed between the cis and trans isomers of **5** (Table I).

Thermal decomposition of the lithium salt of *trans*-**6** afforded a 8:92 mixture of two hydrocarbons in a 95% yield. The minor product was one of the fragmentation products **8** and the major one was assigned as as 1,3,3-trimethyl-4-isobutenylcyclobutene (**12**), a ring-expansion product, on the basis of analysis and spectral and glpc comparisons with a specimen prepared by photocycloaddition of methylmaleic anhydride to **8**, followed by hydrolysis and oxidative decarboxylation (Scheme II). Purification of the crude photoadducts on a silica gel column, followed by an alkaline hydrolysis, afforded a regio- and stereoisomerically pure dicarboxylic acid **19**, in which the location of a methyl group at C_1 was determined by the characteristic nmr signals at τ 7.27 (1 H, s, C_2 H), 6.42 (1 H, d, J = 10 Hz, C_4 H), and 4.80 (1 H, d, J = 10 Hz, C_4 CH=C).[15]

(9) Formation of acetylene was also confirmed, at least qualitatively, as another fragment of this cheletropic reaction.

(10) (a) J. H. Bayless, L. Friedman, F. B. Cook, and H. Shechter, *J. Amer. Chem. Soc.*, **90**, 531 (1968); (b) for solvent effect on the Bamford–Stevens reaction, see ref 2c, pp 30–32.

(11) L. Crombie, R. P. Houghton, and D. K. Woods, *Tetrahedron Lett.*, 4553 (1967); see also ref 6.

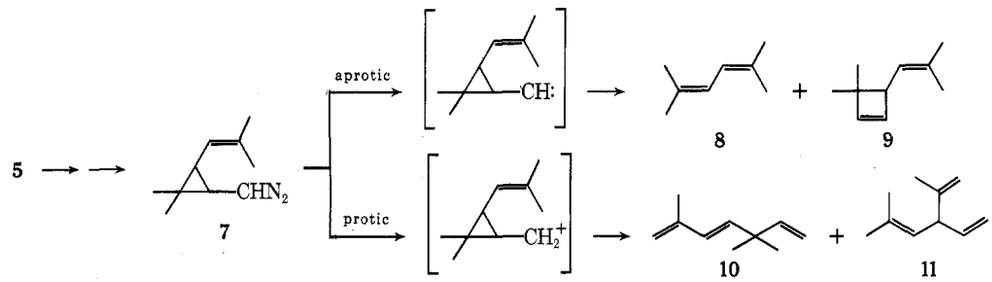
(12) A. F. Thomas and B. Willhalm, *Tetrahedron Lett.*, 3775 (1964), and ref 1a.

(13) Reexamination of the deamination products in acetic acid revealed the formation of **11**, santorina acetate, **10**, and artemisia acetate in a 10:4:29:27 ratio; *cf.* also ref 1a and 6.

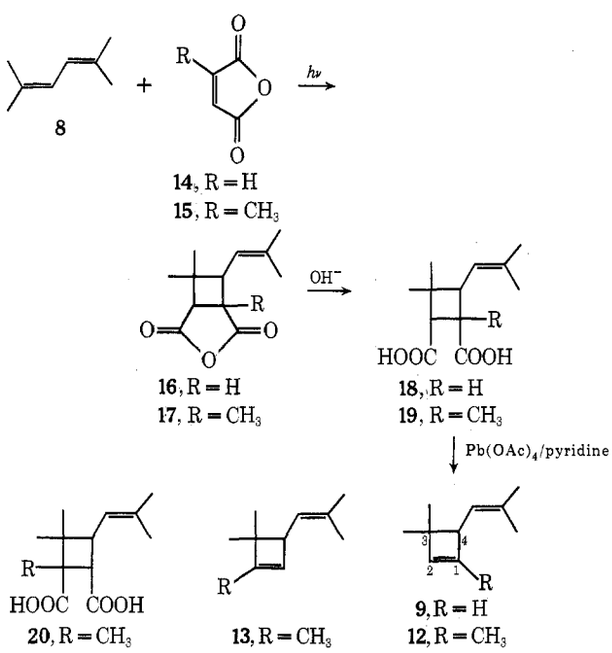
(14) For photolytic decompositions of dimethylcyclopropylidazomethane, see ref 4h.

(15) For vicinal coupling constants in cyclobutanes, see, for example, L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, New York, N. Y., 1969, p 287.

SCHEME I



SCHEME II



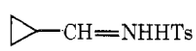
Thus corroborated, diacid **19** was decarboxylated by lead tetraacetate oxidation to give a single olefinic product which was completely identical (ir, nmr, and glpc) with a hydrocarbon **12** from the decomposition of *trans*-**6**.

Thermolysis of *cis*-**6** lithium salt afforded **12** and **8** in a 70:30 ratio, indicating 100% selectivity of the C_1–C_3 bond migration even in the cis isomer as in the trans isomer (Table I).

It is notable that no trace of *cis*- and *trans*-1-vinyl-2,2-dimethyl-3-isobutenylcyclopropanes[7b] as possible hydrogen migration products was produced in the decompositions of both *cis*- and *trans*-**6** lithium salts.

Discussion

In a sharp contrast to a number of cyclopropylcarbenes reported in the literature,[4] *cis*- and *trans*-chrysanthemylcarbenes *via* the Bamford–Stevens reactions of *cis*- and *trans*-**5** provide novel examples where the fragmentation process predominates substantially over the ring-expansion process; even when the parent cyclopropanecarboxaldehyde tosylhydrazone (**21**) is



used as a carbene precursor, the major product is known to be cyclobutene[4a,c] (Table I). The presence of a C_3-isobutenyl substituent might lower the transition-state energy for the fragmentation reaction by virtue of formation of a conjugated diene, assuming that the carbene reaction proceeds *via* either a concerted process or stepwise ones (ion-pair or radical-pair)[16–18] (Chart I).

Unsymmetrically substituted cyclopropylketone tosylhydrazone is known to rearrange to cyclobutenes in two possible directions, but the migration of a less substituted (*i.e.*, less sterically hindered) bond of cyclopropane is prefered.[4i,j,m] The present results that both *cis*- and *trans*-**6** lead to the formation of only a single ring-expansion product **12** with migration of the isobutenyl-substituted bond (C_3–C_1 bond) could not be explainable only by the steric hindrance. A similar steric bulkiness is conceivable for C_2-methyl and C_3-isobutenyl substituents in the cis isomer,[19] from which the observed exclusively selective C_3–C_1 bond migration could never be expected. Hence, it could be concluded that the electronic effect of a C_3-isobutenyl substituent should play an important role at the transition state. Such a remarkable substituent effect is commonly observed in the ring-opening reactions of cyclopropane attached to an electron-deficient carbon such as carbonium ion.[1,20]

Finally, we wish to discuss the considerable difference of the product distributions between the aldehyde and ketone tosylhydrazones **5** and **6**. The diversity of cyclopropylcarbene reactions, such as fragmentation

(16) The concerted process seems to be most likely as shown recently by a successful prediction of forbiddeness–allowedness of the rearrangement from correlation diagrams of reacting cyclopropylcarbene (see ref 4p). However, the possibility of a stepwise process should also be considered in general.

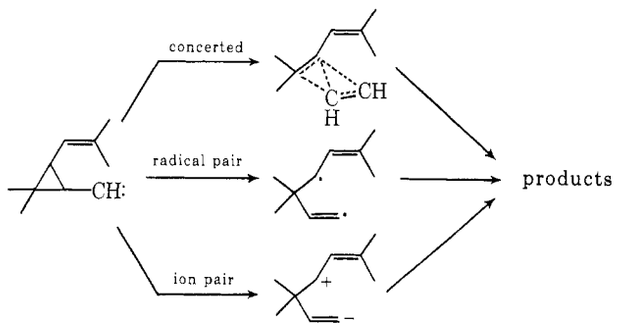
(17) For an ion-pair mechanism, *cf.* ref 4q.

(18) For a radical-pair mechanism, see M. Jones, Jr., J. D. Reich, and L. T. Scott, *J. Amer. Chem., Soc.*, **92**, 3118 (1970).

(19) The evidence rests on the nmr study concerning a diastereotopic phenomenon in the chrysanthemyl system. We examined nmr spectra of several chrysanthemyl derivatives such as **1** [R = CH_2CONH_2, $CH_2N(CH_3)_2$, CH_2NH_2, CH_2OH, CH_2OAc, $CH_2OCOC_6H_3(NO_2)_2$-2,4] and dihydrochrysanthemol, all of which have a methylene group attached to an asymmetric C_1 carbon. As an unequivocal difference between the cis and trans isomers, an A_2X pattern for the cis isomers and an ABX pattern for the trans isomers were observed. The difference must be associated with the anisotropy of a cyclopropane ring and unequal conformer populations due to the difference of nonbonded interactions between the methylene group and the substituents (hydrogen, methyl, and isobutenyl). The equivalency of methylene protons in the cis isomers contrary to the nonequivalency in the trans isomers suggests similar steric bulkiness of C_2-methyl and C_3-isobutenyl groups. *Cf.* also (a) J.-L. Pierre, R. Perraud, and P. Arraud, *Bull. Soc. Chim Fr.*, 1537 (1970); (b) J. Edmond, G. Popják, S.-M. Wong, and V. P. Williams, *J. Biol. Chem.*, **246**, 6254 (1971); (c) C. D. Poulter, *J. Amer. Chem. Soc.*, **94**, 5515 (1972).

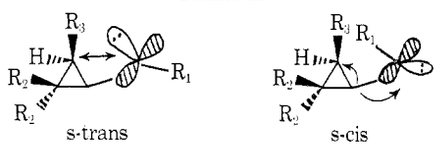
(20) (a) H. M. Walborsky and L. Plonker, *J. Amer. Chem. Soc.*, **83**, 2138 (1961); (b) T. Shono, I. Nishiguchi, and R. Oda, *J. Org. Chem.*, **35**, 42 (1970); (c) for a recent theoretical study, see L. D. Kispert, C. Engleman, C. Dyas, and C. U. Pittman, Jr., *J. Amer. Chem. Soc.*, **93**, 6948 (1971).

CHART I



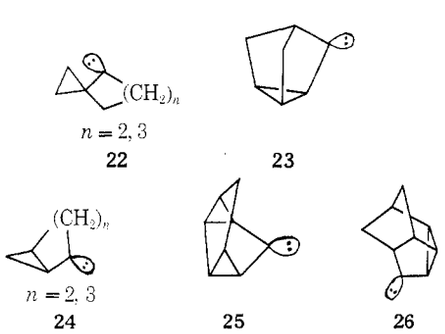
and ring expansion, has been explained by considering mainly strain factors as well as electronic effects,[4q,r] but no conformational effect. We advance here that not only the strain effect but also the conformational effect play a very significant role in determining the cyclopropylcarbene rearrangement reactivity. A maximum interaction of the carbene with the rearranging bond could be possible when the substituent R_1 takes an s-trans-like conformation against the cyclopropane ring, while in an s-cis-like conformation, the interaction is apparently unfavorable as illustrated in Chart II.[21]

CHART II



$R_1 = H, CH_3$; $R_2 = CH_3$; $R_3 = CH=C(CH_3)_2$

The known results of intramolecular rearrangement of geometrically constrained cyclopropylcarbene can be rationalized by considering the conformational effect. For example, spirocarbene (**22**) where an s-trans conformation is geometrically fixed is known to undergo the ring expansion exclusively.[4l,22] On the contrary, cyclopropylcarbenes such as **23**,[23] **24**,[4q] **25**,[24] and **26**,[25]



where an s-cis conformation is inevitably fixed by the geometrical constraint, undergo predominantly the fragmentation reaction.

For the present crysanthemyl systems, an s-trans conformation is expected to be more favored for the carbenes from *cis*- and *trans*-**6** than for the carbenes from *cis*- and *trans*-**5**.[26] Therefore, the observed predominant ring expansion of chrysanthemylmethylcarbenes from **6** could be rationalized by the conformational effect. A somewhat larger fragmentation for the cis isomer (30%) than the trans one (8%) may result in a steric hindrance to the ring expansion of the former, *i.e.*, the steric crowdedness at the transition state for the ring expansion even with an s-trans-like conformation hinders to some extent the ring expansion, permitting the fragmentation *via* the s-trans conformation also.[27]

Thus, the substituent effect of an isobutenyl group at C_3 is concluded to play a remarkable role electronically as well as sterically in the cyclopropylcarbene reactivity. The conformational effect of the carbene against a cyclopropane ring is postulated as a primarily controlling factor to determine the cyclopropylcarbene rearrangement aptitude.

Experimental Section[28]

***cis*- and *trans*-2,2-Dimethyl-3-isobutenylcyclopropanecarboxaldehydes (*cis*- and *trans*-3).**—*trans*-Chrysanthemol (*trans*-**2**, 6.00 g, 38.9 mmol) was added to a pyridine–CrO_3 complex solution (the Sarett reagent)[29] prepared from pyridine (200 ml) and chromic anhydride (12 g, 120 mmol) at room temperature. After standing overnight, the mixture was poured onto cold water (500 ml) and extracted with three 200-ml portions of ether. The combined extracts were washed with three 100-ml portions of 10% hydrochloric acid, two 50-ml portions of saturated sodium carbonate aqueous solution, and finally with 100-ml of water. After being dried over anhydrous sodium sulfate, the extract was concentrated *in vacuo* and distilled to afford the aldehyde (*trans*-**3**) as a colorless oil (3.83 g, 65%), bp 57–58° (2.5 mm) [lit.[30] bp 43–44° (0.1 mm)].

The cis aldehyde (*cis*-**3**) was obtained similarly from *cis*-chrysanthemol (*cis*-**2**) as a colorless oil (58%), bp 58–60° (2.5 mm) [lit.[30] bp 63–64° (2.0 mm)].

***cis*- and *trans*-2,2-Dimethyl-3-isobutenylcyclopropyl Methyl Ketones (*cis*- and *trans*-4).**—To a stirred and refluxing solution of *trans*-chrysanthemic acid (*trans*-**1**, 6.0 g, 38.9 mmol) in dry ether (30 ml) was added an ethereal methyllithium solution prepared from methyl bromide (9.8 g, 103 mmol) and metallic lithium (1.3 g, 187 mmol) under nitrogen.[31] After standing overnight at room temperature, the mixture was poured onto ice water (*ca.* 200 ml) and the organic layer was separated, washed with saturated sodium chloride aqueous solution and water successively, and

(21) Zimmerman and Sousa reported recently on the correlation diagrams for cheletropic fragmentation and hydrogen migration of carbenes considering the nodal properties. They also predict the geometrical requirements at the transition states such as an s-cis-like conformation for the fragmentation and a somewhat twisted s-trans-like conformation for the hydrogen migration (alkyl migration); see ref 4p.

(22) K. B. Wiberg, G. J. Burzmaier, and P. Warner, *J. Amer. Chem. Soc.*, **93**, 246 (1971). In these cases the fragmentation is highly unfavorable also owing to the inordinate strain required to generate cyclobutyne and cyclopentyne.

(23) (a) S. J. Cristol and J. K. Harrington, *J. Org. Chem.*, **28**, 1413 (1963); (b) D. M. Lemal and A. J. Fry, *ibid.*, **29**, 1673 (1964).

(24) R. G. Bergman and V. J. Rajadhyaksha, *J. Amer. Chem. Soc.*, **92**, 2163 (1970).

(25) P. K. Freeman and D. M. Balls, *J. Org. Chem.*, **32**, 2354 (1967).

(26) (a) For a conformational study on cyclopropanecarboxaldehyde, see L. S. Bartell and J. P. Guillory, *J. Chem. Phys.*, **43**, 647 (1965); (b) for cyclopropyl methyl ketone, see L. S. Bartell, J. P. Guillory, and A. T. Parks, *J. Phys. Chem.*, **69**, 3043 (1965); (c) for chrysanthemylaldehyde and methyl ketone, see W. G. Dauben and G. W. Shaffer, *J. Org. Chem.*, **34**, 2301 (1969), and ref 7b, footnote 20.

(27) Geometrically this fragmentation process seems to be allowed from the correlation diagram by Zimmerman and Sousa (ref 4p), though energetically the fragmentation *via* this conformation might be less favorable than that *via* the s-cis one.

(28) All melting points were obtained on a hot-stage type micro melting point apparatus and are corrected. Nmr spectra were recorded on a JEOL JNM-C-60HL spectrometer at 60 MHz with TMS as an internal standard, and ir spectra on a JASCO IR-S ir spectrophotometer. High-resolution mass spectra were obtained with a Hitachi RMS-4 mass spectrometer at 80 eV. Glpc analyses were performed on a Varian gas chromatograph Model 1400 and preparative glpc on a Varian Aerograph Model 700. Microanalyses were carried out with a Perkin-Elmer 240 elemental analyzer.

(29) G. I. Poos, G. E. Arth, R. E. Beyler, and L. H. Sarett, *J. Amer. Chem. Soc.*, **75**, 422 (1953).

(30) *Cf.* footnote 9 in ref 7b.

(31) *Cf.* M. J. Jorgenson, *Org. React.*, **18**, 1 (1970).

dried (Na_2SO_4). Removal of solvent *in vacuo* and distillation gave the ketone *trans*-**4** as a colorless oil (3.5 g, 59%), bp 60–61° (4 mm) [lit.[30,32] bp 90–91° (15 mm)]. The cis ketone (*cis*-**4**) was obtained similarly as a colorless oil (52%): bp 60–62° (4 mm); $n^{21}D$ 1.4780; ir (neat) 1690, 1457, 1415, 1385, 1358, 1193, 970, 842, and 798 cm^{-1}; nmr (CCl_4) τ 4.50–4.90 (mound, 1 H, CH=C), 7.88 (s, 3 H, $COCH_3$), 8.08–8.40 [m, 8 H, C=C-$(CH_3)_2$ and C_1 H and C_1 H], 8.80 and 8.82 (each s, 6 H, C_2 *gem*-dimethyl).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.56; H, 10.82.

***p*-Tosylhydrazones (*cis*- and *trans*-5) of *cis*- and *trans*-3.**—To a stirred solution of *p*-toluenesulfonylhydrazide (2.45 g, 13.1 mmol) in methanol (10 ml) was added *trans*-**3** (2.00 g, 13.1 mmol) at room temperature. After stirring was continued for 2 hr, the mixture was cooled to precipitate colorless crystals which were collected by filtration and recrystallized from methanol to give *p*-tosylhydrazone *trans*-**5** (3.44 g, 82%): mp 100–101°; ir (KBr) 3220 (NH), 1615 (C=N), 1600 (phenyl), and 860 cm^{-1} (CH=C); nmr (CCl_4) τ 1.96 (s, 1 H, NH, disappeared on deuteration), 2.10–2.90 (complex m, 4 H, phenyl protons), 3.03 and 3.55 (each d, J = 8.0 Hz, 0.6 H and 0.4 H, anti and syn CH=NNHTs), 5.20 (broad d, J = 7.5 Hz, 1 H, CH=C), 7.60 (s, 3 H, tosyl CH_3), 8.32 [s, 6 H, C=C$(CH_3)_2$], 8.55–9.10 (m, 2 H, C_1 H and C_3 H), 8.91 and 8.95 (s, 6 H, C_2 *gem*-dimethyl).

Anal. Calcd for $C_{17}H_{24}N_2O_2S$: C, 63.73; H, 7.54; N, 8.74. Found: C, 63.73; H, 7.51; N, 8.76.

Similarly *cis*-**5** was prepared from *cis*-**3** and *p*-toluenesulfonylhydrazide. Since crystallization of the crude product was difficult, an analytical sample was obtained after purification on a silica gel column ($CHCl_3$) followed by preparative tlc (silica gel, $CHCl_3$) as a colorless oil: ir (neat) 3230 (NH), 1615 (C=N), 1600 (phenyl), 860 cm^{-1} (CH=C); nmr (CCl_4) τ 1.10 (broad s, 1 H, NH, disappeared on shaking with D_2O), 2.10–2.95 (m, 5 H, phenyl protons and CH=NNHTs), 5.12 (d, J 7.5 Hz, 1 H, CH=C), 7.61, (s, 3 H, tosyl CH_3), 8.38 [s, 6 H, C=C$(CH_3)_2$], 8.65–9.35 (m, overlapped with strong singlet signals at τ 8.88 and 8.99, 8 H, C_2 *gem*-dimethyl and C_1 H and C_3 H).

Anal. Calcd for $C_{17}H_{24}N_2O_2S$: C, 63.73; H, 7.54; N, 8.74. Found: C, 63.48; H, 7.51; N, 8.41.

***p*-Tosylhydrazones (*cis*- and *trans*-6) of *cis*- and *trans*-4.**—*trans*-**4** (2.32 g, 13.9 mmol) was treated similarly with *p*-toluenesulfonylhydrazide (2.60 g, 13.9 mmol) in methanol (15 ml) to afford the *trans*-tosylhydrazone (*trans*-**6**) as colorless crystals (3.22 g, 69%): mp 141–142.5°; ir (KBr) 3250 (NH), 1630 (C=N), 1600 (phenyl), and 860 cm^{-1} (CH=C); nmr (CCl_4) τ 2.55 (broad s, 1 H, NH), 2.13–2.87 (complex m, 4 H, phenyl protons), 5.18 (broad d, J = 8.0 Hz, 1 H, CH=C), 7.60 (s, 3 H, tosyl CH_3), 8.12 and 8.18 (each s, 1 H and 2 H, syn and anti TsNHN=CCH_3), 8.31 [s, 6 H, C=C$(CH_3)_2$], 8.45–9.45 (m, 8 H, C_1 H, C_3 H, and C_2 *gem*-dimethyl).

Anal. Calcd for $C_{18}H_{26}N_2O_2S$: C, 64.64; H, 7.84; N, 8.37. Found: C, 64.96; H, 7.77; N, 8.41.

Similar treatment of *cis*-**4** gave *cis*-**6** as colorless crystals (58%): mp 136–137°; ir (KBr) 3230 (NH), 1640 (C=N), 1600 (phenyl), and 845 cm^{-1} (CH=C); nmr ($CDCl_3$) τ 2.12–2.83 (m, 5 H, phenyl protons and NH, the integration decreased to *ca.* 4 H on shaking with D_2O), 5.23 (broad d, J = 8.0 Hz, 1 H, CH=C), 7.62 (s, 3 H, tosyl CH_3), 8.15 and 8.36 (each s, 1 H and 2 H, syn and anti TsNHN=CCH_3), 8.27 [s, 6 H, C=C$(CH_3)_2$], 8.84, 8.94, 9.19, and 9.28 (each s, 6 H, C_2 *gem*-dimethyl), and 8.0–9.0 (m, 2 H, C_1 H and C_3 H).

Anal. Calcd for $C_{18}H_{26}N_2O_2S$: C, 64.64; H, 7.84; N, 8.37. Found: C, 64.48; H, 7.73; N, 8.61.

Decompositions of Tosylhydrazones (*cis*- and *trans*-5 and -6) Alkali Salts. General Procedure.—Tosylhydrazone alkali salt prepared from the corresponding tosylhydrazone (*cis*- and *trans*-**5** or -**6**) and an appropriate base (1.1 equiv) was decomposed by heating at 90–120° under a reduced pressure of nitrogen in a reaction flask fitted with a distillation head connected directly to a trap followed by another trap of the same size. The distillate collected in the traps at −73° was analyzed on glpc by using a 6 ft × $^2/_{25}$ in. column packed with silicone SE-30 (3%) on Varaport 30 at 60–80°. For preparative glpc, a 6 ft × $^8/_{25}$ in. U-shaped column packed with silicone SE-30 (10%) on 60–80 mesh Chromosorb W was used. For other conditions, see Table I.

(32) R. H. Eastman and S. K. Freeman, *J. Amer. Chem. Soc.*, **77**, 6642 (1955).

(1) To a solution of *cis*-**5** (or *trans*-**5**) (320 mg, 1.00 mmol) in dry THF (1 ml) was added *n*-butyllithium solution in *n*-hexane (0.70 ml of 10% w/v solution, 1.01 mmol) at 0° under nitrogen atmosphere. After standing for 0.5 hr at room temperature, the solvent was removed *in vacuo* to leave colorless solids which were heated at 90–110° to yield a volatile, oily product (51 mg, 43%) (60 mg, 51% from *trans*-**5**). The crude product was analyzed on glpc as a mixture of two hydrocarbons (Table I). The major product eluted first on preparative glpc was identified as 2,5-dimethyl-2,4-hexadiene (**8**) by comparisons of its ir and nmr spectra and glpc retention time with those of a commercially available authentic specimen. Isolation of the minor second product on glpc was unsuccessful because of its thermolability. However, analysis of ir and nmr spectral data of a mixture of this product and **8**, and glpc retention times in comparison with a specimen prepared from **8** and maleic anhydride as described below permitted the assignment of this second product as 3,3-dimethyl-4-isobutenylcyclobutene (**8**) (for physical data of **9**, see below).

(2) Tosylhydrazones *cis*- and *trans*-**6** were decomposed according to method 1 above to afford a mixture of two hydrocarbons (72 and 95% from *cis*- and *trans*-**6**, respectively) which were isolated on preparative glpc. The first component was identical with **8** by spectral and glpc comparisons. The second component, assigned as 1,3,3-trimethyl-4-isobutenylcyclobutene (**12**), had the following physical data: $n^{18}D$ 1.4691; ir (CCl_4) 1660, 1640, and 865 cm^{-1}; nmr (CCl_4) τ 4.35 (q, J = 1.5 Hz, 1 H, C_2 H), 5.00 [d, septuplet, J = 9.0 and 1.5 Hz, 1 H, CH=C$(CH_3)_2$], 7.06 (d, J = 9.0 Hz, 1 H, C_4 H), 8.25 (d, J = 1.5 Hz, 3 H, C_1 CH_3), 8.37 and 8.44 [each d, J = 1.5 Hz, each 3 H, C=C$(CH_3)_2$], 8.86 and 9.07 (each s, each 3 H, C_3 *gem*-dimethyl) (irradiation at the signal at τ 8.25 changed the quartet at τ 4.35 to a sharp singlet); mass spectrum *m/e* (rel intensity) 150 (10, M^+), 109 (100), 91 (36), 81 (54).

Anal. Calcd for $C_{11}H_{18}$: C, 87.92; H, 12.08. Found: C, 88.14; H, 11.86.

(3) To a solution of *trans*-**5** (960 mg, 3.00 mmol) in methanol (7 ml) was added sodium methoxide (162 mg, 3.00 mmol) under nitrogen. The mixture was stirred for 0.5 hr and the solvent was removed *in vacuo* to afford colorless solids which were subjected to thermal decomposition as above under the conditions in Table I. An oily product (220 mg) collected at a trap at −73° was analyzed and purified on glpc. The first and second fractions were identified as **8** and **9**, respectively, by means of method 1. The third fraction was characterized as **2,5-dimethyl-3-vinyl-1,4-hexadiene (santorina triene)** (**11**) by comparison of its ir and nmr spectra with reported ones.[12] The fourth fraction was identified as **2,5,5-trimethyl-1,3,6-heptatriene (artemisia triene)** (**10**) by comparison of glpc retention time and ir and nmr spectra with those of a specimen prepared by an alternative method.[6]

(4) A suspension of *trans*-**5** sodium salt (90 mg, 0.26 mmol) in dry ether (30 ml) in a quartz tube was irradiated with stirring under nitrogen steam at room temperature from a 100-W high-pressure mercury lamp for 3 hr and the product was analyzed on glpc (Table I).

3,3-Dimethyl-4-isobutenylcyclobutene (9) from 8 and Maleic Anhydride.—A solution of **8** (9.00 g, 81.8 mmol), maleic anhydride (1.50 g, 15.2 mmol), and benzophenone (500 mg) in ether (100 ml) was irradiated under a slow nitrogen steam with a 100-W high-pressure mercury lamp using a cylindrical Pyrex jacket cooled by running water for 5 hr. The solvent was removed by evaporation and excess **8** was removed by distillation at 60–80° under reduced pressure (25 mm). An oily residue was chromatographed on a silica gel column with benzene as an eluent to afford crude 1:1 adduct **16** (2.10 g, *ca.* 66%) accompanied by an unidentified solid product (0.22 g). **16** exhibited ir (neat) absorptions at 1805 and 1780 (anhydride) and 1660 cm^{-1} (isobutenyl), and nmr (CCl_4) signals at τ 4.92 (d, J = 8.0 Hz, 1 H, CH=C) and 6.33–7.00 (m, 3 H, cyclobutane ring protons). A mixture of **16** (2.0 g) and 7% aqueous potassium hydroxide (20 ml) was stirred overnight at room temperature. The mixture was washed with ether (20 ml) and the aqueous layer was neutralized with 10% hydrochloric acid and extracted two times with 20-ml portions of ether. The combined extracts were dried (Na_2SO_4) and evaporated to give the dicarboxylic acid **18** as colorless solids (1.50 g, 68%) which were recrystallized from *n*-hexane–ether to afford an analytical sample as colorless crystals: mp 141–143°; ir (KBr) 1720, 1700 (COOH), and 850 cm^{-1} (CH=C); nmr ($CDCl_3$) τ −0.06 (broad s, 2 H, COOH), 4.66 (broad d, J = 10 Hz, 1 H, CH=C), 6.43 (t, J = 10 Hz, 1 H, C_1 H), 6.92 (d, J = 10

Hz, 1 H, C_2H), 6.92 (t, J = 10 Hz, C_4H), 8.25 and 8.38 [each s, each 3 H, $C{=}C(CH_3)_2$], and 8.74 (s, 6 H, C_3 *gem*-dimethyl) (the triplet signal at τ 6.92 changed to a doublet on irradiation at the τ 4.66 signal); mass spectrum *m/e* (rel intensity) 226 (18, M^+), 126 (100), 111 (88), and 110 (56).

Anal. Calcd for $C_{13}H_{20}O_4$: C, 64.98; H, 8.39. Found: C, 64.84; H, 8.33.

A mixture of **18** (200 mg, 0.884 mmol) and lead tetraacetate (500 mg, 1.12 mmol) in dry pyridine (4 ml) was warmed at 80° for 1 min.[33] After evolution of carbon dioxide ceased, the mixture was quickly poured onto ice–water (50 ml) and extracted with petroleum ether (bp 39–44°, 30 ml). The extract was washed five times with 30-ml portions of water and dried (Na_2SO_4). After removal of solvent, the residual oil was purified by flask to flask distillation (bath temperature 40°, 2 mm, Dry Ice trap) to give the olefin **9** (20 mg, 16%) as an oil: ir (CCl_4) 1660, 1645, and 870 cm^{-1} (C=C); nmr (CCl_4) τ 4.02 and 4.16 (each d, J = 3.0 Hz, each 1 H, C_1H and C_2H), 4.99 [broad d, J = 9.5 Hz, 1 H, $CH{=}C(CH_3)_2$], 6.92 (d, J = 9.5 Hz, 1 H, C_4H), 8.28 and 8.38 [each s, each 3 H, $CH{=}C(CH_3)_2$], 8.81 and 9.04 (each s, each 3 H, C_3 *gem*-dimethyl); mass spectrum *m/e* (rel intensity) 136 (100, M^+), 105 (45), 91 (50), and 79 (35).

Anal. Calcd for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 88.30; H, 11.69.

1,3,3-Trimethyl-4-isobutenylcyclobutene (12) from Methylmaleic Anhydride (15) and 8.—A solution of **8** (11.0 g, 99.8 mmol), **15** (2.20 g, 19.6 mmol), and benzophenone (650 mg) in ether (100 ml) was irradiated as above for 7 hr. Purification of the crude product on a silica gel column eluting with benzene afforded 1:1 adduct **17** as an oil (2.30 g) and unidentified solids (980 mg). The adduct **17** had ir (neat) absorptions at 1850, 1780 (anhydride), and 1660 (C=C) cm^{-1}, and nmr signals (CCl_4) at τ 4.81 and 5.13 [d, J = 9.5 Hz, $CH{=}(CH_3)_2$], 6.89 and 7.23 (d, J = 9.5 Hz, C_4H), and 7.33 and 7.23 (s, C_2H). The appearance of the signals in pairs (each *ca.* 2:1 ratio) indicated that the adduct **17** is a mixture of two stereoisomers (syn and anti).

A mixture of **17** (550 mg, 2.47 mmol) and 3% aqueous KOH (15 ml) was stirred overnight at room temperature. The aqueous layer was washed with ether (20 ml), neutralized with 10% hydrochloric acid, and extracted twice with 20-ml portions of ether. The combined extracts were dried (Na_2SO_4) and evaporated to afford colorless solids (420 mg, 71%) which were recrystallized from *n*-hexane–ether to give the diacid **19** as crystals: mp 164–165°; ir (KBr) 1720 and 1670 cm^{-1} (COOH); nmr ($CDCl_3$) τ −0.94 (broad s, 2 H, COOH), 4.80 (broad d, J = 10 Hz, 1 H, CH=C), 6.42 (d, J = 10 Hz, 1 H, C_4H), 7.27 (s, 1 H, C_2H), 8.28 [s, 6 H, $C{=}C(CH_3)_2$], 8.53 (s, 3 H, C_1CH_3), 8.78 and 8.87 (each s, each 3H, C_3 *gem*-dimethyl); mass spectrum *m/e* (rel intensity) 240 (18, M^+), 140 (60), 125 (72), and 110 (100).

Anal. $C_{13}H_{20}O_4$: C, 64.98; H, 8.39. Found: C, 64.84; H, 8.33.

A mixture of **19** (90 mg, 0.38 mmol) and lead tetraacetate (250 mg, 0.57 mmol) in dry pyridine (3 ml) was warmed at 80° for 15 min. The mixture was poured onto 10% hydrochloric acid (20 ml) and extracted two times with 25-ml portions of ether. The combined extracts were washed with water and dried (Na_2SO_4). Removal of the solvent gave an oil which was purified by flask to flask distillation (bath temperature 80–100°, 25 mm) to afford the olefin **12** (10 mg, 18%).

Registry No.—*cis*-**1**, 15259-78-6; *trans*-**1**, 827-90-7; *cis*-**2**, 18383-59-0; *trans*-**2**, 18383-58-9; *cis*-**3**, 20104-06-7; *trans*-**3**, 20104-05-6; *cis*-**4**, 20104-10-3; *trans*-**4**, 20104-09-0; *cis*-**5**, 42077-36-1; *trans*-**5**, 42077-37-2; *cis*-**6**, 42077-38-3; *trans*-**6**, 42077-39-4; **8**, 764-13-6; **9**, 42077-40-7; **12**, 42077-41-8; **15**, 616-02-4; **16**, 42077-42-9; **17**, 42077-43-0; **18**, 42077-44-1; **19**, 42077-45-2; *p*-toluenesulfonylhydrazide, 1576-35-8; maleic anhydride, 108-31-6.

(33) *Cf.* R. Criegee, "Newer Methods of Preparative Organic Chemistry," Vol. 2, Academic Press, New York, N. Y., 1963, p 368.

Molecular Design by Cycloaddition Reactions. VI.[1] Observation of the Enone-π-methane Moiety in Photochemical [1,3] and [3,3] Sigmatropic Rearrangements

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Photolyses (Pyrex, >290 nm) of several substituted tropone adducts are investigated. Mechanisms for [1,3] and [3,3] sigmatropic rearrangements of thus-produced bicyclo[3.2.2]nonadienone systems (enone-π-methane moiety) are discussed.

Recently much interest has arisen in the photochemical rearrangement of the enone-π-methane moiety.[2-7]

We have found that the incorporation of heteroatoms into the bicyclo[3.2.2]nonadienone system causes some changes in its photochemical behavior;[8] irradiation of tropone–4-phenyl-1,2,4-triazoline-3,5-dione adduct in methanol afforded two products by different [3,3] sigmatropic rearrangement followed by addition of methanol. Previously, we have also reported that irradiation of Diels–Alder adducts of tropolone and epoxy-bridged cyclic olefins in methanol led to diketones by successive [1,3] sigmatropic rearrangement[9] in contrast to previous reports[3,5,8] of the light-induced rearrangement of tropone adducts in nucleophilic solvents. Thus, the hydroxyl group at the bridgehead position (α to carbonyl group) has been shown to cause a marked variation in the photochemical behavior of this system, but the mechanism was not elucidated. From these facts it seems that substituents play an important role in the photochemistry of the bicyclo[3.2.*x*]dienone system.

With a hope of providing some additional data for understanding these substituent effects on the photochemical behavior, we have investigated the photochemistry of the cycloadducts of 1,4-epoxy-1,4-di-

(1) Part V of this series: T. Sasaki, K. Kanematsu, and K. Hayakawa, *J. Amer. Chem. Soc.*, **95**, 5632 (1973).

(2) O. L. Chapman and J. D. Lassila, *J. Amer. Chem. Soc.*, **90**, 2449 (1968).

(3) O. L. Chapman, M. Kane, J. D. Lassila, R. L. Loeschen, and H. E. Wright, *J. Amer. Chem. Soc.*, **91**, 6856 (1969).

(4) J. Ciabattoni, J. E. Crowley, and A. S. Kende, *J. Amer. Chem. Soc.*, **89**, 2778 (1967).

(5) (a) A. S. Kende, Z. Goldschmidt, and P. T. Izzo, *J. Amer. Chem. Soc.*, **91**, 6858 (1969); (b) A. S. Kende and Z. Goldschmidt, *Tetrahedron Lett.*, 783 (1970).

(6) T. Tezuka, R. Miyamoto, T. Mukai, C. Kabuto, and Y. Kitahara, *J. Amer. Chem. Soc.*, **94**, 9280 (1972).

(7) H. Hart and G. M. Love, *J. Amer. Chem. Soc.*, **93**, 6266 (1971).

(8) T. Sasaki, K. Kanematsu, and K. Hayakawa, *J. Chem. Soc. C*, 2142 (1971).

(9) T. Sasaki, K. Kanematsu, and K. Hayakawa, *J. Chem. Soc., Perkin Trans. 1*, 1951 (1972).