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# Synthesis and Spectral Properties of Chloro-substituted Triptycenes

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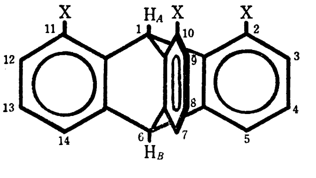
A series of 2-, 7-, 10-, and 11-chloro-substituted triptycenes were prepared by means of the addition of benzyne or 3-chlorobenzyne to anthracene and its derivatives for studying the effect of chloro-substituent on electronic and NMR spectra. It was found that the intensity of the longest wavelength bands in the chlorotriptycenes could be explained in terms of superposition of three benzenoid chromophores, and that the calculated value of chloro-group on magnetic anisotropy was in good agreement with the values reported.

Owing to its rigid cage structure which enables $\sigma$-type overlap between three isolated $\pi$-electron systems, triptycene has been given much attention since the first synthesis by Bartlett *et al.*[1] Thereafter many derivatives have been synthesized[2] for the investigation of electronic, NMR, and CD spectral properties.

A stepwise introduction of a particular substituent at 2-, 10-, and 11-positions of triptycene (I) is interesting for the study of the effect of the substituent on the electronic absorption spectrum of triptycene. Such derivatives are suitable for exploring the magnetic anisotropy of the substituent by comparison of the chemical shift of bridgehead proton $H_A$ with that of the other one $H_B$.



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In the present paper we will report on the synthesis and the spectral, electronic and NMR properties of several chlorotriptycenes.

## Results and Discussion

*Synthesis* The synthesis of mono-, di-, and trichlorotriptycenes was carried out according to the reaction sequence shown in Chart 1. Chloro-substituted anthracenes, III, IV, and V, were prepared from the corresponding anthraquinone derivatives by reduction with zinc and aqueous ammonia.[3] The mono- and di-chlorotriptycenes were obtained in two ways, by the reaction of the corresponding chloroanthracenes with benzyne generated from anthranilic acid according to the procedure of Friedman,[4] and by the reaction of anthracene and 1-chloroanthracene with 3-chlorobenzyne generated from 6-chloroanthranilic acid. The fact that both methods give identical products, 2-chlorotriptycene (VI) and dichlorotriptycenes (VII and VIII), indicates intermediary formation of 3-chlorobenzyne from 6-chloroanthranilic acid. 2,7,11-Trichlorotriptycene (IX) was prepared by the addition of 3-chlorobenzyne to 1,5-dichloroanthracene (IV), while an isomer, 2,10,11-trichlorotriptycene (X) was obtained along with IX by use of 1,8-dichloroanthracene (V) in place of IV. The properties and yields of the above chlorotriptycenes are summarized in Table 5.

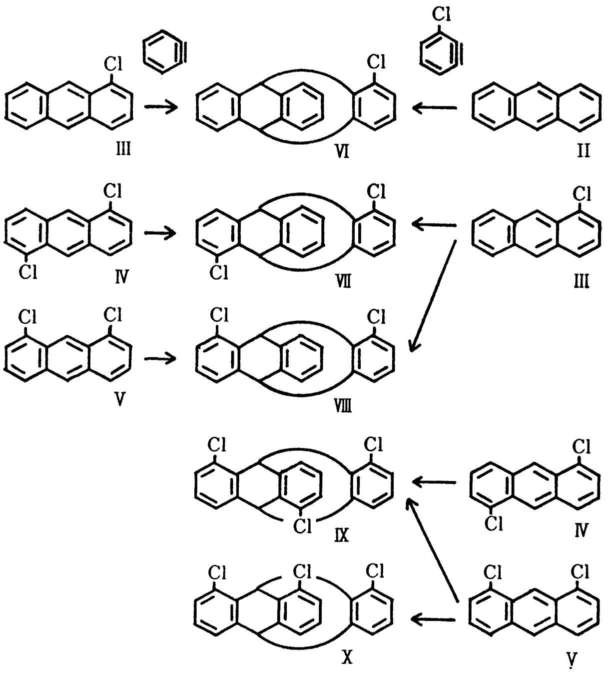
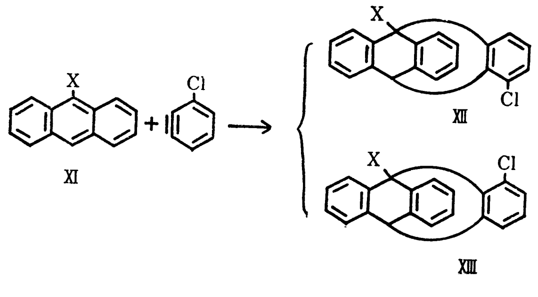


Chart 1

In general, a mixture of two isomeric triptycenes, quasi-*trans* and quasi-*cis*, is obtained by the reaction of 3-chlorobenzyne with the substituted anthracenes devoid of center of symmetry, *i.e.*, III, V, and XI; for example, a mixture of quasi-*trans* (XII) and quasi-*cis* (XIII) from XI as follows.



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[1] P. D. Bartlett, M. J. Ryan, and S. G. Cohen, *J. Amer. Chem. Soc.*, **64**, 2649 (1942).

[2] For review, see B. H. Klanderman, *Org. Chem. Bull.*, **37**, No. 1 (1965).

[3] H. Schilling, *Ber.*, **46**, 1066 (1913).

[4] L. Friedman and F. M. Logullo, *J. Amer. Chem. Soc.*, **85**, 1549 (1963); *J. Org. Chem.*, **34**, 3089 (1969).

As the isomers are distinguishable from the chemical shifts (Table 4) of the bridgehead protons in NMR spectra, the ratio of the isomers can be determined by comparison of their peak areas. The ratios obtained are shown together with those of 9-substituted anthracenes in Table 1. It is difficult to attribute these ratios to steric requirement of substituents. The inductive effect of the substituents would be mainly operative in determining the ratios.

Table 1. Ratios of isomeric triptycenes yielded by the reaction with 3-chlorobenzyne

| Anthracene | | Triptycene derivative quasi-*trans*/quasi-*cis* |
|---|---|---|
| 1-Chloro- | (III) | 1 |
| 1,8-Dichloro- | (V) | 1.9 |
| 9-Chloro- | (XI) | 1.9 |
| 9-Methyl- | (XI) | 1 |
| 9-Ethyl- | (XI) | 1 |
| 9-*i*-Propyl- | (XI) | 0.8 |

*Electronic Spectra* Two different interpretations have been given on the electronic spectra of triptycene and its derivatives up to the present. On the basis of appreciable spectral difference between triptycene and triphenylmethane, Bartlett and Lewis ascribed the difference to the intramolecular charge transfer in the former.[5] On the other hand, Wilcox, Jr., and Craig gave the explanation that the electronic spectrum of triptycene could be regarded as the superposition of three benzenoid chromophores on the ground of crude MO calculation.[6]

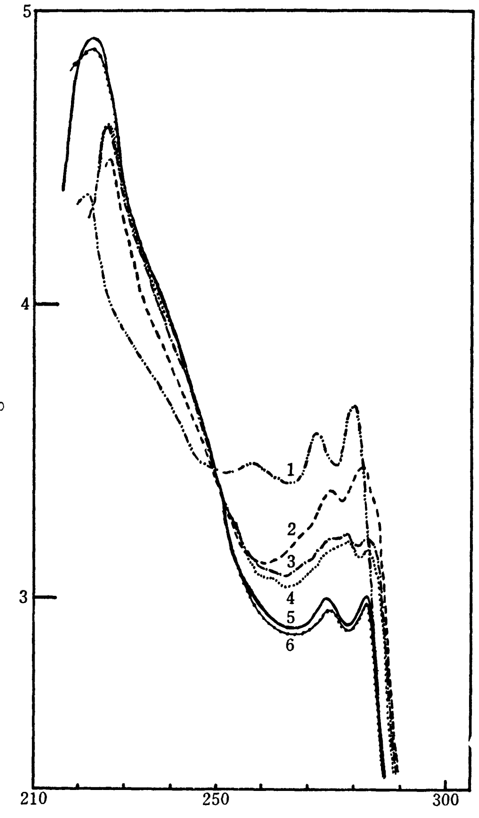

Fig. 1. Electronic spectra of triptycene and chlorotriptycenes in dioxane.
1, Triptycene(Tr); 2, 2-Cl-Tr(VI); 3, 2,7-$Cl_2$-Tr(VII); 4, 2,10-$Cl_2$-Tr(VIII); 5, 2,7,11-$Cl_3$-Tr(IX); 6, 2,10,11-$Cl_3$-Tr(X)

The spectra of chloro-substituted triptycenes are shown along with those of the parent compound triptycene in Fig. 1 and Table 2. They show that all the longest wavelength bands of chlorotriptycenes appear at the same position, but the intensity of the bands at 260—280 mμ decreases with the increase of the number of chloro-substituent. It seems that this phenomenon can be explained by Platt's quantitative approach to the intensities of the $^1L_b$ band in polysubstituted benzenes.[7] He assigned to each substituent a quantity called the spectroscopic moment $m$, which has units of (centimeter moles/liter)$^{1/2}$ and from which the increase or the decrease in the maximum extinction $\varepsilon$ can be calculated by the following vector-addition formula for two substituents.

$$\varepsilon - \varepsilon_0 \sim m_i^2 + m_j^2 - 2m_i m_j \cos\theta \qquad (1)$$

where $\varepsilon_0$ is the vibrational intensity of benzene itself and $\theta$ is the angle between the axes through each substituent and bisecting the ring.

To calculate the intensity, triptycene is divided into three *o*-xylene chromophores, and 2-chlorotriptycene is divided into one 3-chloro-*o*-xylene and two *o*-xylene chromophores in the same manner. Then the relative intensities of *o*-xylene and 3-chloro-*o*-xylene are res-

Table 2. Absorption maxima and intensity of triptycene and chlorotriptycenes in dioxane

| | $\lambda_{\max}$ mμ ($\varepsilon$) |
|---|---|
| I: X=H | 220.5(28300), 256.5(3010), 263$^{a)}$(2640), 271(3870), 278.5(4740) |
| VI | 224(32500), 273(2280), 280(2820) |
| VII | 224(43800), 269(1280), 274(1550), 278(1600), 282(1600) |
| VIII | 224(42500), 278(1580), 282(1460) |
| IX | 221(76000), 273(960), 281.5(1000) |
| X | 221(80200), 273.5(925), 282(975) |

a) Inflection

Table 3. Calculated and observed values for the intensity of the longest wavelength absorption bands of chlorotriptycenes

| Triptycene | | ε-Value | |
|---|---|---|---|
| | | Calcd | Obsd |
| 2-Cl- | (VI) | 3339 | 2820 |
| 2,7-$Cl_2$- | (VII) | 1938 | 1600 |
| 2,10-$Cl_2$- | (VIII) | 1938 | 1460 |
| 2,7,11-$Cl_3$- | (IX) | 537 | 1000 |
| 2,10,11-$Cl_3$- | (X) | 537 | 975 |

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[5] P. D. Bartlett and E. S. Lewis, *J. Amer. Chem. Soc.*, **72**, 1011 (1950).

[6] C. F. Wilcox, Jr., *J. Chem. Phys.*, **33**, 1874 (1960); C. F. Wilcox, Jr., and A. C. Craig, *J. Org. Chem.*, **26**, 2491 (1961).

[7] J. R. Platt, *J. Chem. Phys.*, **19**, 263 (1951).

pectively 49 and 1, estimated by Eq. (1) and the moments of methyl and chlorine groups (7 and 6).[7] Assuming the $\varepsilon$-values of *o*-xylene chromophore is one third of $\varepsilon$-value of triptycene ($\varepsilon=4740$) and $\varepsilon_0$ is 150,[7] $\varepsilon-\varepsilon_0$ value of 3-chloro-*o*-xylene is $(4740/3-150)\times 1/49$. Thus the $\varepsilon$-value of the longest wavelength bands of chlorotriptycenes were calculated as shown in Table 3.

The calculated values also show the decreasing tendency of the intensities with the number of chloro-substituent. A moderately good agreement between observed and calculated values was obtained. The small difference between both values is possibly due to the replacement of the spectroscopic moment of bridgehead carbon simply by that of methyl group.

Consequently, we suppose that the intensity of $^1L_b$ bands of chlorotriptycenes can be accounted for in terms of the superposition of three benzenoid chromophores, which supports Wilcox, Jr.'s interpretation on the UV spectra of triptycene.

*NMR Spectra* The NMR spectra of triptycene and its derivatives were first reported by Theilacker *et al.*[8] and later analyzed in detail by Smith and Shoulders,[9] and Kidd *et al.*[10] The spectrum of triptycene in carbon disulfide reveals an $A'_2B'_2$ pattern of aromatic protons centered at 2.96 $\tau$ and a singlet of two bridgehead tertiary protons at rather low field of 4.79 $\tau$. Supposing that a substituent is introduced at 2- or 3-position of triptycene, bridgehead proton should shift to higher or lower field owing to the anisotropy of the substituent. Thus the magnitude of such shifts will allow us to estimate the shielding effect of the substituent by comparison with the other bridgehead proton as in structure (I). Table 4 shows the chemical shifts of bridgehead protons of chlorotriptycenes. The spectra of chlorotriptycenes (VI—X) were all measured in arsenic trichloride because of poor solubility of trichloroderivatives (IX and X) in the usual organic solvents. The table reveals that with the increase of the number of chlorine atoms the resonance position of the bridgehead proton regularly shifts to lower field by average 0.43 ppm.[11]

TABLE 4. CHEMICAL SHIFTS ($\delta$) OF BRIDGEHEAD PROTONS OF CHLOROTRIPTYCENES IN $AsCl_3$ AND AVERAGE INTERNAL CHEMICAL SHIFT PER CHLORINE ATOM

| Triptycene | | No. of Cl | | | | $\Delta\sigma$/Cl |
|---|---|---|---|---|---|---|
| | | 0 | 1 | 2 | 3 | |
| 2-Cl- | (VI) | 5.49 | 5.90 | | | −0.41 |
| 2,7-$Cl_2$ | (VII) | | 5.92 | | | |
| 2,10-$Cl_2$- | (VIII) | 5.52 | | 6.37 | | −0.43 |
| 2,7,11-$Cl_3$- | (IX) | | 5.93 | 6.38 | | −0.45 |
| 2,10,11-$Cl_3$- | (X) | 5.53 | | | 6.89 | −0.45 |
| | | | | | average | −0.43 |

A difference in net shielding, or the internal chemical shift $\Delta\sigma$, between two protons $H_A$ and $H_B$ in a molecule can generally be expressed by the equation

$$\Delta\sigma = \sigma_A - \sigma_B = \Delta\sigma_d + \Delta\sigma_w + \Delta\sigma_e \tag{2}$$

where $\Delta\sigma_d$ is magnetic anisotropy effect, $\Delta\sigma_w$ is the van der Waals effect and $\Delta\sigma_e$ is electric field effect. In reference to the X-ray analysis[12] the geometry of chlorotriptycenes was drawn from which the distance $r$ between a bridgehead proton nearer to chlorine atom and the midpoint of C–Cl bond, the distance R between the proton and the chlorine atom, and the angle $\theta$ given by the line represented as $r$ and C–Cl bond axis were measured, as shown in Fig. 2.

The electric field effect $\Delta\sigma_e$ in Eq. (2) is calculated by the equation of Buckingham[13]

$$\Delta\sigma_e = -2\times 10^{-12}E_z - 10^{-18}E^2, \tag{3}$$

and the electric field term $E$ is estimated by the following equation, assuming the point charge.

$$E = \mu/R^2\cdot l, \tag{4}$$

where $\mu$ is the dipolemoment of chlorobenzene (1.56 D) and $l$ is the distance between chlorine atom and the center of the benzene ring (Fig. 2).

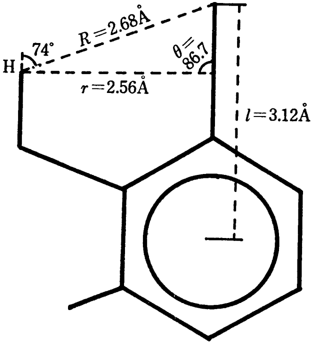

Fig. 2. Measured distances ($R$, $r$, and $l$) and angles in chlorotriptycenes.

The steric compression effect $\Delta\sigma_w$ is estimated from the following equation which was presented by Bothner-By and modified by Nakagawa.[14]

$$\Delta\sigma_w = (-[R]/R^6)\times 7 \tag{5}$$

where [R] is atomic refraction. The value $\Delta\sigma_d$ (−0.03 ppm) which is left in substracting $\Delta\sigma_e$ (−0.29 ppm) and $\Delta\sigma_w$ (−0.11 ppm) from the observed value $\Delta\sigma$ may be ascribed to the long range shielding due to the magnetic anisotropy of the substituent. $\Delta\sigma_d$ is related with the measured values of $\theta$ and $r$ by the following McConnell equation.[15]

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8) W. Theilacker, K. Albrecht, and H. Uffmann, *Chem. Ber.*, **98**, 428 (1965).

9) W. B. Smith and B. A. Shoulders, *J. Phys. Chem.*, **69**, 2022 (1965).

10) K. G. Kidd, G. Kotowycz, and T. Schaefer, *Can. J. Chem.*, **45**, 2155 (1967).

11) Because of difficulty in quantitative evaluation for solvent effect, the value in arsenic trichloride will be taken in the following calculations.

12) K. Ozeki, N. Sakabe, and J. Tanaka, Symposium on Molecular Structure held by The Chemical Society of Japan, Summary 3B25, Tokyo, October 1968; K. J. Palmer and D. H. Templeton, *Acta Crystallogr.*, **B24**, 1048 (1968).

13) A. D. Buckingham, *Can. J. Chem.*, **38**, 300 (1960).

14) A. A. Bothner-By, *J. Mol. Spectrosc.*, **5**, 52 (1960); N. Nakagawa, "Interpretation of NMR Spectra," Kyoritsu, Tokyo (1966), p. 98.

15) H. J. McConnell, *J. Chem. Phys.*, **27**, 226 (1957).

TABLE 5. ANALYTICAL DATA, SOLVENTS IN REACTION AND YIELDS OF CHLOROTRIPTYCENES

| Triptycene | Formula | Anal |  |  |  |  |  | Mp °C | Recryst. Solvent | Yield % | Reaction solvent |
|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  | Calcd % |  |  | Found % |  |  |  |  |  |  |
|  |  | C | H | Cl | C | H | Cl |  |  |  |  |
| 2-Cl- (VI) | $C_{20}H_{13}Cl$ | 83.19 | 4.54 | 12.28 | 83.12 | 4.27 | 12.37 | 225.0—225.5[a)] | $C_2H_5OH$ | 1) 30<br>2) 16 | 1)<br>2) $CH_2Cl_2$-THF[c)] |
| 3-Cl- | $C_{20}H_{13}Cl$ | 83.19 | 4.54 | 12.28 | 83.12 | 4.54 | 12.12 | 167.5—168.0[b)] | Pet. ether | 1) 2 | 1) DME[c)] |
| 2,7-$Cl_2$- (VII) | $C_{20}H_{12}Cl_2$ | 74.32 | 3.74 | 21.94 | 74.00 | 3.54 | 21.70 | 258.0—258.5[a)] | $C_2H_5OH$ | 1) 42<br>2) 8 | 1) $CH_2Cl_2$-THF[c)]<br>2) DME[c)] |
| 2,10-$Cl_2$- (VIII) | $C_{20}H_{11}Cl_2$ | 74.32 | 3.74 | 21.94 | 74.13 | 3.54 | 21.77 | 299.5—300.0[a)] | $C_6H_6$ | 1) 75<br>2) 8 | 1) $CH_2Cl_2$-THF[c)]<br>2) DME[c)] |
| 2,7,11-$Cl_3$- (IX) | $C_{20}H_{11}Cl_3$ | 67.16 | 3.10 | 29.74 | 66.80 | 3.47 | 29.98 | 303—307[a)] | $C_2H_5OH$ | 1) 9<br>2) 16 | 1) DME[c)]<br>2) DME[c)] |
| 2,10,11-$Cl_3$- (X) | $C_{20}H_{11}Cl_3$ | 67.16 | 3.10 | 29.74 | 67.72 | 3.14 | 29.41 | 413—415[a)] | $C_6H_{12}$ |  |  |

a) in sealed tube. b) lit[4)] mp 168—169°C. c) THF=tetrahydrofuran; DME=dimethoxyethane.
1) benzyne method. 2) chlorobenzyne method.

$$\Delta\sigma_d = (1/3r^3)\Delta\chi(1-3\cos^2\theta) \qquad (6)$$

A calculated value of $\Delta\chi$, $-1.6\times10^{-30}$ cm³/molecule, is in good agreement with the values reported by Schaeffer and Yonemoto[16)] ($5\times10^{-30}$ cm³/molecule) and by Flautt[17)] ($1.5\times10^{-30}$ cm³/molecule).

Two bridgehead protons of 3-chlorotriptycene show a singlet peak, or no internal chemical shift, probably due to the smaller difference of distances between both protons and the substituent in 3-substituted triptycene than in 2-substituted one.

These results imply that our assumption is reasonable, and that the triptycene derivatives are fairly suitable compounds for the study of magnetic anisotropy, due to the presence of appropriate reference proton in the rigid molecular structure.

## Experimental

All melting points are uncorrected. The IR and UV spectra were measured on a Jasco autorecording spectrometer DS-402G and on a Hitachi EPS-3T, respectively. The NMR spectra were measured on a Hitachi Perkin-Elmer R-20 spectrometer (60 MHz) using TMS as an internal standard. A frequency counter was used to measure the frequency separation between signals.

*Mono-, Di-, and Tri-chlorotriptycenes.* Preparation of mono-, di-, and tri-chlorotriptycenes was carried out using the Diels-Alder reaction of anthracene derivatives with benzyne or 3-chlorobenzyne, generated from anthranilic or 6-chloroanthranilic acid respectively (Chart 1). All the reactions were carried out according to the procedure of Friedman and Logullo.[4)] 3-Chlorotriptycene was synthesized by the reaction of anthracene with 4-chlorobenzyne generated from 5-chloroanthranilic acid.

2-Chlorotriptycene (VI) obtained by two methods shows an identical melting point and spectral properties. The reaction of 1-chloroanthracene with 3-chlorobenzyne gave a mixture of dichlorotriptycenes, VII and VIII. Attempts to separate VII and VIII from the mixture were unsuccessful. However, the chromatography on alumina of the reaction mixture of 1,8-dichloroanthracene (V) with 3-chlorobenzyne resulted in the separation of the trichlorotriptycenes, IX and X. An early benzene fraction was evaporated and recrystallized from alcohol to give 2,7,11-trichlorotriptycene (IX). Crystals obtained from the latter fraction were treated with cyclohexane to remove IX from slightly soluble isomer, 2,10,11-trichlorotriptycene (X) and were recrystallized from cyclohexane to give pure X.

The analytical data, melting points and yields of several chlorotriptycenes obtained are summarized in Table 5.

*Reaction of 3-Chlorobenzyne with 9-Alkyl- and 9-Chloro-anthracenes.* All reactions of 3-chlorobenzyne with 9-alkyl- and 9-chloro-anthracenes were undertaken according to the general procedure[18)] described in the following case of 9-methylanthracene.

To a solution of 9-methylanthracene[19)] (2.0 g, 10 mmol) and *i*-amyl nitrite (2.0 m*l*, 15 mmol) in dimethoxyethane (20 m*l*) was dropwise added a solution of 6-chloroanthranilic acid (2.6 g, 15 mmol) in dimethoxyethane (10 m*l*) for 30 min under refluxing and stirring. After further reflux for 10 min and addition of *i*-amyl nitrite (2 m*l*), an additional solution of 6-chloroanthranilic acid (2.6 g) in dimethoxyethane (10 m*l*) was added dropwise to the mixture for 30 min under reflux. The mixture was refluxed for 20 min with stirring to complete the reaction and cooled, and the solvent was removed *in vacuo*. The residue obtained was treated with maleic anhydride (2.0 g) in xylene (25 m*l*) under reflux for 1 hr. After evaporation of xylene the residue was chromatographed on alumina (50 g) with benzene. A part (150 m*l*) of the effluent (700 m*l*) was evaporated to dryness in a vacuum and the residue was dissolved in deuterochloroform to measure NMR spectrum. The ratio of quasi-*trans*/quasi-*cis* in the product was determined from half-width of bridgehead proton signals in both isomers.

The authors wish to express their appreciation to Professor Masazumi Nakagawa of Osaka University for his continued encouragement through this work.

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16) T. Schaeffer and T. Yonemoto, *Can. J. Chem.*, **42**, 2318 (1964).

17) T. J. Flautt and W. F. Erman, *J. Amer. Chem. Soc.*, **85**, 3212 (1963).

18) *Cf.* L. F. Fieser, "Organic Experiments," 3rd Ed., D. C. Heath Co., Boston (1964), p. 314.

19) A. Sieglitz and R. Marx, *Ber.*, **56**, 1619 (1923).