October, 1980] © *1980 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, *53*, *2977—2980 (1980)* 2977

Restricted Rotation Involving the Tetrahedral Carbon. XXXIII.[1] Restricted Rotation about a C_{sp^3}–C_{sp^2} Bond in 10,10-Disubstituted 9-(2,6-Xylyl)-9,10-dihydroanthracene Derivatives[2]

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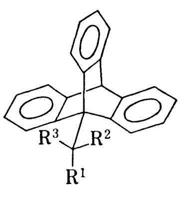
(Received April 12, 1980)

A series of 10,10-disubstituted 9-(2,6-xylyl)-9,10-dihydroanthracene derivatives have been prepared and their conformations and barriers to internal rotation about the C_{xylyl}–C_9 bond have been examined. These compounds exist predominantly as a pseudo-equatorial form in the ground state for rotation. A large effect is inserted by the substituents in 10 position on barriers to rotation and is interpreted in terms of a rotation-inversion mechanism rather than a simple rotation mechanism for the methyl-exchange process which is observed by ^{1}H NMR spectra. The highest barrier to rotation has been found in the compound having two peri-chloro groups and a hydroxyl group in 9-position. The high barrier is ascribed to destabilization of the transition state, where 9-aryl group takes axial conformation, due to the three electronegative groups which are forced to be arranged parallelly in quite a near region. The change of 9-OH to 9-H thus decreases the barrier to rotation when peri-chlorines are present, while the increase in barrier is observed as in the case of 9-arylfluorenes and 9-arylxanthenes when they are absent.

It is well known that the barrier to rotation of 9-alkyltriptycenes (**1**) are extraordinarily high and in some cases rotational isomers have been isolated as stable entities at room temperature.[3] Barriers to rotation of aryl groups in 9-aryltriptycenes are, on the other hand, lower than those expected.[4] Although the molecular model of 9-(*o*-tolyl)triptycenes (**2**) indicated the existence of extremely high repulsion between the methyl and a peri hydrogen in the transition state for rotation, the barriers were in the range of 54—63 kJ mol^{-1} depending on the substituents in the peri position. These facts were interpreted in terms of destabilization of the ground state due to repulsive interaction between 6′ and peri hydrogens. This means that the removal of a benzo group from 9-aryltriptycene, which leads to 9-aryl-9,10-dihydroanthracene skeleton (**3**), eliminates the repulsion mainly in the ground state and should lead to an increase in barriers to rotation. But a previous paper which dealt with restricted rotation of the aryl group in 9-(2,6-xylyl)xanthenes (**4**), 10-oxa analogs of **3**, showed relatively low barriers to rotation.[5] McKinley *et al.* explained the low barriers in this system, comparing with those of the structurally similar 9-mesitylfluorene derivatives (**5**),[6] on the basis of the difference in the direction of the substituents: the aryl group in the xanthene system takes an axial conformation both in the ground state and in the transition state for rotation. If the aryl group is axial in the boat form of the 9,10-dihydroanthracene type molecules,[7] the steric repulsion between 1,8-substituents of the xanthene ring and 2′,6′-substituents of the aryl ring will not increase in the transition state for rotation in contrast to the case of the 9-arylfluorene system.



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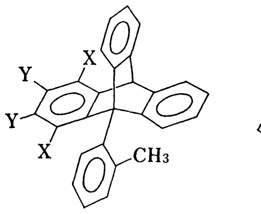

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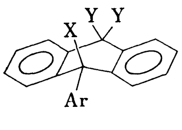

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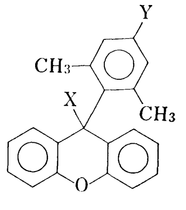
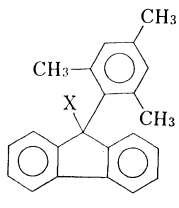


a X=OH
Y=H
b X=H
Y=CH$_3$

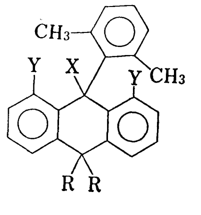
4



a X=OH
b X=H

5

The consideration described above leads to the idea that the barrier to rotation of the 9-aryl group in a 9,10-dihydroanthracene type molecule may be increased if the 9-aryl group is forced to take an equatorial conformation. It seems possible to realize such a situation by the introduction of two substituents in the 10 position. If a bulky group in the 9-position takes an axial conformation, it opposes a substituent in the 10 position which is also axial. Therefore, introduction of two bulky substituents in the 10 position, which assures that one of the two groups is always axial irrespective of the ring inversion, a bulky substituent in the 9 position will inevitably take the equatorial conformation. Under such expectation, we synthesized several 10,10-disubstituted 9-aryl-9,10-dihydroanthracenes (**6**—**11**) and measured the barriers to rotation about the C_9–C_{ar} bond by dynamic NMR method. This paper reports the results of the investigation and discusses the mechanism for rotation.



6 X=OH, Y=H, R=CH$_3$
7 X=H, Y=H, R=CH$_3$
8 X=OH, Y=Cl, R=CH$_3$
9 X=H, X=Cl, R=CH$_3$
10 X=OH, Y=H, R=PhCH$_2$
11 X=OH, Y=Cl, R=PhCH$_2$

Experimental

General. Melting points are uncorrected. ^{1}H NMR spectra were recorded either on a Hitachi R-20B spectrometer operating at 60 MHz or on a Varian EM 390 spectrometer at 90 MHz. IR spectra were measured on a Hitachi EPI-G3 grating infrared spectrophotometer. High and low temperature ^{1}H NMR spectra were measured in hexachlorobutadiene and chloroform-*d* solutions, respectively. The probe temperature was measured by the peak separation of methanol or ethylene glycol or by a thermocouple.

Syntheses. 9-(2,6-Xylyl)-10,10-dimethyl-9,10-dihydroanthracen-9-ol (6): To a vigorously stirred tetrahydrofuran solution of 2,6-xylylmagnesium bromide, prepared from 1.0 g (0.0054 mol) of 2-bromo-*m*-xylene and 0.144 g (0.0060 mol) of magnesium, was added 0.299 g (0.00135 mol) of 10,10-dimethylanthrone[8] at 0 °C. The reaction mixture was stirred for 3 h at room temperature, heated with stirring at 80 °C for 1 h, cooled, and treated with aqueous ammonium chloride. The organic layer was separated and the water layer was extracted with ether. The combined ether solution, after dried over sodium sulfate, was evaporated and the resulting oil was separated by chromatography on silica gel. Elution with hexane and benzene (10 : 1) gave white crystals which were recrystallized from hexane. The yield was 78% based on anthrone. The melting point was 153—154 °C. Found: C, 87.76; H, 7.48%. Calcd for $C_{24}H_{24}O$: C, 87.76; H, 7.37%. NMR(CDCl$_3$, δ at 0 °C): 1.35 (3H, s), 1.70 (3H, s), 1.83 (3H, s), 1.9 (1H, s), 2.92 (3H, s), 7.0—7.8 (11H, m).

9-(2,6-Xylyl)-10,10-dimethyl-9,10-dihydroanthracene (7). To a solution of 102 mg (0.31 mmol) of **6** in 10 ml of acetic acid was added 2.0 ml of 57% hydriodic acid. The solution was stirred for 5 h at room temperature. The reaction mixture was poured into water and extracted with ether. The ether layer was washed with aqueous sodium hydrogencarbonate and then with aqueous sodium hydrogensulfite, and dried over sodium sulfate. After evaporation of the solvent, the products were separated by chromatography on silica gel. Elution with hexane followed by recrystallization from ethanol afforded 79 mg (81%) of white fluorescent crystals, mp 133—134 °C. Found: C, 92.18; H, 7.78%. Calcd for $C_{24}H_{24}$: C, 92.26; H, 7.74%. NMR (CDCl$_3$, δ): 1.40 (3H, s), 1.54 (3H, s), 1.90 (3H, s), 2.57 (3H, s), 5.80 (1H, s), 6.6—7.8 (11H,m).

1,8-Dichloro-9-(2,6-xylyl)-10,10-dimethyl-9,10-dihydroanthracen-9-ol (8), mp 199—200 °C, was prepared by treating 2,6-xylyllithium, prepared from 1.0 g (0.0054 mol) of 2-bromo-*m*-xylene and 0.081 g (0.012 mol) of lithium, with 0.103 g (0.00035 mol) of 1,8-dichloro-10,10-dimethylanthrone[9,10] in 30 ml of ether. The reaction mixture was separated by chromatography on silica gel. The white crystals thus obtained were recrystallized from ethanol. The yield was 63% based on anthrone. Found: C, 72.85; H, 5.44; Cl, 17.38%. Calcd for $C_{24}H_{22}Cl_2O$: C, 72.55; H, 5.58; Cl, 17.85%. This compound could not be obtained from the Grignard reaction as in the case of compound **6**. NMR (CDCl$_3$, δ): 1.40 (3H, s), 1.62 (3H, s), 1.93 (3H, s), 2.9 (1H, s), 3.10 (3H, s), 6.5—7.6 (9H, m).

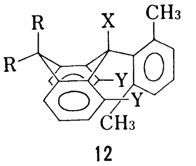
1,8-Dichloro-9-(2,6-xylyl)-10,10-dimethyl-9,10-dihydroanthracene (9), mp 206—207 °C, was similarly prepared by the reaction of **8** with 57% hydriodic acid in acetic acid followed by similar treatment as **7**. Recrystallization from hexane gave white crystals in 78% yield. Found: C, 75.77; H, 5.86; Cl, 18.63%. Calcd for $C_{24}H_{22}Cl_2$: C, 75.59; H, 5.82; Cl 18.60%. NMR-(CDCl$_3$, δ): 1.51 (3H, s), 1.63 (3H, s), 2.00 (3H, s), 2.87 (3H, s), 5.90 (1H, s), 6.6—7.6 (9H, m).

9-(2,6-Xylyl)-10,10-dibenzyl-9,10-dihydroanthracen-9-ol (10), mp 216—217 °C, was prepared by treating 2,6-xylylmagnesium bromide, prepared from 3.2 g (0.0173 mol) of 2-bromo-*m*-xylene and 0.411 g (0.0173 mol) of magnesium, with 2.0 g (0.0057 mol) of 10,10-dibenzylanthrone[8] in 50 ml of THF. The reaction mixture was separated by chromatography on silica gel. Elution with hexane and benzene (10 : 1) gave white crystals which were recrystallized from ethanol. The yield was 55% based on anthrone. Found: C, 89.76; H, 6.46%. Calcd for $C_{36}H_{32}O$: C, 89.96; H, 6.71%. NMR (CDCl$_3$, δ): −0.2 (1H, s), 0.26 (3H, s), 2.55 (3H, s), 3.45 (2H, s), 3.86 (2H, s), 6.1—7.6 (19H, m), 8.1 (2H, dd).

1,8-Dichloro-9-(2,6-xylyl)-10,10-dibenzyl-9,10-dihydroanthracen-9-ol (11), mp 283—285 °C, was synthesized by treating 2,6-xylyllithium, prepared from 2.20 g (0.012 mol) of 2-bromo-*m*-xylene and 173 mg (0.025 mol) of lithium, with 1.22 g (0.0028 mol) of 1,8-dichloro-10,10-dibenzylanthrone in 30 ml of ether. The product was recrystallized from benzene–hexane. The yield was 60% based on anthrone. Found: C, 78.92; H, 5.26; Cl, 12.76%. Calcd for $C_{36}H_{30}Cl_2O$: C, 78.68; H, 5.50; Cl, 12.90%. NMR (CDCl$_3$, δ): −0.2 (1H, s), 0.35 (3H, s), 2.78 (3H, s), 3.30 (2H, s), 5.00 (2H, s), 6.1 (2H, m), 6.3 (1H, dd), 6.7—7.6 (14H, m), 8.1 (2H, dd).

Results and Discussion

Ground State Conformation. Before discussing the barriers to rotation of these compounds, it is necessary to consider the ground state conformation. These compounds could exist as two conformers, pseudo-equatorial (**12**) and pseudo-axial (**13**), with respect to 9-aryl orientation. The molecular model indicates that, while extremely large repulsion exists in **13**, such large repulsive interaction can not be expected in **12** and suggests that the 9-aryl group takes the conformation which bisects the 9,10-dihydroanthracene ring. That the preferred conformation of these compounds is pseudo-equatorial is clearly demonstrated by the ^{1}H NMR spectra, especially in the case of **10** and **11**. In both compounds one of the methyl signals appeared at an abnormally high magnetic field. In addition, the hydroxyl signals of these compounds also appeared at quite a high field (δ=−0.2). The high chemical shifts of these protons can be explained by the 9-aryl equatorial form with the conformation of benzyl groups which is discussed below. Two benzyl groups are arranged in such a manner that the two bulky benzene rings take the conformation anti to each other to avoid severe steric interaction. As a result one benzene ring of the benzyl group faces the methyl in the 2′ position and another the OH group, making these protons shift to quite a high field. In fact there are no such signals in 10,10-dimethyl derivatives **6** and **8**. Thus the most plausible conformation of **10** and **11** are considered to be **14**. Another piece of evidence for the conformation can be supplemented by the IR spectra. As are shown



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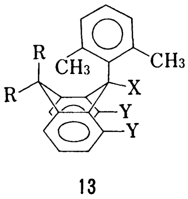

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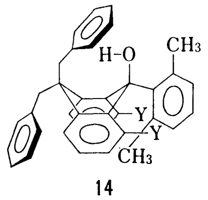

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Table 1. ν_{OH} Absorption[a)]

Compound	**6**	**8**	**10**	**11**
ν_{OH}/cm^{-1}	3596	3586	3547	3542

a) Carbon tetrachloride solutions of which concentrations were *ca.* 10 mmol l^{-1}

in Table 1, those compounds which carry benzyl groups exhibit ν_{OH} absorptions at around 3545 cm^{-1}, whereas those carrying methyl groups in the 10 position at around 3590 cm^{-1}. The latter absorption is characteristic of tertiary benzylic alcohols[11)] but the former is too low to assign to the normal tertiary benzylic alcohols. Instead, the existence of the OH⋯π interaction[12)] is suggested. Then the benzylic phenyl and the hydroxyl groups must be located in proximity. The existence of two aromatic protons which appeared at a field lower than δ 8.0 as a double doublet can also be explained by this conformation. These signals are assigned to the protons in 4 and 5 positions, because in **14** they reside in the deshielding zone of the benzene ring of the benzyl group.

In the case of the 10,10-dimethyl derivatives (**6**—**9**), it is very difficult to decide whether or not the 9-aryl groups of these compounds take the equatorial conformation on the basis of their ^{1}H NMR spectra, because there are no so characteristic signals as to suggest a conformation. But comparison of barriers to rotation of **6** and **7** with those of the corresponding xanthene derivatives **4a** and **4b** clearly indicates that the 9-aryl groups also take the equatorial conformation, the reason of which will be mentioned in the later part of this paper.

Barriers to Rotation. In every compound examined, two methyl signals in 2′ and 6′ positions broadened when the temperature was raised. However, no change in chemical shifts and spectral widths was observed in the signals in 10 position. This clearly shows that the coalescent phenomenon of this system is not due to the slow inversion of 9,10-dihydroanthracene ring but due to the restricted rotation of the 9-aryl ring.

In Table 2, activation free energies of these compounds including structurally similar **4** and **5** are listed together with the coalescence temperatures and the chemical shift differences between two methyl signals in 2′ and 6′ positions. Inspection of Table 2 reveals that the replacement of two methyl groups in 10 positions by benzyl groups causes the increase in energy barrier by 17.6 kJ mol^{-1} (**6**→**10**) and by more than 4.6 kJ mol^{-1} (**8**→**11**). Since the substituents in 10 positions are located far away from the two methyls in the pseudo-equatorial 9-aryl group, the increase in energy observed here seems to be too large as the substituent effect on barriers to rotation.

Table 2. Chemical shifts and barriers to rotation

Compd	2′-CH$_3$	6′-CH$_3$	10-R	T_c/°C	$\Delta G^{\neq}_c$/ kJ mol^{-1}
4a	1.35	2.93		−20	45.6[a)]
4b	1.63	2.58		95	73.6[a)]
5a	1.15	2.90		145	84.5[b)]
5b	1.13	2.69		>190	>104.6[b)]
6	1.35	2.92	1.70, 1.83	48	64.4
7	1.40	2.57	1.54, 1.90	126	82.0
8	1.40	3.10	1.62, 1.93	172	90.4
9	1.63	2.87	1.51, 2.00	36	62.8
10	0.26	2.55	3.45, 3.86	138	82.0
11	0.35	2.78	3.30, 4.00	>200	>95.0

a) Data from McKinley *et al.*[5)] b) Data from Rieker and Kessler.[6c)]

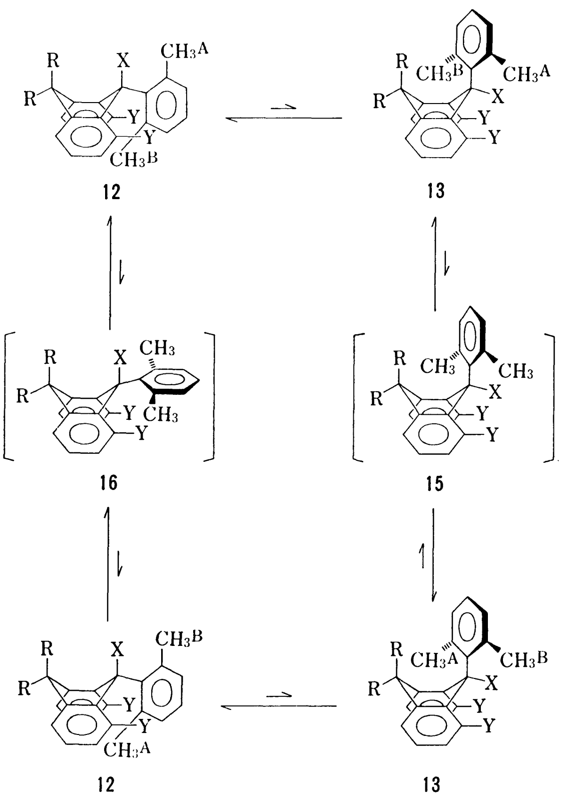

Fig. 1. Mechanism for the exchange of two methyls in the 2,6-xylyl group.

Two paths may be possible as the methyl-exchange mechanism as shown in Fig. 1. One is a simple rotation process during which the 9-aryl group is fixed in the equatorial form. The conformation of the transition state of this process is shown as **16**. The other is an inversion-rotation process which indicates that the methyl-exchange occurs through inversion of the 9,10-dihydroanthracene ring followed by rotation in the pseudo-axial conformation and then inversion to the methyl-exchanged ground state. The conformation of the transition state in this process is **15**. If the former is the case, the substituent effect in 10 position is, as mentioned, too large. In fact extremely large repulsion is expected between the xylyl group and 1,8-substituents in the conformation **16**. The barrier would have been very high in this case. If, on the other hand, the latter is occuring, the large substituent effect can be explained on the basis of the bulkiness of the benzyl groups in 10 position. In the transition state for the

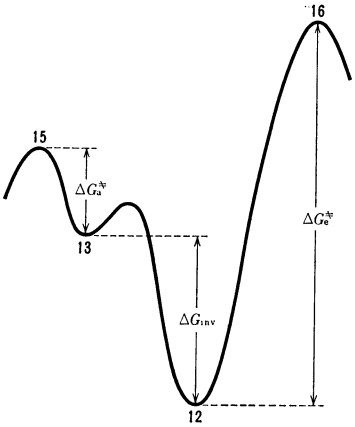

Fig. 2. Free energy profile for the rotation in 10,10-disubstituted 9-(2,6-xylyl)-9,10-dihydroanthracenes.

exchange, the two methyl groups in the pseudo-axial 9-aryl ring interact with the atoms in 1,8-positions as shown in **15**. In such a conformation two benzyl groups in **10** and **11** can not be arranged as in the ground state **14**; inside benzyl group takes the conformation in which the bulky benzene ring rotates away from the 9-aryl ring to avoid steric interaction and the rotation causes, in turn, repulsion between the two benzyl groups to result in an increase in energy of this state. In compounds **6** and **8**, on the other hand, such an additional increase in energy caused by the interaction between the two methyl groups in 10 position does not occur in the transition state for rotation. This may be the reason why **10** and **11** have higher barriers to rotation than those of the corresponding **6** and **8**. The energy profile in this system thus becomes the one described in Fig. 2, where ΔG_{inv}, $\Delta G_a^{\neq}$, and $\Delta G_e^{\neq}$ stand for the difference in free energy between **12** and **13**, the barrier to rotation in the pseudo-axial state, and that in the pseudo-equatorial state, respectively.

The reason why we take $\Delta G_a^{\neq}$ smaller than ΔG_{inv} is as follows. If we assume that two methyls exchange only through the inversion of dihydroanthracene ring as described above, the free energy of activation ($\Delta G^{\neq}$) in Table 2 are given by

$$\Delta G^{\neq} = \Delta G_{\text{inv}} + \Delta G_a^{\neq}.$$

Since the barrier to rotation of the xylyl group in structurally similar **4a**, where the 9-aryl group is axial both in the ground and in the transition state for rotation, was reported to be 45.6 kJ mol^{-1}, $\Delta G_a^{\neq}$ in this system is expected to be far lower than this value because of the existence of two substituents in 10 position which destabilize the aryl-axial form **13**. Therefore, the main portion of $\Delta G^{\neq}$ is occupied by ΔG_{inv}. A similar discussion has been made recently by Miller for the restricted rotation in 3-mesityl-1*H*,3*H*-naphtho[1,8-*de*]pyrans.[13] The above discussion clearly indicates that the ground state conformation of 10,10-dimethyl derivatives (**6**—**9**) is also equatorial. If the 9-aryl groups of these compounds were axial, the $\Delta G^{\neq}$ should have been equal to $\Delta G_a^{\neq}$ which must be lower than that of **4a**. Actually, however, the reverse is true in this system.

Introduction of two chloro groups in 1 and 8 positions causes a strange effect on barriers to rotation: the increase in energy by more than 13.0 kJ mol^{-1} (**10**→**11**) and by 26.0 kJ mol^{-1} (**6**→**8**) was observed in the 9-OH derivatives, while the decrease in energy by as much as 19.2 kJ mol^{-1} was found in the 9-H derivatives (**7**→**9**). These results may be explained as follows. Introduction of two chloro groups raises the energy state of both the ground state **12** and the transition state **15** for rotation. But the degree of the increase is much greater in the latter than in the former when X is OH, because in **15** three bond dipoles are forced to be arranged parallelly in quite a narrow region. Since such a repulsion in **15** is not expected in the 9-H compound (**9**), the increase in energy of the ground state is large relative to the transition state, resulting in a low barrier to rotation.

The change in barriers, observed on the change in the 9-substituent from OH to H, is also interesting. In the case of a pair of **6** and **7**, the increase in energy of *ca.* 17.6 kJ mol^{-1} is ascribed mainly to the stabilization of the ground state. Such a stabilization of the ground state due to loss of repulsion between 9-OH and 2′-methyl is well known in **4** and **5**. On the contrary, relatively large decrease in rotational barrier (27.6 kJ mol^{-1}) was found when **8** was changed to **9**. Probably, the role of parallel arrangement of the three dipoles in the transition state of **8** exceeds that of the increase in the steric interaction in the ground state of **8** in contribution to the barrier to rotation.

References

1) Preceding paper: G. Yamamoto, M. Suzuki, and M. Ōki, *Angew. Chem. Int. Ed. Engl.*, submitted.

2) Presented in part as a preliminary form: M. Nakamura and M. Ōki, *Tetrahedron Lett.*, **1979**, 527.

3) M. Ōki, *Angew. Chem. Int. Ed. Engl.*, **15**, 87 (1976).

4) M. Nakamura and M. Ōki, *Bull. Chem. Soc. Jpn.*, **48**, 2106 (1975).

5) S. V. McKinley, P. A. Grieco, A. E. Young, and H. H. Freedman, *J. Am. Chem. Soc.*, **92**, 5900 (1970).

6) a) E. A. Chandross and C. F. Sheley, Jr., *J. Am. Chem. Soc.*, **90**, 4345 (1968); b) T. H. Siddall, III, and W. E. Stewart, *J. Org. Chem.*, **34**, 233 (1969); c) A. Rieker and H. Kessler, *Tetrahedron Lett.*, **1969**, 1227.

7) P. W. Rabideau, *Acc. Chem. Res.*, **11**, 141 (1978) and references cited therin.

8) D. Y. Curtin, R. C. Tuites, and D. H. Dybvig, *J. Org. Chem.*, **25**, 155 (1960).

9) E. De B. Barnett and M. A. Matthews, *J. Chem. Soc.*, **123**, 2549 (1923).

10) D. Y. Curtin and Z. M. Holubec, *J. Org. Chem.*, **34**, 3093 (1969).

11) M. Ōki and H. Iwamura, *Bull. Chem. Soc. Jpn.*, **35**, 1552 (1962).

12) M. Ōki and H. Iwamura, *Bull. Chem. Soc. Jpn.*, **33**, 681 (1960).

13) A. Miller, *J. Org. Chem.*, **44**, 1934 (1979).