H, NH), 7.3 (s, 5 H, C_6H_5); ^{13}C NMR 28.2 (q, $C(CH_3)_3$), 50.0 (t, $CHCH_2$), 52.2 (q, OCH_3), 53.4 (t, $NCH_2C_6H_5$), 53.8 (d, $CHCH_2$), 79.9 (s, $C(CH_3)_3$), [aromatic carbons at] 127.0 (para), 128.0 (ortho), 128.4 (meta), 140.0 (ipso), 155.4 (s, NCOO), 172.4 (s, $COOCH_3$), MS (70 eV) *m/e* 234, 175, 149, 132, 120, 91 (100), 77, 65, 57, 51, 41.

Registry No. 2, 4248-19-5; 3, 55477-80-0; 4, 99532-92-0; $C_6H_5CH_2NH_2$, 100-46-9; methyl pyruvate, 600-22-6.

Synthesis and Properties of the Cyclohexa[*cd*]perylenium Tetrafluoroborate. A Homologue of the Phenalenium Ion

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The odd-alternant phenalenyl system 1 has intrigued both experimental and theoretical chemists due to its unique electronic structure.[1] Although there is much current interest in the species consisting of the phenalenyl system,[2] little is known for the extended odd-alternant systems related to 1.[3] Cyclohexa[*cd*]perylenyl system (2), in which two phenalenyl skeletons share their active (starred) sites of 1,3-positions on the one hand and of 1,9-positions on the other, can be regarded as a higher homologue of 1 from various points of view. First, both 1 and 2 are odd-alternant hydrocarbons. Second, simple Hückel molecular orbital theory predicts that 2 has 1 nonbonding and 11 bonding molecular orbitals with the energies given in Figure 1. The cyclohexa[*cd*]perylenium ion (2^+) thus possesses 22 π-electrons which exactly fill pairwise the 11 bonding molecular orbitals. The additional one or two electrons of the radical ($2^\cdot$) or the anion (2^-) occupy the nonbonding molecular orbital. Hence all three species should possess the same magnitude of π-electron energy and also the same delocalization energy. Third, the charge density distribution in 2^+ and 2^- are found at positions 1, 3, 4, 5a, 6, 8, 9, 11, 11b, and 13 (starred atoms) and zero at the remaining positions (unstarred atoms). The central carbon atoms, C_α and C_β (see Figure 1), have no charge since the nonbonding MO coefficients at these atoms vanish, even though these are starred atoms. In connection with our study on the phenalenyl system we now report the synthesis and some properties of 2^+.

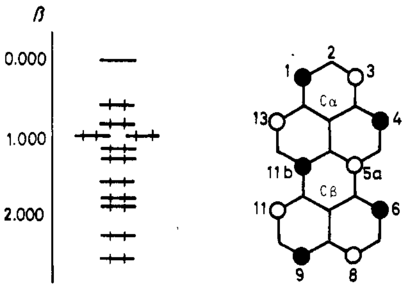


Figure 1. Hückel molecular orbital energies and nonbonding MO coefficients of 2.

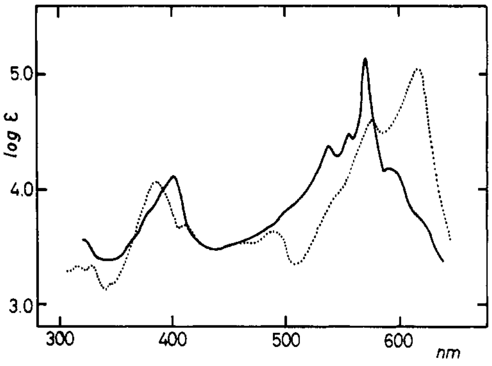
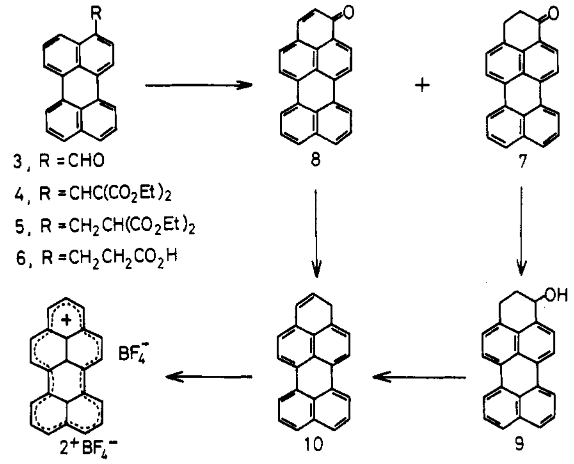


Figure 2. UV-vis spectra of 2^+(—) and 8 (···) in CF_3COOH.

Knoevenagel reaction of 3-perylenecarboxaldehyde (3),[4] obtained from perylene with phosphoryl chloride and *N*-methylformanilide in 94% yield with diethyl malonate led to 76% yield of α,β-unsaturated diester 4, mp 206 °C. Reduction of 4 by zinc-acetic acid yielded 5 in 92% yield.



On hydrolysis and subsequent decarboxylation of 5, β-(3-perylenyl)propionic acid (6), mp 273 °C, was obtained in almost quantitative yield. Treatment of 6 with phosphorous pentachloride in benzene under reflux followed by treatment with anhydrous tin(IV) chloride at 5~10 °C for 1 h gave 7 (42%), orange prisms, mp 185 °C, and 8 (8%), violet powder, mp >300 °C. 8 was also obtained from 7 by dehydrogenation with DDQ in benzene. Reduction of 7 with $NaBH_4$ gave the alcohol 9 in 85% yield, yellow powder, mp 170~5 °C. The hydrocarbon 10, a common potential precursor to 2^+, $2^\cdot$, and 2^-, was derived from 9 with β-naphthalenesulfonic acid in benzene or from 8 by reduction with DIBAL-H. However, 10 could not be isolated in pure form due to its pronouced sensitivity toward air and heat. Hydride abstraction from the freshly prepared crude hydrocarbon 10 with triphenylmethyl tetrafloroborate in dichloromethane at room temperature immediately gave the desired cation salt ($2^+BF_4^-$) as a deep red powder, mp > 300 °C, which can be stored without any change under atmospheric conditions.

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[1] For reviews, see Reid, D. H. *Q. Rev. Chem. Soc.* **1965**, *19*, 274. Hünig, S.; Wolff, E. *Chimia* **1968**, *22*, 33. Murata, I. "Topics in Nonbenzenoid Aromatic Chemistry"; Nozoe, T., Breslow, R., Hafner, K., Ito, S., Murata, I. Eds.; Hirokawa: Tokyo, 1973; Vol. 1, p 191. Murata, I.; Nakasuji, K. *Isr. J. Chem.* **1980**, *20*, 244. Nakasuji, K. *Yuki Gosei Kagaku Kyokai Shi* **1985**, *43*, 145.

[2] Nakasuji, K.; Yoshida, K.; Murata, I. *J. Am. Chem. Soc.* **1983**, *105*, 5136 and references therein.

[3] Murata, I.; Yamamoto, K.; Hara, O. *Tetrahedron Lett.* **1974**, 2047. Hara, O.; Yamamoto, K.; Murata, I. *Ibid.* **1977**, 2431. Hara, O.; Tanaka, K.; Yamamoto, K.; Nakazawa, T.; Murata, I. *Ibid.* **1977**, 2435. Yamamoto, K.; Matsue, Y.; Hara, O.; Murata, I. *Ibid.* **1982**, *23*, 877.

[4] Buu-Hoi, Ng. Ph.; Long, C. T. *Recl. Trav. Chim. Pays-Bas* **1956**, *75*, 1221. Buckly, D. A.; Thomas, H. R. Ger. Offen. 2456538.

0022-3263/86/1951-0251$01.50/0

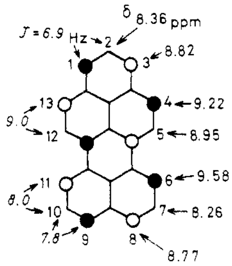

Figure 3. ^1H NMR parameters for 2^+.

As illustrated in Figure 2, the electronic spectra of 2^+ and 8 in trifluoroacetic acid exhibited the pronounced red shifts compared to the phenalenium ion (400 nm)[5] and phenalenone (404 nm),[6] respectively, suggesting the fully delocalized structure with extended conjugation. In spite of the fact that a unit positive charge resides over the 10 peripheral starred carbon atoms, the ^1H NMR chemical shifts of 2^+ in deuteriotrifluoroacetic acid (Figure 3) are comparable to those of the tropylium ion (δ 9.20 in CD_3CN)[7] and the phenalenium ion (δ 9.30 and 8.46 in $AsCl_3$).[8] This provides evidence for the existence of a strong induced diamagnetic ring current associated with the perimeter of 2^+. As expected the protons on the starred carbon atoms resonated at considerably lower magnetic field than those of the others. The fairly downfield chemical shift of H-5 and H-12 compared to the other protons attached to the unstarred carbon atoms is mainly due to the location of these protons at bay regions. The chemical shifts and the comparative uniformity of the coupling constants show the cation 2^+ to have fully delocalized structure with C_{2v} symmetry.

Measurement of the reduction potential of 2^+ by cyclic voltammetry showed two step reversible reductions (E_1 ($2^+/2^\cdot$) = 0.21 V, E_2 ($2^\cdot/2^-$) = −0.89 V vs. SCE). The first reduction potential (E_1) of 2^+ is more negative than that of the phenalenium ion (0.7 V).[9] This fact indicates that 2^+ is thermodynamically more stable than 1^+ in conformity with the extensive delocalized structure.[10]

The studies on the corresponding anion 2^- and radical $2^\cdot$ are currently in progress.

Experimental Section

All melting points were uncorrected. ^1H NMR spectra were obtained on a Hitachi R-24A spectrometer (60 MHz) and a Varian XL-100 spectrometer (100 MHz). Infrared spectra were recorded on a JASCO DS-701G spectrophotometer. Ultraviolet spectra were taken on a Shimazu UV-240 spectrophotometer. Cyclic voltammgrams (CV) were measured on a Yanaco polarographic analyzer P-1100 with Watanabe WX-1000 XY recorder in dichloromethane containing 2^+ (0.5 mg/10 mL) and n-Bu_4NClO_4 (0.1 M) at room temperature under nitrogen using a standard calomel electrode as a reference electrode and a Pt electrode as a working electrode. Sweep rate was 100 mV s^{-1}.

3-Perylenecarboxaldehyde (3). From 6.16 g (24.4 mmol) of perylene was obtained 6.40 g (94.2 %) of **3** according to the literature procedure:[3] mp 238 °C (recrystallized from benzene; lit. mp 236 °C), MS, m/e 280 (M^+, 280); ^1H NMR ($CDCl_3$, 60 MHz) δ 10.20 (s, 1 H), 9.05 (d, 1 H), 8.25 ~7.22 (m, 10 H).

Diethyl (3-Perylenylmethylene)propanedioate (4). A mixture of **3** (6.25 g, 22.3 mmol), diethyl malonate (4.64 g, 29.0 mmol), and piperidine (2 mL) in dry benzene (100 mL) was heated under reflux for 48 h. The solvent was evaporated in vacuo, and the residue was chromatographed on silica gel. Elution with benzene–hexane (1:1) gave unreacted **3** and unidentified red needles; further elution with benzene gave **4** as red needles (6.86 g, 75.8%); mp 206 °C (recrystallized from benzene): ^1H NMR ($CDCl_3$, 60 MHz) δ 8.24~7.15 (m, 12 H), 4.50~4.00 (m, 4 H), 1.53~1.01 (m, 6 H). Found: C, 79.70; H, 5.22. Calcd for $C_{28}H_{22}O_4$: C, 79.59; H; 5.26.

Diethyl (3-Perylenylmethyl)propanedioate (5). A mixture of **4** (6.50 g, 15.3 mmol), zinc dust (18 g), and acetic acid (400 mL) was refluxed for 3 h. After cooling, the reaction mixture was poured into a mixture of water and benzene. After shaking, the organic layer was separated and dried over magnesium sulfate. The solvent was evaporated, and the residue was chromatographed on silica gel by eluting with benzene to give **5** as yellow powder (6.01 g, 92.1%): mp 138 °C; ^1H NMR ($CDCl_3$, 60 MHz) δ 8.01~7.11 (m, 11 H), 4.10 (q, 4 H), 3.82~3.43 (m, 3 H), 1.16 (t, 6 H). Found: C, 79.33; H, 5.67. Calcd for $C_{28}H_{24}O_4$: C, 79.21; H, 5.71.

β-(3-Perylenyl)propionic Acid (6). Hydrolysis of **5** (5.60 g, 13.2 mmol) by aqueous potassium hydroxide (2%, 130 mL) in a mixture of benzene (100 mL) and ethanol (400 mL) in the usual manner gave the dicarboxylic acid which, without purification, was refluxed in o-dichlorobenzene (150 mL) for 1 h to effect decarboxylation. After the mixture was cooled, **6** was separated as yellowish brown needles (4.13 g, 96.5%): mp 273 °C dec; IR (KBr) 1705, 1591, 1500, 1432, 1378, 1302, 1210, 827, 811, 765 cm^{-1}. Found: C, 84.97; H, 5.20. Calcd for $C_{23}H_{16}O_2$: C, 85.15; H, 4.98.

1*H*-2,3-Dihydrocyclohexa[*cd*]perylen-1-one (7) and Cyclohexa[*cd*]perylen-1-one (8). Phosphorous pentachloride (4.10 g, 19.7 mmol) was added to a suspension of **6** (4.13 g, 12.7 mmol) in benzene (120 mL) at 10 °C; the mixture was refluxed for 1 h. After the mixture was cooled in an ice bath, anhydrous tin(IV) chloride (7 mL) in benzene (20 mL) was added during 15 min at 5 °C and stirred at 5~10 °C for 1 h. Cold concentrated HCl (15 mL) was added, and the mixture was refluxed for 0.5 h with vigorous stirring. The product was extracted with CH_2Cl_2 and purified by chromatography on silica gel. Elution with CH_2Cl_2 gave **7** (1.65 g, 42.3%) as orange powder; mp 185 °C. Further elution with AcOEt gave **8** (0.32 g, 8.2%) as reddish violet powder; mp >300 °C. **7**: IR (KBr) 1670, 1592, 1502, 1322, 1105, 823, 768 cm^{-1}. Found: C, 90.31; H, 4.50. Calcd for $C_{23}H_{14}O$: C, 90.16; H, 4.62. **8**: IR (KBr) 1630, 1586, 1555, 1385, 1367, 1290, 1235, 1130, 834, 810, 758 cm^{-1}. Found: C, 90.92; H, 3.84. Calcd for $C_{23}H_{12}O$: C, 90.76; H, 3.94.

1*H*-2,3-Dihydrocyclohexa[*cd*]perylen-1-ol (9). Sodium borohydride (0.5 g, 13.2 mmol) was added to a suspension of **7** (1 g, 3.27 mmol) in ethanol (300 mL), and the mixture was stirred at room temperature for 6 h. After usual workup, **9** was obtained as yellow powder (0.86 g, 85.2%): mp 170~175 °C; ^1H NMR (CD_2Cl_2, 60 MHz) δ 8.30~8.14 (m, 4 H), 7.78~7.30 (m, 6 H), 5.10 (t, 1 H), 3.30~3.12 (m, 2 H), 2.29~2.08 (m, 2 H). Found: C, 89.72; H, 5.20. Calcd for $C_{23}H_{16}O$: C, 89.57, H, 5.24.

Cyclohexa[*cd*]perylenium Tetrafluoroborate ($2^+BF_4^-$). A mixture of **9** (0.3 g, 1 mmol), β-naphthalenesulfonic acid (0.05 g, 0.24 mmol), and dry benzene (100 mL) was refluxed for 5 min under nitrogen. The reaction mixture was passed through a short column of deactivated alumina to afford yellow solution. The solvent was evaporated in vacuo, and the residue was dissolved in CH_2Cl_2 (50 mL). To this solution was added triphenylmethyl tetrafluoroborate (0.2 g, 0.6 mmol) in CH_2Cl_2 (20 mL) and stirred for 1 h. Dark red precipitates were filtered and recrystallized from CH_2Cl_2 gave pure $\mathbf{2^+BF_4^-}$ (0.08 g, 33.3%): mp >300 °C; IR (KBr) 1613, 1572, 1413, 1285, 1247, 1090~1030, 849, 815, 755, 700 cm^{-1}; ^1H NMR (CF_3COOD, 100 MHz) δ 9.58 (d, 2 H, H-6,11, J = 8.0 Hz), 9.22 (d, 2 H, H-4,13, J = 9.0 Hz), 8.95 (d, 2 H, H-5,12, J = 9.0 Hz), 8.82 (d, 2 H, H-1,3, J = 6.9 Hz), 8.77 (d, 2 H, H-8,9, J

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(5) Pettit, R. *Chem. Ind. (London)* **1956**, 1306; *J. Am. Chem. Soc.* **1960**, *82*, 1972.

(6) Sugihara, Y.; Hashimoto, K.; Yoshikawa, M.; Murata, I. *Tetrahedron Lett.* **1982**, *23*, 1925.

(7) Fraenkel, G.; Carter, R. E.; McLachlan, A.; Richards, J. H. *J. Am. Chem. Soc.* **1960**, *82*, 5846. Schaeffer, T.; Schneider, W. G. *Can. J. Chem.* **1963**, *41*, 966. Leto, J. R.; Cotton, F. A.; Waugh, J. S. *Nature (London)* **1957**, *180*, 978.

(8) Prinzbach, H.; Freudenberger, V.; Scheidegger, U. *Helv. Chim. Acta* **1967**, *50*, 1087.

(9) Haddon, R. C.; Wudl, F.; Kaplan, M. L.; Marshall, J. H.; Cais, R. E.; Bramwell, F. B. *J. Am. Chem. Soc.* **1978**, *100*, 7629.

(10) This conclusion rests on the reasonable assumption that the corresponding radicals have about the same energy. If this is true, then comparison of the second reduction potentials (−0.89 V for $2^\cdot$ and −0.9 V for $1^{\cdot 9}$) indicates that the anions have about the same energy. There are other examples[9] where structural changes have large effects on cation stability and small effects on anion stability.

= 7.8 Hz), 8.36 (t, 1 H, H-2, $J_{1,2} = J_{2,3} = 6.9$ Hz), 8.26 (d, d, 2 H, H-7,10, $J_{7,8} = J_{9,10} = 7.8$ Hz, $J_{6,7} = J_{10,11} = 8.0$ Hz).

Registry No. $2^+\cdot BF_4^-$, 99706-25-9; **3**, 35438-63-2; **4**, 99706-18-0; **5**, 99706-19-1; **6**, 99706-20-4; **7**, 99706-21-5; **8**, 99706-22-6; **9**, 99706-23-7; perylene, 198-55-0; *N*-methylformanilide, 93-61-8; diethyl malonate, 105-53-3; β-naphthalenesulfonic acid, 120-18-3; triphenylmethyl tetrafluoroborate, 341-02-6.

An Efficient Synthesis of (±)-Abscisic Acid

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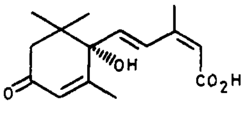
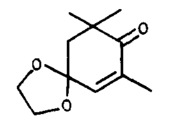
Abscisic acid 1 is a natural product extensively distributed in higher plants and has the important function of regulating the plants' dormancy state, permitting survival in adverse conditions.[1]



1



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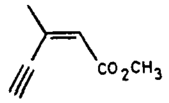
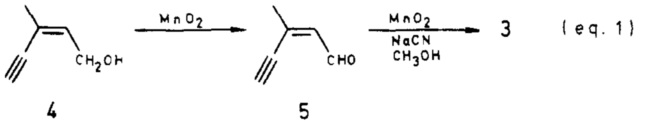


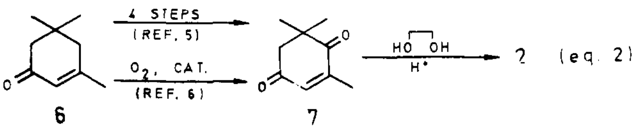
3

Several syntheses of 1 have been described previously.[2] The observed low to moderate yields are presumably attributable to the highly functionalized molecule. We describe herein an efficient synthesis of (±)-1 from intermediates 2 and 3 as outlined below.

Allylic oxidation of the commercial alcohol 4 (eq 1) afforded aldehyde 5.[3] Subsequent oxidation of 5 in the presence of cyanide ion and methanol[4] gave the desired ester 3.[5]

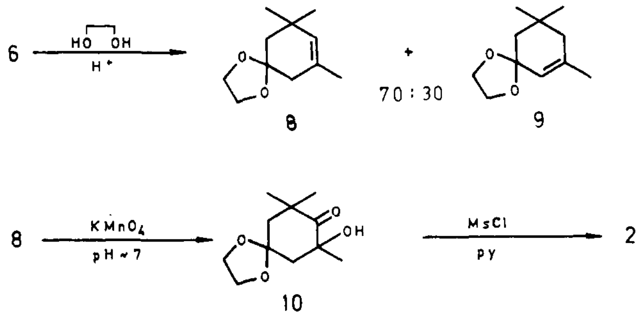


A five-step synthesis of compound 2 from isophorone 6 (eq 2) has been described by Marx and Sondheimer.[6] A direct conversion of isophorone to intermediate 7 by air oxidation has also been reported.[7] However, this latter route could not be effected in our hands without extensive polymerization, leading to low yields of 7. An alternate three-step synthesis of 2 from isophorone was realized as projected in Scheme I.

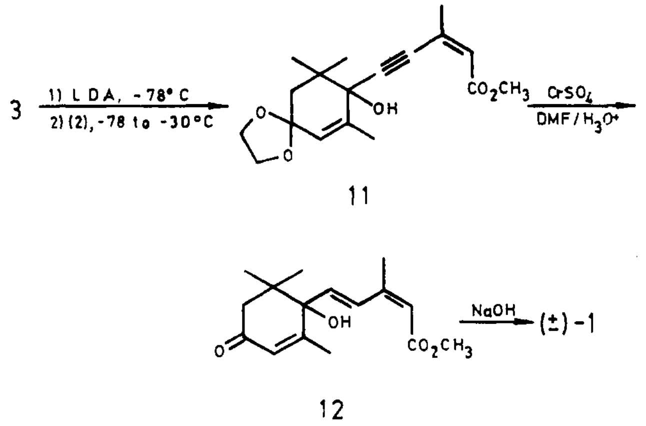


Treatment of isophorone with ethylene glycol and acid in toluene[8] afforded a 70:30 mixture of ketals 8 and 9 in 88.5% yield. The ketals were readily separated by fractional distillation. Potassium permanganate oxidation of 8 in neutral medium gave 10 (72.5%). Dehydration of 10 was accomplished with methanesulfonyl chloride in refluxing pyridine to afforded enone 2 (63%).

Scheme I



Scheme II



Reaction of the lithium salt of 3 (Scheme II) with enone 2 (−78 → −30 °C) afforded a quantitative yield of 11. Subsequent reduction of 11 with chromium (II) sulfate[10] resulted in a complex mixture of products from which the methyl ester of (±)-abscisic acid 12 was isolated in 35% yield. Saponification of 12 afforded racemic abscisic acid (80%) as a white crystalline solid.

Experimental Section

Melting points were determined on a Reichert Kofler block melting point apparatus. All melting points and boiling points

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[†] FFCLRP-USP.
[‡] IQ-USP.

(1) (a) Milborrow, B. V. *Annu. Rev. Plant Physiol.* **1974**, *25*, 259–307. (b) Nakanishi, K.; Goto, T.; Itô, S.; Natori, S.; Nozoe, S. "Natural Products Chemistry"; Kodansha-Academic Press: Tokyo and New York, 1974; Vol. 1, p 180. (c) Burden, R. S.; Taylor, H. F. *Pure Appl. Chem.* **1976**, *47*, 203–209.

(2) (a) Cornforth, J. W.; Milborrow, B. V.; Ryback, G. *Nature (London)* **1965**, *206*, 715. (b) Mousseron-Canet, M.; Mani, J. C.; Dalle, J. P.; Olivê, J. L. *Bull. Soc. Chim. Fr.* **1966**, *12*, 3874–3878. (c) Roberts, D. L.; Heckman, R. A.; Hege, B. P.; Bellin, S. A. *J. Org. Chem.* **1968**, *33*, 3566–3569. (d) Findlay, J. A.; Mackay, W. D. *Can. J. Chem.* **1971**, *49*, 2369–2371. (e) Oritani, T.; Yamashita, K. *Tetrahedron Lett.* **1972**, 2521–2524. (f) Shibasaki, M.; Terashima, S.; Yamada, S. *Chem. Pharm. Bull.* **1976**, *24*, 315–322. (g) Mayer, H. L.; Rigassi, N.; Schwieter, U.; Weedon, B. C. L. *Helv. Chim. Acta* **1976**, *59*, 1424–1427.

(3) Derguini, F.; Balogh-Nair, V.; Nakanishi, K. *Tetrahedron Lett.* **1979**, 4899–4902.

(4) Corey, E. J.; Gilman, N. W.; Ganem, B. E. *J. Am. Chem. Soc.* **1968**, *90*, 5616–5617.

(5) Gelencser, E.; Dlouky, T.; Zotchik, N. V.; Rubtsov, I. A. Deposited Document VINITI 380-78 1978; *Chem. Abstr.* **1979**, *91*, 157800*n*.

(6) Marx, J. N.; Sondheimer, F. *Tetrahedron, Suppl.* **1966**, *No. 8*, 1–7.

(7) Seuret, M.; Widmer, E. (F. Hoffman-La Roche & Co. AG) Belg. Pat. 830723, 1975.

(8) The ketalization of isophorone was described by Babler, Malek, and Coghlan,[9] using a Dean–Stark trap to remove water. We found it preferable to distill out the azeotrope, water/toluene, or for larger amounts to use ethyl orthoformate. Ketal 9 can be converted into a mixture of 8 and 9 in the same original ratio (70:30) by simply stirring at room temperature in dry toluene with a catalytic amount of *p*-toluenesulfonic acid. This mixture can be treated as before to yield additional amounts of 8.

(9) Babler, J. H.; Malek, N. C.; Coghlan, M. J. *J. Org. Chem.* **1978**, *43*, 1821–1823.

(10) (a) Castro, C. E.; Stephens, R. D. *J. Am. Chem. Soc.* **1964**, *86*, 4358–4363. (b) Hanson, J. R.; Premuzic, E. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 247–252. (c) Hanson, J. R. *Synthesis* **1974**, 1–8.

0022-3263/86/1951-0253$01.50/0