($CDCl_3$) δ 1.32 (t, 3, CH_3), 2.18 (s, 6, CH_3), 3.72 (q, 2, $-CH_2-$), 7.21 (s, 1, H-2 imidazole). Anal. Calcd for $C_7H_{12}N_2$: C, 67.74; H, 9.77; N, 22.50. Found: C, 67.79; H, 10.01; N, 22.38.

1-Carbethoxy-2-ethyl-4-methylimidazole (8). To a solution of 11.0 g (0.1 mol) of 2-ethyl-4(5)-methylimidazole and 11 g (0.11 mol) of triethylamine in 100 ml of acetonitrile was added dropwise with stirring at 0–5° a solution of 10.8 g (0.1 mol) of ethyl chloroformate in 30 ml of ether. After stirring for an additional 1 hr at 0° the reaction mixture was filtered. Upon washing, drying, and evaporation of the organic phase 17.3 g (95%) of 8 remained as a colorless oil: NMR ($CDCl_3$) δ 1.32 (t, 3, CH_3), 1.37 (t, 3, CH_3), 2.18 (s, 3, CH_3), 3.01 (q, 2, CH_2), 4.41 (q, 2, CH_2), 7.04 (s, 1, H-5). No traces of isomer could be detected.

On decarboxylation of 8 under the conditions used for 6 (210°), 51% of product was obtained, bp 81–85° (0.1 mm). Anal. Calcd for $C_8H_{14}N_2$: C, 69.56; H, 10.14; N, 20.28. Found: C, 69.59; H, 10.29; N, 20.12.

The NMR spectrum and TLC revealed the presence of two isomeric imidazoles in the ratio 3:1 (based on integrals). The major isomer could be identified as the normal product 1,2-diethyl-4-methylimidazole: NMR ($CDCl_3$) δ 1.38 (t, 3, CH_3), 1.41 (t, 3, CH_3), 2.25 (s, 3 CH_3), 2.64 (q, 2, CH_2), 3.87 (q, 2, CH_2), 6.58 (s, 1, H-5). The minor compound must be assigned as the isomeric 1,2-diethyl-5-methylimidazole: NMR ($CDCl_3$) δ 1.31 (t, 3, CH_3), 1.37 (t, 3, CH_3), 2.24 (s, 3, CH_3), 2.63 (q, 2, CH_2), 3.87 (q, 2, CH_2), 6.64 (s, 1, H-4).

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Registry No.—**1a,** 288-32-4; **1b,** 1072-62-4; **1c,** 50995-95-4; **1d,** 36947-68-9; **1g,** 670-96-2; **1h,** 693-98-1; **2a,** 19213-72-0; **2b,** 56468-36-1; **2c,** 56468-37-2; **2d,** 56468-38-3; **2e,** 56468-39-4; **2f,** 56468-40-7; **2g,** 56468-41-8; **2h,** 56468-42-9; **3a,** 105-39-5, **3e,** 13361-35-8; **4a,** 7098-07-9; **4b,** 51807-53-5; **4c,** 56468-43-0; **4d,** 56468-44-1; **4e,** 56468-45-2; **4f,** 46056-02-4; **4g,** 56468-46-3; **4h,** 21202-52-8; **5,** 56468-47-4; **6,** 56468-48-5; **7,** 56468-49-6; **8,** 56468-50-9; 4,5-dimethylimidazole, 2302-39-8; 2-ethyl-4(5)-methylimidazole, 931-36-2; 1,2-diethyl-4-methylimidazole, 56468-51-0; 1,2-diethyl-5-methylimidazole, 56468-52-1.

Supplementary Material Available. NMR data for all compounds will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number JOC-75-3279.

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Conformational Analysis of the Dibenzo[*a,g*]quinolizidines by Spectroscopic Methods

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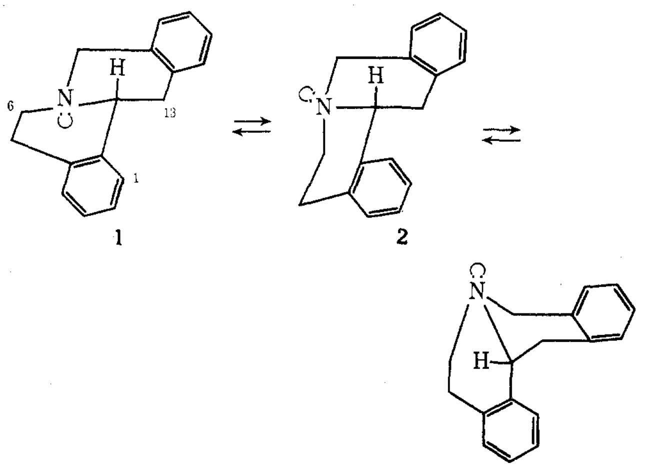
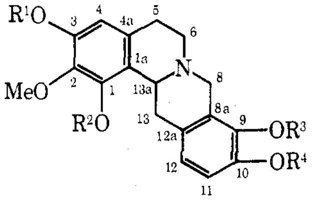
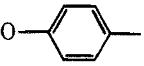
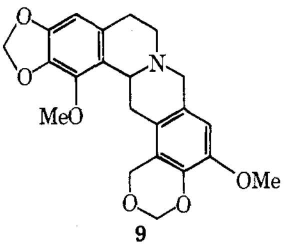
The dibenzo[*a,g*]quinolizidine structure forms the skeleton of the tetrahydroprotoberberine alkaloids. If rings B and C of the dibenzo[*a,g*]quinolizidine assume half-chair conformations, it exists in the equilibrium of one trans (1) and two cis conformation (2 and 3). The unsubstituted di-



1 **2** **3**



4, R¹ = R³ = R⁴ = Me; R² = H
5, R¹ = R³ = H; R² = R⁴ = Me
6, R¹ = R³ = Me; R² = H; R⁴ = COBr
7, R¹ = R² = R³ = R⁴ = Me
8, R¹ = R³ = Me; R² = R⁴ = H



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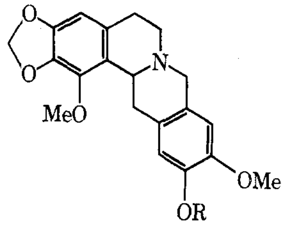
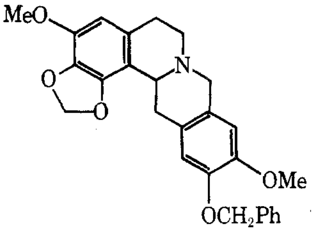


10, R = CH_2Ph
11, R = H



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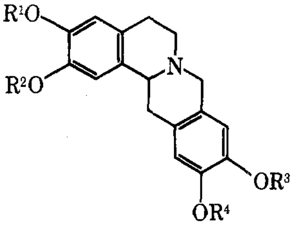
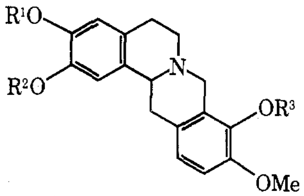
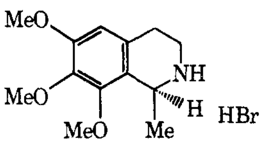


13, R¹ = R² = R³ = R⁴ = Me
14, R¹ + R² = R³ + R⁴ = CH_2



15, R¹ + R² = CH_2; R³ = Me
16, R¹ = R² = Me; R³ = H



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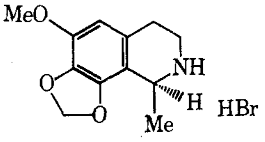

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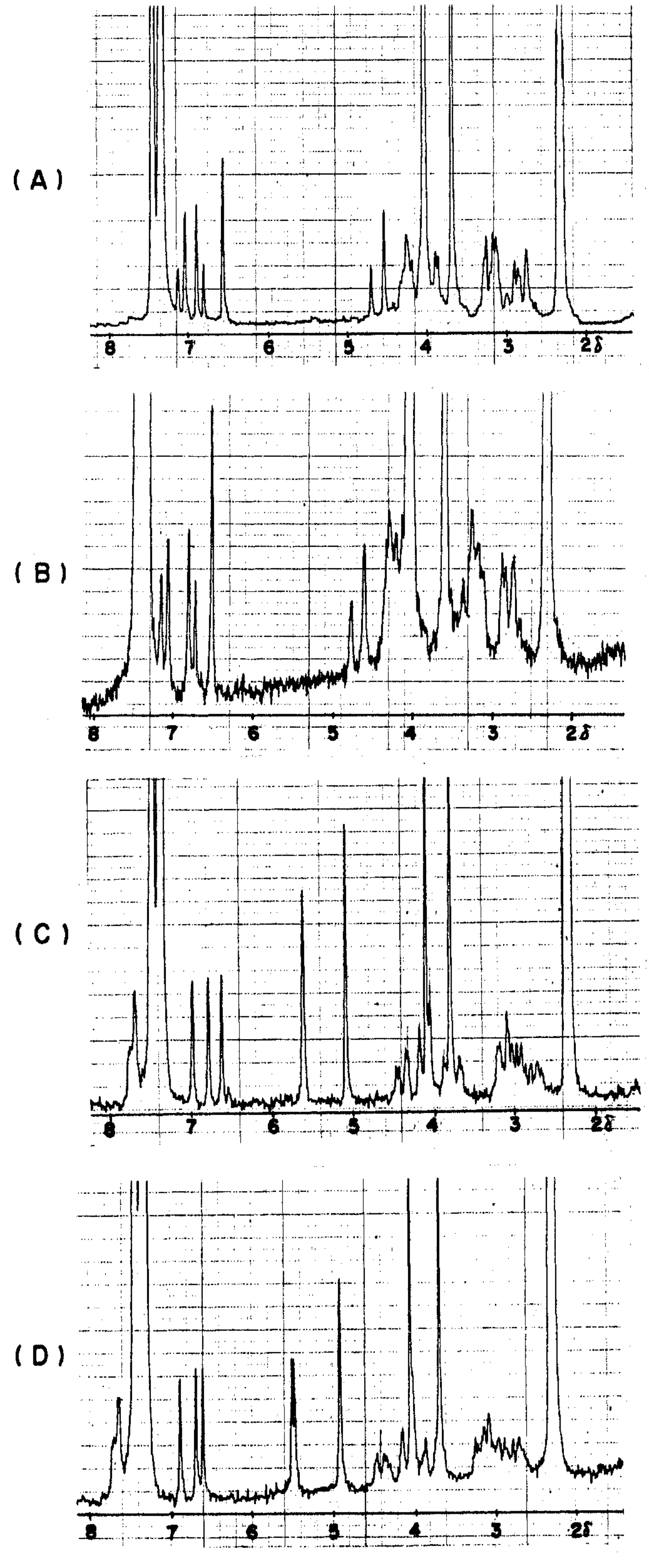

Figure 1. Proton NMR spectra of tetrahydroprotoberberines in deuteriotoluene at room temperature and −88°: (A) *O*-methylcapaurine (**7**) at room temperature; (B) *O*-methylcapaurine (**7**) at −88°; (C) the base **10** at room temperature; (D) the base **10** at −88°.

benzo[*a*,*g*]quinolizidine exists mainly in the thermodynamically stable *trans*-quinolizidine.[1] X-Ray analyses of the hydrobromides of (−)-capaurine (**4**) and (±)-isocapaurimine (**5**) and (−)-capaurimine *p*-bromobenzoate (**6**) by us revealed that they exist in the *cis*-quinolizidine form (**2**) in the crystalline state.[2-4] It was considered that an energetically unfavorable nonbonded interaction of the C-1 substituent with the C-13 hydrogens destabilized the trans form (**1**). Such an unfavorable interaction still remains in the other cis form (**3**), which may be the least preferred one. Thus, cis form **2** becomes more important for the 1-substituted tetrahydroprotoberberines. In the course of the synthesis of orientalidine (**9**),[5] we observed that (±)-3-methoxy-1,2-methylenedioxytetrahydroprotoberberine derivatives, for example **12**, showed strong Bohlmann bands in their ir spectra. We therefore became interested in the conformational analysis, using spectroscopic methods, of the dibenzo[*a*,*g*]quinolizidines varying oxy substituents in the A and D rings, and now wish to describe our findings.

Ir Spectroscopy. The presence or absence of Bohlmann bands in the ir spectra in solution has been utilized to distinguish the *trans*- from *cis*-quinolizidines,[6,7] although some workers have found that these absorptions were not definitive.[8,9] The ir spectra of (−)-*O*-methylcapaurine (**7**) and (±)-1-methoxy-2,3-methylenedioxytetrahydroprotoberberines (**9**, **10**, and **11**)[5] in chloroform solution did not show Bohlmann bands between 2700 and 2900 cm^{-1}. On the other hand, (±)-3-methoxy-1,2-methylenedioxytetrahydroprotoberberines showed considerably strong absorptions between 2700 and 2900 cm^{-1}, comparable to that of 1-nonsubstituted tetrahydroprotoberberines. It was therefore assumed that these derivatives exist mainly in the trans conformation in solution.

When the ir spectra of the tetrahydroprotoberberines were taken in the crystalline states, peculiar behavior was observed. Crystals of (−)-capaurimine *p*-bromobenzoate (**6**), whose X-ray analysis revealed the *cis*-quinolizidine,[4] and (−)-capaurimine (**8**) in potassium bromide did not show absorptions between 2700 and 2900 cm^{-1}. On the other hand, (±) compounds (**10**, **12**), optically active (−)-capaurine (**4**), and (−)-*O*-methylcapaurine (**7**) showed strong absorptions in the same region. However, the racemates of capaurine (**4**) and *O*-methylcapaurine (**7**), prepared by the racemization of the corresponding optically active compounds with Adams catalyst,[10] showed no Bohlmann-type absorptions. The ir spectra of some tetrahydroprotoberberines between 2400 and 3100 cm^{-1} are given in supplementary pages. Bohlmann bands in the crystalline state provide ambiguous criteria, and there is a possibility that the conformation of the 1-substituted tetrahydroprotoberberines in the crystalline state may depend upon the crystal structure (see paragraph at end of paper regarding supplementary material).

Proton NMR Spectroscopy. The angular proton of a trans conformation in benzo[*a*]- and indolo[*a*]quinolizidines resonates at a higher field than δ 3.8 ppm, whereas cis conformations are characterized by a signal below 3.8 ppm for this proton.[11] However, it is normally difficult to observe the signal due to the angular proton from the proton NMR spectra of the tetrahydroprotoberberines in deuteriochloroform solution, because the signals due to methoxyl groups appeared around 3.8 ppm. When the spectra were taken in deuteriotoluene, the signals due to the angular protons were shifted downfield and separated from the signals due to the methoxyl groups. The chemical shifts of the angular proton and the protons at the C-8 position of some tetrahydroprotoberberines in deuteriotoluene are shown in Table I, together with the coupling constants. (−)-*O*-Methylcapaurine (**7**), (±)-orientalidine (**9**), and (±)-**10** showed the angular proton at 4.26, 4.24, and 4.37 ppm, respectively, as a quartet (J = 12 and 4 Hz). On the other hand, the angular proton of the bases (**12** and **14**) appeared at 3.96 and 3.50 ppm, respectively, as a quartet (J = 15 and 4 Hz). From the above chemical shifts, it is estimat-

Table I[a]
Chemical Shifts and Coupling Constants of the Protons at C-13a and C-8 Positions of Some Tetrahydroprotoberberines in Deuteriotoluene at Room Temperature

Compd	13a-H, ppm (*J*, Hz)	8-H eq, ppm (*J*, Hz)	8-H ax, ppm (*J*, Hz)
7	4.26 (4 and 12)	4.62 (16)	4.16 (16)
9	4.24 (4 and 12)	4.12 (15)	*b*
10	4.37 (4 and 12)	4.25 (16)	3.95 (16)
12	3.96 (4 and 15)	4.02 (15)	3.76 (15)
14	3.50 (4 and 15)	3.74 (15)	3.49 (15)

[a] The δ values were calculated from the signal due to the methyl group of toluene, 2.32 ppm. [b] The signal was not distinguishable.

Table II[a]
Carbon-13 Chemical Shifts of Tetrahydroprotoberberines

Carbon	7	8	10	11	12	13	14	15	16
C-1	151.9	146.4[c]	147.5	147.8	142.4	108.5[b]	105.6	105.5	109.1
C-2	140.2	143.6	134.5	134.5	133.4	147.3	146.1	145.9[c]	147.5
C-3	150.1	150.6[c]	140.2	140.4	145.3	147.3	146.1	146.1[c]	147.5
C-4	107.4	104.0	102.9	103.1	107.0	111.3	108.5	108.4	111.5
C-4a	130.6[b]	131.3	128.6	128.5	129.5	126.6	127.9	127.7	127.0
C-5	30.0	30.6	30.1	30.1	30.0	29.0	29.6	29.6	29.2
C-6	48.3	49.3	47.1	46.9	51.1	51.3	51.3	51.4	51.5
C-8	53.3	53.6	57.2	57.3	58.0	58.2	58.7	54.0	53.7
C-8a	128.3[b]	127.9[b]	126.6[b]	124.8[b]	126.8[b]	126.2	127.4	127.7[b]	121.4
C-9	150.9	146.4[c]	109.7	108.7	109.8	109.5[b]	106.5	150.2	141.6
C-10	145.3	146.6[c]	146.6	145.3	146.8	147.3	146.1	145.0	144.2
C-11	110.9	114.2	147.9	144.3	148.0	147.3	146.1	110.9	109.1
C-12	124.0	125.3	114.3	114.6	114.5	111.3	108.5	123.9	119.3
C-12a	128.6[b]	128.5[b]	127.6[b]	127.3[b]	127.8[b]	126.2	127.4	128.6[b]	128.1
C-13	33.0	32.9	31.9	31.6	34.0	36.3	37.1	36.5	36.5
C-13a	55.5	56.0	54.9	54.7	57.1	59.5	59.9	59.6	59.4
C-13b	124.2	117.9	123.6	123.9	114.1	129.6	130.9	130.8	129.9
$-OCH_3$	60.6 (× 2)	61.2	59.2	59.5	56.5	55.8 (× 4)		60.1	56.2 (× 3)
	60.1	60.9	56.0	56.1	56.3			55.8	
	55.8 (× 2)	56.3							
$-OCH_2O$			100.5	100.7	101.2		100.8 (× 2)	100.7	
$-OCH_2Ph$			70.9		71.2				
$-OCH_2C_6H_5$			137.2		137.3				
			128.3		128.5				
			127.1		127.4				
			126.4		126.8				

[a] All shifts are in parts per million from Me_4Si. [b,c] The assignments may be reversed.

ed that the former three compounds adopt predominantly the cis conformation. The splitting pattern of the angular proton suggests that the cis form is not **3**, but **2**. The difference between the chemical shifts of 3-methoxy-1,2-methylenedioxytetrahydroprotoberberine (**12**) and **14** is due to the anisotropy of the oxygen substituent at the C-1 position. This was confirmed by ^{13}C NMR spectroscopy (vide infra). Furthermore, the protons at C-8 in (−)-*O*-methylcapaurine (**7**) appeared at low field owing to the presence of the methoxyl group at the C-9 position.

Proton NMR spectroscopy of the tetrahydroprotoberberines in deuterioacetone or deuteriotoluene was also studied at variable temperatures. The proton NMR spectra in deuterioacetone from −90° to room temperature showed no change. When the compounds **7, 10, 12,** and **13** were measured in deuteriotoluene from −90 to 100°, the chemical shifts of some signals in all the spectra gradually changed, but separate conformations were not observed. For example, the proton NMR spectra of **7** and **10** in deuteriotoluene at room temperature and −88° are shown in Figure 1. It is therefore assumed that the equilibration between *cis* and *trans*-quinolizidines is very fast.

^{13}C NMR Spectroscopy. The assignments of the ^{13}C chemical shifts of some tetrahydroprotoberberines are based on the comparison of the spectra[12–14] and on the splitting patterns which are observed in the off-resonance decoupled spectra. The values are shown in Table II.

It was expected that some of the carbons of the *cis*-quinolizidines would resonate at a higher field than in the *trans*-quinolizidine owing to γ effects.[15] Although the chemical shifts of C(5), C(8), and C(13a) in the dibenzo[*a,g*]quninolizidine are expected to be influenced directly by the substituents on the adjacent benzene ring, the preferential conformation can be determined by the comparison of the chemical shift of C(6). (±)-Tetrahydroprotoberberines (**13–16**), which have a hydrogen at C-1 position, showed the signal due to C(6) at about 51.4 ± 0.1 ppm even if the pattern of the substitutents on ring A and D is changed. (±)-3-Methoxy-1,2-methylenedioxytetrahydroprotoberberine (**12**) also showed the signal at 51.1 ppm, indicating the preferential *trans*-quinolizidine. The fact is consistent with the presence of Bohlmann bands in chloroform solution and the chemical shift of the angular proton in deuteriotoluene, which has been already methioned above. Based on these results and in consideration of the results of X-ray analyses of *O*-methylanhalonidine hydrobromide (**17**) and anhalonine hydrobromide (**18**),[16] the methylenedioxy group at the peri position does not cause as serious an interaction as either the hydroxy or the methoxy group.

For (−)-capaurimine (**8**), (−)-*O*-methylcapaurine (**7**), and (±) compounds (**10 and 11**), the signal due to C(6) appeared at 49.3, 48.3, 47.1, and 46.9 ppm, respectively. Owing to the steric interaction between the C-1 OR and C-13 hydrogens, these four compounds must be shifted over toward the cis form (**2**), because the C-6 signal always appears at a lower field (~δ 51.4, as shown above), when the system exists in the *trans*-quinolizidine form. It seems that the conformation of tetrahydroprotoberberines having a substituent at C-1 position is governed by the degree of steric interaction between the C-1 substituent and C-13 hydrogens. The chemical shift due to C(6) would depend upon the position of equilibrium between cis form **2** and trans form **1**. Therefore it was estimated that (−)-capaurimine (**8**) exists as a mixture of cis and trans in the equilibrium. This is consistent with the observation of weak absorptions in the region of 2800–2700 cm^{-1} of the ir spectrum of (−)-capaurimine in solution[17] and the finding by Shamma and his coworkers that (−)-capaurimine showed an intermediate rate for methiodide formation as compared with the cis and trans model compounds.[18] Estimation of the position of equilibrium by the ^{13}C chemical shifts have been recently reported.[19,20]

It is probably worthwhile to mention the difference of the C(8) chemical shifts between the 9,10- and 10,11-substituted tetrahydroprotoberberines. The C(8) of the 9,10-substituted compounds appeared at a higher field than 54.0 ppm, while the C(8) of the 10,11-substituted ones resonates at a lower field than 57.0 ppm. The steric perturbation by the C-9 substitutent caused this difference, a fact which is useful for the structure determination of the natural products.

Experimental Section

Ir spectra were taken in chloroform or potassium bromide with a Hitachi EPI-3 recording spectrometer. Proton NMR spectra were taken with a JNM-PS-100 spectrometer operating at 100 MHz. ^{13}C NMR spectra were obtained in deuteriochloroform (0.3–0.7 *M*) with a JNM-PFT-100 system equipped with a JNM-PS-100 spectrometer operating at 25.15 MHz. Optical rotations were measured with a JASCO PIP-SL automatic polarimeter.

Racemization of (−)-*O*-Methylcapaurine (7). To a suspension of 30 mg of Adams catalyst in 10 ml of methanol which was previously saturated with hydrogen, 30 mg of (−)-*O*-methylcapaurine (**7**) was added. The mixture was shaken for 50 hr at room temperature and atmospheric pressure. After filtration of the catalyst, the combined filtrate and washing were evaporated and the residue was recrystallized from methanol to give 20 mg of (±)-*O*-methylcapaurine as colorless needles, mp 142–144° (lit.[21] mp 140–142°), $[\alpha]^{25}D$ 0° (MeOH). The ir (in $CHCl_3$) and NMR (in $CDCl_3$) spectra were superimposable on those of (−)-*O*-methylcapaurine.

Racemization of (−)-Capaurine (4). To a suspension of 60 mg of Adams catalyst in 10 ml of methanol which was previously saturated with hydrogen, 60 mg of (−)-capaurine (**4**) was added and the mixture was shaken for 96 hr under the same condition as above and worked up as before to give 40 mg of (±)-capaurine, mp 207–209° (from methanol) (lit.[21] mp 208°), $[\alpha]^{25}D$ 0° (methanol). The ir (in $CHCl_3$) and NMR (in $CDCl_3$) spectra were superimposable on those of the optically active compound (**4**).

Acknowledgments. We wish to express our gratitude to Dr. K. Takahashi and Dr. T. Honda, Pharmaceutical Institute, Tohoku University, for their help in the preparation of samples. We also thank Dr. T. Kobari, Mitsui Pharmaceutical Co. Ltd., Miss R. Kato and Miss R. Suenaga of this institute, and Mr. m. Kunugi of JEOL Ltd. for the spectral measurements.

Registry No.—(−)-**4**, 478-14-8; (±)-**4**, 478-15-9; (±)-**5**, 56437-89-9; (−)-**6**, 30758-82-8; (−)-**7**, 6033-73-4; (±)-**7**, 6033-71-2; (−)-**8**, 30758-81-7; (±)-**9**, 56437-90-2; (±)-**10**, 52346-06-2; (±)-**11**, 52346-07-3; (±)-**12**, 56437-91-3; (±)-**13**, 13407-95-9; (±)-**14**, 36295-42-8; (±)-**15**, 29074-38-2; (±)-**16**, 7762-76-7.

Supplementary Material Available. The ir spectra in potassium bromide for compounds (±)-**4**, **-7**, **-10**, **-12**, and **-13** and (−)-**4**, **-6**, **-7**, and **-8** will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C., 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number JOC-75-3280.

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A New Synthesis of Benzo[*a*]pyrene-6,12-quinone[1]

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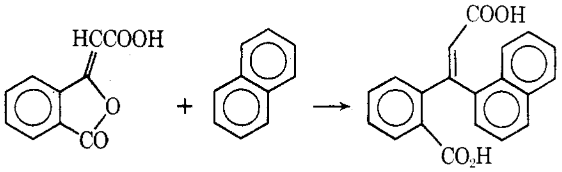
The condensation of phthalideneacetic acid (**1**) with naphthalene in anhydrous hydrogen fluoride to yield benzo[*a*]pyrene-6,12-quinone (**2**) has been described.[3] An unsaturated acid, A, was suggested[3] as an intermediate in the formation of **2**. Because of previous work on the thermal rearrangement of 1-ethoxyvinyl esters of *o*-benzoylbenzoic acids[4] we were led to study the pyrolysis of 1-ethoxyvinyl *o*-(1-naphthoyl)benzoate (**3**) in the hope of obtaining **4**, a compound which might be convertible to A. Although we were unable to obtain A by pyrolysis of **4** or of the hydrolysis product **5**, we did obtain 3-carboethoxymethyl-3-(1-naphthyl)phthalide (**4**), which could be hydrolyzed to 3-(*o*-carboxyphenyl)-3-hydroxy-3-(1-naphthyl)propanoic acid (**5**) and reduced to ethyl 3-(*o*-carboxyphenyl)-3-(1-



1 A