stirred for 7 hr at that temperature. After allowing to warm to room temperature, carbon monoxide was bubbled through the mixture for 1 hr to dispel any remaining nickel carbonyl. Anhydrous ethanol (30 ml) was added and the solution was distilled under reduced pressure to give 4.20 g of yellowish white crystals [bp 120–140° (0.7 mm)]. This was identified to be *trans-N,N*-dimethylcinnamamide by glpc and ir comparison with an authentic sample (yield 96.0%). *N,N*-Dimethyl-3-cyclohexene carboxylic acid amide [bp 98–99° (0.5 mm)] obtained from 3-bromocyclohexene was identified by the ir ($\nu_{C=O}$ 1645 cm^{-1}), the mass spectrum (*m/e* P = 153, 81, 72), and the nmr spectrum [τ 8.2–8.5 (m, 5 H), 7.3 (s, 6 H), 6.9 (m, 1 H), 4.5–4.7 (m, 2 H)]. *N,N*-Dimethylcrotonamide was isolated by preparative glpc and identified by the ir (conjugated $\nu_{C=O}$ and $\nu_{C=C}$ 1620 and 1665 cm^{-1}), the mass spectrum (*m/e* P = 113, 98, 69, 41), and the nmr spectrum [τ 8.3 (d, 3 H), 7.1 (s, 6 H), 3,9 (d, 1 H), 2.5 (m, 1 H)]. The other *N,N*-dimethyl acid amides cited in Table I were identified by glpc and ir comparison with authentic samples.

Reaction of 1 with Benzophenone.—To the THF solution (60 ml) of 1 prepared from 25 mmol of lithium dimethylamide and 37 mmol of nickel carbonyl was added 4.55 g (25 mmol) of benzophenone in 20 ml of THF and the mixture was stirred for 20 hr at 67°. After hydrolysis with 30 ml of 3 *N* hydrochloric acid at room temperature, the solution was concentrated by removal of the THF under reduced pressure and was extracted with ether. The ethereal extract was washed with water saturated with sodium chloride until a neutral solution was obtained and dried with anhydrous magnesium sulfate. The extract was distilled under reduced pressure after removal of the ether to give fraction 1, bp 120–125° (0.7 mm), 3.32 g, and fraction 2, bp 140–145° (0.7 mm), 0.50 g. Fraction 1 consisted of the recovered benzophenone. By recrystallization of fraction 2 using petroleum ether–benzene, white crystals of α-phenyl-*N,N*-dimethylmandelamide (mp 103°) were obtained. This compound was identified by the ir (KBr ν_{OH} 3300 cm^{-1}, $\nu_{C=O}$ 1620 cm^{-1}), the mass spectrum (*m/e* P = 255, 183, 105), the nmr spectrum [τ 7.3 (broad, 6 H), 4.1 (s, 1 H, this peak disappeared on adding D_2O), 2.7 (s, 10H)], and the elemental analysis. The yield was 30% based on benzophenone converted.

Anal. Calcd for $C_{16}H_{17}NO_2$: C, 75.27; H, 6.71; N, 5.49. Found: C, 75.18; H, 6.66; N, 5.38.

Reaction of 1 with Benzaldehyde.—Treatment of 2.65 g (25 mmol) of benzaldehyde with 1 (25 mmol) by the method mentioned above resulted in formation of 1.68 g of *N,N*-dimethylbenzamide (84.2% based on benzaldehyde converted), which was identified by glpc, ir comparison with an authentic sample, the mass spectrum (*m/e* P = 149, 105), and the nmr spectrum [τ 7.0 (s, 6 H), 2.6 (s, 5 H)].

Reaction of 1 with Acetophenone.—To the ether solution of 1 (25 mmol) was added 6.00 g (50 mmol) of acetophenone and the solution was stirred for 24 hr at 18°. After hydrolysis with 30 ml of 3 *N* hydrochloric acid, the solution was extracted with ether. The extract was washed with water, saturated with sodium chloride, dried with anhydrous magnesium sulfate, and then was distilled under reduced pressure. The first fraction [bp 115° (80 mm), 2.50 g] was acetophenone recovered and the second fraction [bp 150–185° (2 mm), 2.61 g] was shown to contain 2.50 g of α-methylchalcone by a glpc analysis. This compound was isolated by preparative glpc and identified by the ir (conjugated $\nu_{C=O}$ and $\nu_{C=C}$, 1660 and 1600 cm^{-1}), the mass spectrum (*m/e* P = 222, 115, 105), and the nmr spectrum [τ 7.5 (s, 3 H), 2.9 (s, 1 H), 2.0–2.8 (m, 10 H)] (77.2% based on acetophenone converted). In the same reaction using THF as a solvent (67°, 10 hr), 3.00 g (25 mmol) of acetophenone was converted to 2.23 g of 1-methyl-1,3,5-triphenyl-2-benzoylcyclohexadiene-2,4 (mp 134–135° from petroleum ether–benzene). This was identified by the ir ($\nu_{C=O}$ 1670 cm^{-1}, $\nu_{C=C}$ 1640 and 1620 cm^{-1}), the mass spectrum (*m/e* P = 426, 411, 321, 105), the nmr spectrum [τ 8.4 (s, 3 H), 6.9 (s, 2 H), 3.9 (s, 1 H), 2.5–3.1 (m, 20 H)], and the elemental analysis.

Anal. Calcd for $C_{32}H_{26}O$: C, 90.10; H, 6.14. Found: C, 90.06; H, 6.01.

Registry No.—1, 30304-90-6; *trans-N,N*-dimethylcinnamamide, 17431-39-9; *N,N*-dimethyl-3-cyclohexenecarboxylic acid amide, 30318-35-5; α-phenyl-*N,N*-dimethylmandelamide, 30318-36-6; α-methylchalcone, 4258-37-1; 1-methyl-1,3,5-triphenyl-2-benzoylcyclohexadiene-2,4, 24233-07-6.

The Question of Ring Inversion in 2,3,6,7-Tetramethoxy-9,10-dihydroanthracene[1,2]

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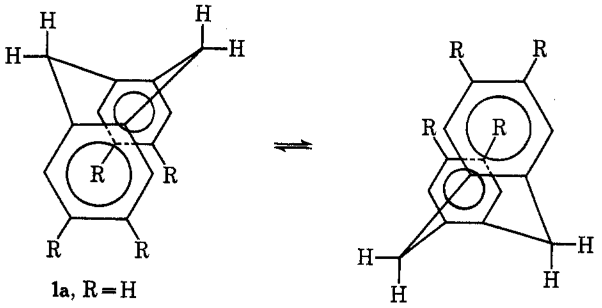
9,10-Dihydroanthracene (**1a**) undergoes a rapid boat-to-boat ring inversion at a rate which exceeds the limits of nmr time scale observability, even at low temperatures.[3,4] However, it was recently reported[5] that 2,3,6,7-tetramethoxy-9,10-dihydroanthracene (**1b**), together with the 2,7-dimethoxy and 1,2,3,5,6,7-hexamethoxy analogs, does not undergo this rapid ring-inversion process[6] and shows distinct axial and equatorial methylene protons characteristic of a rigid boat conformation. We felt that it would be highly unusual, and, if true, extremely important that substituents so far from the center ring could exert such a strong influence on the inversion process and that a reinvestigation was in order.



1a, R = H

b, R = OCH_3

The methoxy derivatives originally studied by nmr were prepared by a modified method of Robinson.[7] It has subsequently been suggested, however, that Robinson's procedure involving the condensation of veratrole with formaldehyde does not produce any dihydroanthracenes.[8] In fact, the related reaction of veratryl alcohol with acid[9] leads to the trimer "cyclotriveratrylene."[10]

For our purposes, we wanted to prepare an appropriate system by the simplest route available, free from possible side reactions. We began with the

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[1] This investigation was supported, in part, by a grant from the Eli Lilly Co., Indianapolis, Ind.

[2] Some preliminary experiments were carried out at the Ben May Laboratory for Cancer Research, University of Chicago.

[3] W. B. Smith and B. A. Shoulders, *J. Phys. Chem.*, **69**, 2022 (1965). See also D. Y. Curtin, C. G. Carlson, and C. G. McCarty, *Can. J. Chem.*, **42**, 565 (1964).

[4] A planar conformation seems to be a less likely explanation. See, in addition to ref 1, A. W. Brinkman, M. Gordon, R. G. Harvey, P. W. Rabideau, J. B. Stothers, and A. L. Ternay, *J. Amer. Chem. Soc.*, **92**, 5912 (1970).

[5] F. G. Jimenez, M. C. Perezamador, and J. R. Alcayde, *Can. J. Chem.*, **47**, 4489 (1969).

[6] Studied from −20 to +55°.

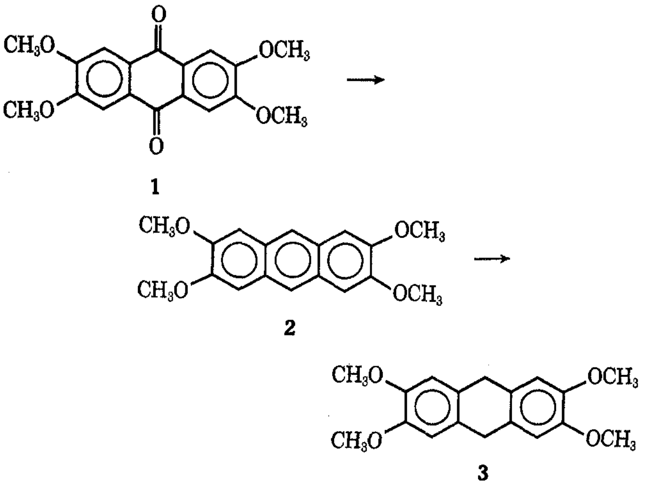
[7] G. M. Robinson, *J. Chem. Soc.*, **107**, 267 (1915).

[8] C. Casinovi and A. Oliverio, *Ann. Chim. (Rome)*, **46**, 929 (1956), and references therein.

[9] Conditions very similar to ref 3: A. S. Lindsey, *J. Chem. Soc.*, 1685 (1965).

[10] This system shows distinct methylene protons even at high temperatures.[9]

readily available 2,3,6,7-tetramethoxyanthraquinone[11] (2), which was converted by Zn/OH$^-$ to the anthracene **3**, showing correct molecular weight (mass spectroscopy) and consistent nmr and infrared spectra. Reduction of **3** with lithium–ammonia[12] led to **1b**[14] (correct molecular ion).



1

2

3

The nmr spectrum (CCl$_4$) of **1b** showed an aromatic singlet at δ 6.68 (4 H) and two partially overlapping singlets at 3.78 (total 16), representing the 12 methoxy protons and the 4 methylene protons. At 100 MHz, the two singlets were sufficiently well resolved to permit adequate integration (12:4) with the methylene protons appearing as a singlet 2.5 Hz upfield from the methoxy signal. Thus, the equivalence of the four methylene protons is consistent with a rapid inversion process and demonstrates that methoxy substituents have no unusual effect on this process.

Experimental Section

2,3,6,7-Tetramethoxyanthraquinone.—The anthraquinone was prepared by the dichromate oxidation of 2,3,6,7-tetramethoxy-9,10-dimethylanthracene according to published procedure.[11]

2,3,6,7-Tetramethoxyanthracene.—The aforementioned anthraquinone (4 g) was refluxed for 48 hr with zinc dust (10 g) in 100 ml of 10% aqueous sodium hydroxide.[15] The solid residue was filtered, washed, dried, and boiled in 75 ml of nitrobenzene. Filtration and refrigeration gave crystals (0.5 g): mp 371–373° (lit.[8] 376°); nmr (CDCl$_3$) δ 7.95 (s, Ar-9,10, 2), 7.3 (s, Ar, 4), and 4.0 (s, OCH$_3$, 12).

2,3,6,7-Tetramethoxy-9,10-dihydroanthracene.—The anthracene above (0.15 g) was suspended in 65 ml of dry ether and added to 100 ml of refluxing ammonia. An excess of lithium metal was added and the dark blue-green solution was stirred for 30 min. Solid ammonium chloride was then added and the reaction was worked up by ether extraction. This gave 50 mg of a white solid which recrystallized from methanol: mp ~230° (lit.[8] 230–250°, dependent on rate of heating); mass spectra m/e 300 (calcd for C$_{18}$H$_{20}$O$_4$, 300.4); nmr described in text.

Registry No.—**3**, 26952-97-6.

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[11] P. Boldt, *Ber.*, **100**, 1270 (1967).

[12] A modified Birch reduction for which complications and side reactions in anthracene systems are virtually unknown.[13]

[13] R. G. Harvey, *Syn.*, 161 (1970).

[14] Our material appears identical with that reported in ref 8 shown not to be the same as ref 7.

[15] E. L. Martin, *J. Amer. Chem. Soc.*, **58**, 1438 (1936). Yields are improved (55%), however, by added copper sulfate. See L. Fieser and M. Fieser, Ed., "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967, p 1282.

The Methanolysis of Phenyl-Substituted Benzhydryl Chlorides

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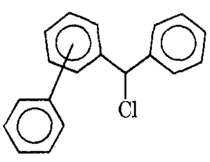
Neighboring group participation[2] in solvolytic displacement reactions of ortho-substituted benzhydryl and benzyl systems has been reported for a number of nucleophilic groups (*e.g.*, COOC$_6$H$_5$,[3] COOCH$_3$,[3] COOH,[3] NO$_2$[4]). In these cases[3,4] the rate of solvolysis is greater for the ortho compound than for the para compound. In cases where there is an absence of participation, the ortho/para rate ratio is less than unity (*e.g.*, CH$_3$,[3] OCOCH$_3$,[3] OCOC$_6$H$_5$,[3] halogen,[5] OCH$_3$)[6].

In view of the great interest in phenyl participation in solvolysis reactions,[2,7] we wish to disclose our studies with *o*-, *m*-, and *p*-phenyl-substituted benzhydryl chlorides.



1, *o*-C$_6$H$_5$
2, *m*-C$_6$H$_5$
3, *p*-C$_6$H$_5$

The benzhydryl chlorides **1**, **2**, and **3** were prepared by hydrogen chloride and/or thionyl chloride treatment of the corresponding carbinols, the syntheses of which are described in the Experimental Section and illustrated in Scheme I for **1**.

The rates and activation parameters for the methanolysis of **1**, **2**, and **3** and benzhydryl chloride itself (**4**) at several temperatures are tabulated in Table I. The products in each case were isolated and identified as the unrearranged methyl ethers. As seen from Table I, the ortho/para rate ratio (**1**/**3**) is less than unity (0.16) and this, coupled with the lack of rearrangement, clearly indicates the absence of phenyl participation in **1**. It was felt that, if phenyl participation during methanolysis of **1** were occurring, 9-phenylfluorene (**5**) would have formed. In fact, it was observed that treatment of *o*-phenylbenzhydrol (**10**) with thionyl chloride or hydrogen chloride above room temperature gave **5**.[8] Apparently, under the milder meth-

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[2] B. Capon, *Quart. Rev., Chem. Soc.*, **18**, 45 (1964).

[3] A. Singh, L. J. Andrews, and R. M. Keefer, *J. Amer. Chem. Soc.*, **84**, 1179 (1962).

[4] A. D. Mease, M. J. Strauss, I. Horman, L. J. Andrews, and R. M. Keefer, *ibid.*, **90**, 1797 (1968).

[5] G. M. Bennett and B. Jones, *J. Chem. Soc.*, 1815 (1935).

[6] M. Simonetta and G. Favini, *ibid.*, 1840 (1954).

[7] For a leading reference, see A. F. Diaz and S. Winstein, *J. Amer. Chem. Soc.*, **91**, 4300 (1969).

[8] The acid-catalyzed rearrangement of **10** to **5** has been reported: H. H. Hatt, A. Pilgrim, and E. F. M. Stephenson, *J. Chem. Soc.*, 478 (1941).