Alkyldihydroaryllithiums. V. Alkylation of 10-Alkyl-9,10-dihydroanthracenyllithiums with Alkyl Iodides

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The structural assignments for *cis*- and *trans*-9-isopropyl-10-methyl-9,10-dihydroanthracene (DHA = dihydroanthracene) have been determined by means of nmr nuclear Overhauser enhancement (NOE) experiments. These hydrocarbons may be formed stereoselectively by reaction of the appropriate 9-lithio-10-alkyl-9,10-DHA with an alkyl iodide. NOE experiments on *cis*- and *trans*-9-isopropyl-10-methyl-9,10-DHAs confirm the structural assignments made previously in this laboratory.

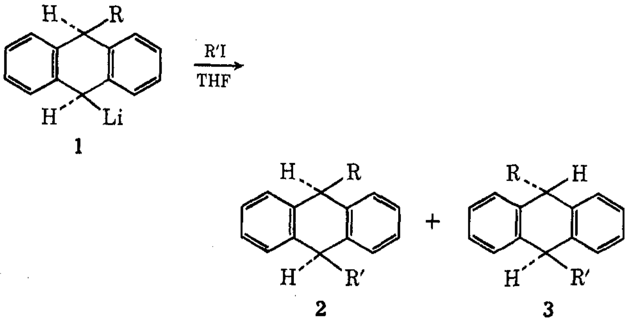
The reaction of 9-lithio-10-alkyl-9,10-dihydroanthracenes (**1**) with alkyl halides is reported to produce stereospecifically *cis*-9,10-dialkyl-9,10-dihydroanthracenes (DHA = dihydroanthracene) when **1** is prepared by the addition of alkyllithium reagents to anthracene.[2] This report differs from one of our earlier observations that 9-lithio-10-isopropyl-9,10-DHA reacts with isopropyl iodide to give a mixture of *trans*- and *cis*-9,10-diisopropyl-9,10-DHAs.[3] The predominant product was assigned trans stereochemistry based on carbon–deuterium ir stretching absorptions and nmr coupling constants for the isopropyl methinyl meso hydrogens. It is important to resolve this difference in stereochemical assignments because it implies that the reaction of **1** with alkyl halides not only is nonstereospecific, but also nonstereoselective.

The difference between the two earlier reports may be that the intermediates, **1**, were generated by two different methods (method A, addition of RLi reagent to anthracene, and method B, lithiation of a 9-alkyl-9,10-DHA). We decided to compare the product ratios secured by the two methods and also to study the effect of reversing the order of introducing the alkyl groups.

It is significant that the two different methods for preparing carbanions **1** both produced the same *cis*-9-methyl-10-ethyl-9,10-DHA after treatment of 9-lithio-10-ethyl-9,10-DHA with methyl halide.[2,4,5]

TABLE I

REACTIONS OF 9-LITHIO-10-ALKYL-9,10-DHA WITH ALKYL IODIDES[a]



	R	R'	cis,[b] %	trans,[c] %
(1)	CH_3–	$(CH_3)_2CH$–	41 ± 2.0	59 ± 2.0
(2)	$(CH_3)_2CH$–	CH_3–	90 ± 1.5	10 ± 1.5

[a] Percentages determined by vapor phase chromatography (H_2 flame ionization) and checked by electronic integration of pmr signals for **2** and **3** in crude reaction mixtures for eq 1. [b] Mp 66°. [c] Mp 76–77°.

TABLE II

ALKYLLITHIUM ADDITIONS TO ANTHRACENE

RLi	+	R'I	→	9-isopropyl-10-methyl-9,10-DHA cis, %	trans, %
$(CH_3)_2CHLi$		CH_3I		90 ± 1.5	10 ± 1.5
CH_3Li		$(CH_3)_2CHI$		40 ± 1.0	60 ± 1.0

Results

Treatment of 9-methyl-9,10-DHA with 1 equiv of *n*-butyllithium in dry THF followed by reaction with isopropyl iodide produced a 59:41 mixture of isomeric 9-isopropyl-10-methyl-9,10-DHAs. (See eq 1 in Table I.) Conversely, metalation of 9-isopropyl-9,10-DHA with *n*-butyllithium in dry THF, followed by reaction with methyl iodide, gave a 90:10 mixture of the 66 and 77° mp isomers. (See eq 2.)

The addition of isopropyllithium to anthracene in dry THF according to method A was followed by reaction with methyl iodide to produce a 90:10 mixture of the same isomers as were secured by method B. See Table II.

Cis stereochemistry has been assigned to the 9-isopropyl-10-methyl-9,10-DHA isomer of mp 66° by virtue of its method of preparation.[2] Among stereoisomeric 9,10-dialkyl-9,10-DHAs, cis stereochemistry was assigned to the higher melting point isomer for the dimethyl,[5] diethyl,[5] and methyl ethyl[3,5] homologs. Examination of Table II shows that isopropyllithium addition to anthracene followed by methyl iodide alkylation gives predominantly the 66° mp compound as reported earlier.[2] However, 10% of its stereoisomer was also obtained, indicating that dialkylation of anthracene *via* method B in THF is a stereoselective rather than a stereospecific reaction. The fact that this compound had a higher melting point than its stereoisomer was not in harmony with previous structural assignments of lower homologs. Fortunately, an unambiguous stereochemistry assignment can be made with the aid of nuclear Overhauser enhancements of the C-9 and C-10 proton signals, as was shown recently for 9-alkyl-9,10-DHAs.[6] Equally fortunate was the conclusion from these NOE experiments that the

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(1) National Science Foundation Undergraduate Research Participant, 1968–1969.

(2) R. G. Harvey and C. C. Davis, *J. Org. Chem.*, **34**, 3607 (1969).

(3) H. E. Zieger, D. J. Schaeffer, and R. M. Padronaggio, *Tetrahedron Lett.*, 5027 (1969).

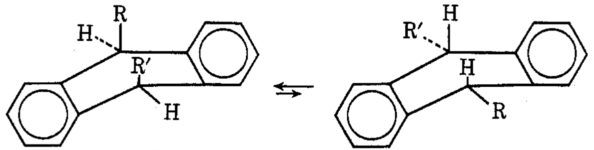
(4) D. J. Schaeffer and H. E. Zieger, *J. Org. Chem.*, **34**, 3958 (1969).

(5) R. G. Harvey, L. Arzadon, J. Grant, and K. Urberg, *J. Amer. Chem. Soc.*, **91**, 4535 (1969).

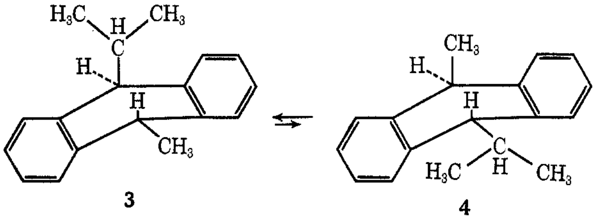
(6) A. W. Brinkman, M. Gordon, R. G. Harvey, P. W. Rabideau, J. B. Stothers, and A. L. Ternay, Jr., *ibid.*, **92**, 5912 (1970).

66° mp compound is the cis isomer and the higher melting point material (77°) is the trans isomer.

Nuclear Overhauser Enhancements.—There is general agreement that the central ring of 9,10-dihydroanthracene has a shallow boat conformation.[5] Furthermore, it has been clearly demonstrated that 9-alkyl-9,10-DHAs with bulky alkyl groups prefer the conformation in which the alkyl group is quasiaxial rather than quasiequatorial.[5,6] In a *cis*-9,10-dialkyl-9,10-DHA the preferred conformation would be expected to have both of the alkyl groups quasiaxial rather than quasiequatorial (*i.e.*, **2a′** rather than **2e′**). A *trans*-9,10-dialkyl-9,10-DHA necessarily must have one of the alkyl groups quasiaxial and the other quasiequatorial. If, as in *trans*-9-isopropyl-10-methyl-9,10-DHA, one of the alkyl groups is large and the other small, then that conformational isomer having the larger alkyl group oriented quasiaxial would be expected to predominate as in **3** rather than **4**. The corollary to the foregoing is that the meso hydrogens in a *cis*-9,10-dialkyl-9,10-DHA would both be quasiequatorial (He′) while the trans isomer would have the meso hydrogen of the carbon bearing the bulky alkyl group in a quasiequatorial orientation ($H_{e'}$) and its counterpart would be quasiaxial ($H_{a'}$).



2a′ **2e′**



3 **4**

The pmr spectra for these two meso hydrogens are easy to distinguish because they possess different chemical shifts and different spin–spin splitting patterns. Both of these effects are traceable to differences between the isopropyl and methyl groups. In practice the simple, first-order low-field quartet and higher field doublet are broadened because of the long range spin–spin interactions with the peri aryl hydrogens (allylic coupling) and because of homoallylic coupling (H–C_9–C=C–C_{10}–H) between the meso protons themselves.

Spin decoupling of the peri aryl hydrogens (at C_1, C_3, C_4, C_8) is expected to produce a nuclear Overhauser enhancement (NOE) of the meso hydrogen intensities which is larger for $H_{e'}$ than for $H_{a'}$ at C_9 or C_{10} because the former are located closer to the peri aryl hydrogens than are the latter. Therefore, the *cis*-9,10-dialkyl-9,10-DHA would be expected to show intensity enhancements of both the C_9 doublet and the C_{10} quartet while the trans isomer should exhibit enhancement only for the C_9 doublet upon spin decoupling of the peri hydrogens. Examination of NOE results in Table III for the benzylic hydrogens of the 9-isopropyl-10-methyl-9,10-DHA isomers leads to the conclusion that the lower melting point isomer possesses cis stereochemistry.[7] For comparison purposes, data for the known[4,8] *cis*- and *trans*-9-ethyl-10-methyl-9,10-DHAs are included in Table III.

TABLE III[a]

NOE RESULTS FOR BENZYLIC PROTONS IN **2** AND **3**

Mp, °C	R-C_9	R-C_{10}	C_9-H	C_{10}-H
66	$(CH_3)_2CH-$	CH_3-	+8.53	+6.78
77	$(CH_3)_2CH-$	CH_3-	+15.3	−0.88
cis (mp 108)	CH_3CH_2-	CH_3-	+16.8	+14.3
trans (mp 33)	CH_3CH_2-	CH_3-	+10.3	+4.1

[a] An average of six integrations was performed for each meso H signal.

Symmetrically dialkylated 9,10-DHAs such as *cis*- and *trans*-9,10-DHAs would not be so amenable to study by NOE as a pair of unsymmetrical stereoisomers because both meso hydrogens (in both isomers) have the same chemical shift. Nevertheless, the cis isomer would be expected to show a larger NOE effect than the trans compound because the latter has half of its meso hydrogens a′ and half e′ while the cis compound populates predominantly one conformer in which both meso hydrogens are oriented e′.

Authentic *cis*-9,10-diisopropyl-9,10-DHA, mp 99.5–105° (lit.[3] mp 109–110°), was prepared as described previously and exhibited a nuclear Overhauser enhancement of 11.8% for the meso hydrogens, while the value for the trans isomer of mp 76–77° was 3.9%.[9]

Long Range Coupling Constants.—Measurement of the long range homoallylic coupling constants (H–C_9–C=C–C_{10}–H) was expected to provide confirmation for the stereochemical assignments, since it had been shown that $J_{a'e'} > J_{e'e'}$ in monoalkyl-9,10-DHAs with values of 1.0–1.3 and 0.40–0.70 Hz, respectively.[6] This expectation was realized when the lower melting point (66°) stereoisomer yielded a homoallylic $J_{H_9,H_{10}} = 0.60$ Hz, while the higher melting point (77°) isomer had $J_{H_9,H_{10}} = 1.3$ Hz.

Discussion

The most startling observation to be made about the data in Tables I and II is that reaction of 9-lithio-10-isopropyl-9,10-DHA with excess methyl iodide gives predominantly *cis*-9-isopropyl-10-methyl-9,10-DHA (**2**) while a comparable reaction with isopropyl iodide produces chiefly *trans*-9,10-diisopropyl-9,10-DHA. Whatever the mechanism for reaction of anthryl carbanions like **1** with alkyl iodides, the formation of both *cis*- and *trans*-9,10-dialkyl-9,10-DHAs in unequal amounts suggests that the intermediate **1** also exists in cis and trans stereoisomeric forms. The reason for this conclusion is based upon the accepted view "that lithium salts like **1** in THF are contact ion pairs."

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[7] This conclusion agrees with the structure assignment of Harvey and Davis[2] but does not follow the pattern of lower homologs wherein the cis isomer was found to be of higher melting point and lower solubility.[5]

[8] Recently an X-ray crystal structure has been completed for the cis compound by Dr. R. H. Stanford, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, Calif. It confirms the stereochemical assignments reached earlier by stereospecific synthesis.[3]

[9] These NOE results provide additional evidence that earlier stereochemistry assignments are correct[3] and that the 9,10-diisopropyl-9,10-DHA obtained from alkylation of dilithioanthracene with isopropyl chloride by R. G. Harvey and L. Arzadon[10] is the trans isomer.

[10] R. G. Harvey and L. Arzadon, *Tetrahedron*, **25**, 4887 (1969).

Consequently, the lithium atom must be oriented either cis or trans to the C_{10} alkyl group.

The fact that the isomer ratios in Table I are the same as those in Table II indicates that *cis*-**1** interconverts with *trans*-**1** because the same equilibrium mixture is obtained by two completely different methods. Additional support for the proposed interconversion of *cis*-**1** and *trans*-**1** may be found in the absolute values for the ratios of **2**:**3** (which are 9:1 and 2:3). If the quenching process involved a delocalized carbanion with some planarity of C_9 with the aromatic rings, then approach of the alkyl iodide from either side of the molecule would give 1:1 ratios of **2** and **3** without regard for the size of the alkyl group at C_{10}. The observed difference in ratios is better understood in terms of the potential existence of two conformational isomers for *cis*-**1** and also two for *trans*-**1**, summarized in Table IV. Clearly, the steric requirements of the isopropyl group would be expected to influence not only the conformer population but also the equilibrium position of the two configurational isomers. When **1** possesses an isopropyl group at C_{10} the cis configuration will predominate over the trans to a much greater extent than it does when a methyl group is at C_{10}. This analysis finds support in an earlier estimate of the conformational populations for 9-methyl-9,10-DHA based on nmr chemical shifts which concluded that 25% of the molecules had the methyl group oriented quasiequatorial.[6] The literature also contains spectroscopic evidence from uv and visible studies on the lithium salts of 10-alkyl derivatives of DHA[11] which is completely in harmony with the existence of two forms for the 10-alkyl derivative but only one absorption for the lithium salt of DHA.

TABLE IV

SUMMARY OF CONFIGURATIONS AND CONFORMATIONS[a]

	Conformer A		Conformer B	
	R	Li	R	Li
cis	a′	a′	e′	e′
trans	a′	e′	e′	a′

[a] a′ = quasiaxial orientation; e′ = quasiequatorial

The most plausible explanation of the difference between methyl iodide and isopropyl iodide reaction with **1** is that they may be reacting by two different mechanisms. One possibility is simple SN2 displacement. An alternate sequence is halogen–metal exchange to form 9-iodo-10-alkyl-9,10-DHAs and alkyllithiums. Rapid coupling of such benzylic iodo compounds with the alkyllithiums would give the products. Precedent for this latter pathway has been reported in recent literature.[12]

The NOE experiments on *cis*- and *trans*-9,10-diisopropyl-9,10-DHAs provide additional experimental evidence for our earlier conclusion[3] that quasiequatorial hydrogens are more shielded than quasiaxial hydrogens in symmetrically dialkylated 9,10-DHAs.

Experimental Section

Nmr Spectra.—NOE measurements were obtained on sealed, vacuum-degassed solutions in deuteriochloroform. Concentrations ranged from 170 to 175 mg/ml. The spectra were obtained on a Varian Associates HA-100 spectrometer operated in the frequency sweep mode. A H-P, V-4315 frequency counter permitted measurement of the line positions within ±0.01 ppm for the chemical shifts.

Gas chromatography was run on a Hewlett-Packard Model 5754 B instrument equipped with a hydrogen flame ionization detector and Disc integrator. A 6 ft × $^1/_8$ in. column of 10% SE-30 on Chromosorb W (DMCS) was used.

Materials.—Ethyllithium (1.2 *M* in benzene), *n*-butyllithium (2.4 *M* in hexane), and isopropyllithium (1.9 *M* in pentane) were secured from Alfa Inorganics. Analysis was accomplished by titration with *sec*-butyl alcohol using phenanthroline indicator.[13] Anthracene and 9-methyl-9,10-DHA were purified and prepared as described previously.[4] 9,10-Dihydroanthracene (Aldrich, 95+ %) was recrystallized from ethanol using decolorizing carbon. It was dried *in vacuo* for 24 hr. Tetrahydrofuran (99.5+ %, Aldrich) was dried by refluxing with lithium aluminum hydride followed by distillation. It was stored at reflux over Na–benzophenone, and was freshly distilled immediately before use. Isopropyl iodide was prepared from isopropyl alcohol according to the literature procedure.[14]

9-Isopropyl-9,10-DHA.—To a solution of DHA (10 g, 0.055 mol) in THF (250 ml) at −60° was added *n*-butyllithium (23 ml, 0.0552 mol). The stirred solution was warmed to 5° during 0.5 hr, cooled to −30°, and treated with an excess of isopropyl iodide. Water (10 ml) was added followed by NaCl. After separation of phases, THF was removed with the rotary evaporator and the resulting oil was crystallized from ethanol using a low-temperature bath to yield 9.0 g (73%) of hydrocarbon, mp 30–33° (lit. mp 28–29°). The 100-MHz pmr spectrum showed δ 7.180 (s, 8 H), 4.120 and 3.790 (C_{10} H_aH_b, $J_{ab} = 19$ Hz), 3.595 (d, C_9H_9, $J = 7.0$ Hz), 1.86 [m, $-C\mathbf{H}(CH_3)_2$], and 0.798 [d, $-CH(C\mathbf{H}_3)_2$]; uv λ_{max} 252.5 mμ (ϵ 4122), 265 (985), 272 (1.053).

Preparation of *trans*-9-Isopropyl-10-methyl-9,10-DHA.—To 10 g of 9-methyl-9,10-DHA (0.052 mol) in 250 ml of THF at −60° was added 21.5 ml of 2.4 *M* *n*-butyllithium (0.052 mol). The temperature was permitted to rise to 0° with magnetic stirring during 30 min. After cooling to −30°, excess isopropyl iodide was added quickly and stirring was continued for 1 hr. Water (25 ml) was added, phases were separated, and THF was removed *in vacuo* to give an oil. Gas chromatography showed the presence of *cis*- and *trans*-9-isopropyl-10-methyl-9,10-DHAs (**2** and **3**) together with starting material. By means of column chromatography over alumina (100 g oven-dried at 120°), 1.48 g of **2** and **3** in hexane was separated with the isomer of longer gas chromatographic retention time being eluted in the earlier column chromatography fractions. After recrystallization from ethanol this isomer had mp 68–70°.

In an identical run, the oil obtained after removal of THF was dissolved in ethanol and seeded with a crystal of the higher melting stereoisomer. The resulting crystals, 6.0 g (47%), mp 68–70°, were recrystallized twice from ethanol, yielding white needles, mp 76–77°.

Anal. Calcd for $C_{18}H_{20}$: C, 91.47; H, 8.53. Found: C, 91.36; H, 8.76.

Nmr ($CDCl_3$) had δ 0.865 [d, 6, $J = 7.0$ Hz, $(C\mathbf{H}_3)_2CH-$], 1.731 [d, 3, $J = 7.3$ Hz, $(C\mathbf{H}_3)C_{10}H$], 1.77 [m, 1, $(CH_3)_2C\mathbf{H}-$)], 3.454 (d, 1, $J = 9.6$ Hz, C_9H), 3.984 (q, 1, $J = 7.7$ Hz, $C_{10}H$), 7.12, 7.15, 7.17, 7.21, 7.27 [m, 8, aromatic H]; uv λ 258 mμ (ϵ 567), shoulder 264.3 (773), 271.5 (794).

Preparation of *cis*-9-Isopropyl-10-methyl-9,10-DHA.—To 10 g of anthracene (0.053 mol) in 250 ml of THF at −60° was added 45 ml of 1.25 *M* isopropyllithium (0.056 mol). The reaction mixture was maintained at −60° for 30 min, after which an excess of methyl iodide was added quickly. Water was added, phases were separated, the THF layer was dried ($MgSO_4$), and the solvent was removed *in vacuo*. The oil was crystallized from ethanol, yielding white crystals, 6.05 g (46%). After recrystallization from ethanol the compound had mp 65–66° (lit.[2] mp 65.5–66.5°).

Anal. Calcd for $C_{18}H_{20}$: C, 91.47; H, 8.53. Found: C, 91.13; H, 8.65.

Nmr ($CDCl_3$) had δ 0.916 [d, 6, $J = 6.9$ Hz, $(C\mathbf{H}_3)_2CH-$], 1.59 [d, 3, $J = 7.7$ Hz, $(C\mathbf{H}_3C_{10}H)$], 1.72 [m, 1, $(CH_3)_2C\mathbf{H}-$], 3.489 (d, 1, $J = 8.8$ Hz, $C_9\mathbf{H}$), 4.043 (q, 1, $J = 7.7$ Hz, $C_{10}H$), 7.16 (m, 8, aromatic H).

These chemical shifts agree well with the literature[2] values.

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(11) D. Nicholls and M. Szwarc, *Proc. Roy. Soc., Ser. A*, **301**, 223 (1969).

(12) R. M. Magid and S. E. Wilson, *Tetrahedron Lett.*, 4925 (1969).

(13) S. Watson and J. F. Eastham, *J. Organometal. Chem.*, **9**, 165 (1967).

(14) A. I. Vogel, "Textbook of Practical Organic Chemistry," 3rd ed, Wiley, New York, N. Y., 1956, p 285.

However, three of the four coupling constants differ substantially from those reported previously.[2] Uv had λ 258 mμ shoulder, 265.5 (ϵ 1026), 272.5 (1036).

cis-**9,10-Diisopropyl-9,10-DHA.**—To 9-isopropyl-9,10-DHA (1.25 g, 5.6 mmol) in dry THF (50 ml) at −60° was added *n*-butyllithium (6.0 mmol). The reaction mixture was stirred at 0° for 1 hr and the reaction was terminated by the rapid addition of excess isopropyl iodide. After separation of salts with water and removal of ether solvents, an nmr spectrum indicated the presence of 12.5% *cis*- and 87.5% *trans*-9,10-diisopropyl-9,10-DHA by integration of the benzylic hydrogen doublets at δ 3.78 (J = 5.0 Hz for the trans isomer) and 3.27 (J = 9.5 Hz for the cis compound). See earlier literature.[3]

After chromatography over dry basic alumina (hexane), 0.85 g of trans-9,10-diisopropyl-9,10-DHA (57%), mp 73–74°, was obtained after recrystallization from ethanol (lit.[3] mp 76–77°); uv 257 mμ (shoulder), 265 (ϵ 647), 272 (588).

In later fractions the cis isomer appeared predominantly as an oil which crystallized upon trituration with ethanol to yield 60 mg of *cis*-9,10-diisopropyl-9,10-DHA (4%, mp 99.5–105°), lit.[3] mp 109–110°; uv λ 258 mμ (ϵ 822), 265 (1084), 272 (1221).

Methyllithium Addition to Anthracene.—Anthracene (0.5 g, 2.8 mmol) in 50 ml of THF was mixed with excess methyllithium (14 mmol) in ether. After refluxing for 4 hr, excess isopropyl iodide was added quickly. After 1 hr stirring, salts were separated with water and gas chromatography showed the presence of five components. The ratio of *cis*- and *trans*-9-isopropyl-10-methyl-9,10-DHA was 40:60 ± 1 as determined by vpc. Unchanged anthracene was recovered.

trans-**9-Ethyl-10-methyl-9,10-DHA.**[15]—Lithium (0.15 g)–ammonia (300 ml) reduction of 9-ethyl-10-methylanthracene (2 g) in THF (120 ml) for 3.5 hr was followed by addition of ethanol (10 ml) and H_2O (10 ml). Solvents were evaporated and the oil obtained from ether–water treatment was recrystallized from absolute ethanol to give 1.3 g of white needles (65%), mp 33–34°.

Anal. Calcd for $C_{17}H_{18}$: C, 91.84; H, 8.16. Found: C, 91.73; H, 8.25; C, 91.75; H, 8.38.

Uv had λ 212.2 mμ (ϵ 19,480), 264.5 (1140), 271.8 (1067); nmr δ 0.887 (t, 3, $\mathbf{CH_3}CH_2$–, J = 7.0 Hz), 1.71 (d, 3, $\mathbf{CH_3}C_{10}H$, J = 6.7 Hz), 3.80 (t, 1, $C_9\mathbf{H}CH_2$–, J = 7.5 Hz), 3.99 (q, 1, $C_{10}\mathbf{H}CH_3$, J = 6.7 Hz), 7.22 (m, 8, aromatic).

These chemical shifts and coupling constants do not agree well with those published previously.[5] This sample was purified by recrystallization before nmr spectroscopy and spectra were obtained on an HA-100 instrument better suited for careful determination of coupling constants. There is no doubt, however, of the identity of this material with that described previously.[5]

Registry No.—*cis*-**2**, 21438-93-7; *trans*-**2**, 33608-27-4; 9-isopropyl-9,10-dihydroanthracene, 17573-50-1; *trans*-9,10-diisopropyl-9,10-dihydroanthracene, 25340-82-3; *cis*-9,10-diisopropyl-9,10-dihydroanthracene, 24316-21-0; *trans*-9-ethyl-10-methyl-9,10-dihydroanthracene, 23660-35-7.

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[15] We thank Mr. Isaac Angres (NSF undergraduate participant) for running this experiment.

The Synthesis of 9,10-Cyclobutenophenanthrene from 9,10-Dimethylene-9,10-dihydrophenanthrene

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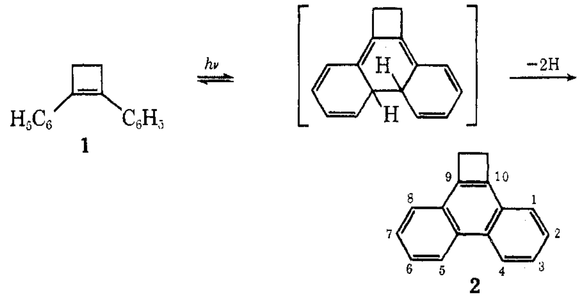
9,10-Dimethylene-9,10-dihydrophenanthrene (**4**) has been prepared from trimethyl(10-methyl-9-phenanthrylmethyl)ammonium chloride (**6**) and characterized by its physical data and the formation of an adduct with maleic anhydride. Irradiation of compound **4** yielded 9,10-cyclobutenophenanthrene (**2**), the proof of structure of which is discussed.

Our interest in 9,10-cyclobutenophenanthrene (**2**) was first aroused during a study of the photochemistry of 1,2-diphenylcyclobutene (**1**), in which it is a possible product (eq 1).[2] We were stimulated to the synthesis of **2** by the subsequent report by Masamune and Kato of diphenyltetrahedrane (**3**).[3] This report drew our attention because of our interest in **3** and because the physical properties attributed to **3** by Masamune and Kato appeared to match better the predicted properties of **2**.[4] We wish now to report the full synthesis and characterization of **2**.



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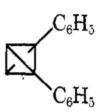

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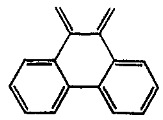

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During the progress of this synthesis, we were able to demonstrate the intermediacy of 9,10-dimethylene-9,10-dihydrophenanthrene (**4**). Previously, this compound had been reported as a reactive intermediate and its presence was inferred only by trapping with various dienophiles.[5] The instability of **4** with respect to dimerization and polymerization prevented our complete characterization of it; however, we were able to obtain its ultraviolet spectrum in dilute solution. The direct observation of **4** in the ultraviolet is to our knowledge the first such observation of an *o*-quinodi-

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[1] Author to whom inquires should be addressed.

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