21720-98-9; IXe, 2861-49-6; IXf, 17643-38-8; IXg, 21721-01-7; Xb, 21721-02-8; Xe, 21721-03-9; 12,12-diethoxycarbonyloctadecene-1, 21721-04-0; 12-methoxycarbonyloctadecene-1, 21721-05-1; 12,12-diethoxycarbonylnonadecene-1, 21721-06-2; 11-methoxycarbonyloctadecene-1, 21721-07-3; 10,10-diethoxycarbonyloctadecyl acetate, 21727-89-9; 8-chlorooctyl acetate, 21727-90-2; 7-bromoheptyl acetate, 21727-91-3.

Acknowledgment.—This work was supported by the U. S. Department of Agriculture, Agricultural Research Service. We are indebted to Miss Sara P. Fore, Southern Utilization Research and Development Division, U. S. Department of Agriculture, for large amounts of parsley seed oil and to Dr. D. A. van Dorp of Unilever Research Laboratories for generous samples of octadecynoic acids.

Alkyldihydroaryllithiums. IV. Stereochemistry of Reactions of 9-Alkyl-9,10-dihydroanthracenyllithiums[1]

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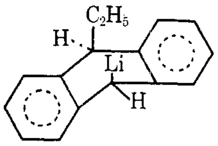
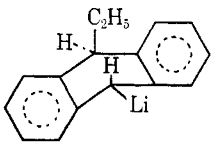
A stereospecific synthesis of *cis*-9-methyl-10-ethyl-9,10-dihydroanthracene from the known *cis*-9,10-dihydro-10-methylanthracene-9-carboxylic acid utilized coupling with lithium dimethylcopper and *cis* tosylate **5c**. The existence of 9-lithio-10-alkyl-9,10-dihydroanthracenes as an equilibrium mixture of *cis* and *trans* stereoisomers is inferred from *cis/trans* product ratio variations obtained with alkyl halides, deuterium oxide, and carbon dioxide.

Recently, we reported that an ethyllithium-N,N,N′,-N′-tetramethyl-*o*-phenylenediamine (TMOPD) complex in cyclohexane adds ethyllithium to anthracene to form a mixture of *cis*- and *trans*-9-lithio-10-ethyl-9,10-dihydroanthracene (dihydroanthracene = DHA) (**1a** and **2a**).[2]



1a



2a

Reaction of these intermediates with methyl iodide gave 88–95% yields of *cis*-9-methyl-10-ethyl-9,10-DHA (**1c**).[3] Treatment of the intermediates with deuterium oxide gave both *cis*- and *trans*-9-deuterio-10-ethyl-9,10-DHA (**1b** and **2b**) as judged by comparison of nmr spectra for the mixed product (Figure 1) with the published spectrum for **1b**.[6] In fact, our early deuterolysis results (*cis/trans* = 39:61 ± 3) corresponded better with data reported by Winkler for the existence of the homologous 10-butyl-9-deuterio-9,10-DHA as nearly a 1:1 mixture of *cis* and *trans* isomers.[7a] The observation of two products under photolytic conditions[7a] or in the presence of bisamine[2] and only one isomer[6,7b] in the absence of uv radiation or bisamine might be interpreted as implying the need for some agent to catalyze the interconversion of **1a** and **2a**. However, neither of these organolithium compounds would be expected to maintain its steriochemical integrity in ether (or THF) at temperatures above 0°.[8] The detection[6,7b] of a single deuterioethyl-DHA isomer was surprising and not in harmony with other results.[2,7a] Accordingly, it was decided to reinvestigate the addition of ethyllithium to anthracene in THF.

Results

Deuterolysis of the adducts formed by addition of ethyllithium to anthracene in THF in the absence of tertiary bisamine gave a 1:1 mixture of *cis*- and *trans*-deuterioethyl-DHA, **1b** and **2b**, regardless of the order of mixing of the intermediates and D_2O. When a dilute solution of D_2O in dry THF was added slowly during 1 hr at $-20°$ to the organolithium intermediates, the *cis/trans* ratio changed to 64:36. The slow mixing result may be attributed to a higher rate of reaction of D_2O with **1a** than with **2a**. An alternate explanation of product variation involving a transmetalation process (*i.e.*, reaction of **2b** with **1a** or **2a**) is not supported by nmr data. Since protolyses with oxygenated acids are known to be faster processes than protonations by weak carbon acids,[9] transmetalation would be expected to be a much slower process than either deuterolysis or equilibration of stereoisomeric organolithium intermediates.[10] If transmetalation was involved, detectable amounts of 9-ethyl-9,10-DHA (**3**) should be observed by nmr; **3** was not detected.

Attempts to secure a single deuterioethyl-DHA isomer by deuterolysis with deuteriotriphenylmethane also gave 57:43 mixtures of **1b** and **2b**.

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(1) Abstracted in part from the Ph.D. thesis of D. J. S. (in preparation). Paper II: *Tetrahedron Lett.*, 3801 (1966). Paper III: *J. Org. Chem.*, **31**, 2977 (1966).

(2) H. E. Zieger and D. J. Schaeffer, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, No. P-155.

(3) We appreciated receiving timely advance notice from Professor R. G. Harvey that alkyl halide quenching of alkyllithium–anthracene adducts affords *cis*-9,10-dialkyl-9,10-DHAs.[4] A *cis* stereochemistry was also assigned by Redford[5] to the 9-methyl-10-ethyl-H,10-DHA of mp 108° using the unproven criterion that *cis*-9,10-dialkyl-9,10-DHAs feature a singlet for the aromatic protons while *trans* isomers exhibit an A_2B_2 (or AA′BB′) pattern.

(4) R. G. Harvey and L. Arzadon, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, No. P-154. NOTE ADDED IN PROOF.—See R. G. Harvey, *et al.*, *J. Amer. Chem. Soc.*, **91**, 4535 (1969).

(5) D. A. Redford, Ph.D. Thesis, The University of Saskatchewan, 1967; University Microfilms, Inc., Ann Arbor, Mich., No. 68-5914; *Dissertation Abstr.*, **28B**, 4074-B (1968).

(6) D. Nicholls and M. Szwarc, *J. Amer. Chem. Soc.*, **88**, 5757 (1966).

(7) (a) H. J. S. Winkler, R. Bollinger, and H. Winkler, *J. Org. Chem.*, **32**, 1700 (1967); (b) D. Nicholls and M. Szwarc, *Proc. Roy. Soc.*, **A301**, 223, 231 (1967).

(8) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, pp 123–127.

(9) Y. Pocker and J. H. Exner, *J. Amer. Chem. Soc.*, **90**, 6764 (1968).

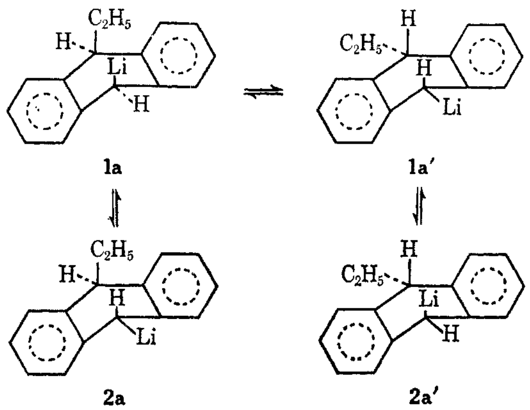
(10) D. E. Applequist and G. N. Chumurny, *ibid.*, **89**, 875 (1967).

Treatment of these organolithium adducts in THF with more selective, more slowly reacting alkyl halides gives exclusively *cis*-9,10-dialkyl-9,10-DHAs, in agreement with another report.[4]

It was anticipated, from statistical considerations alone, that hydrogen–metal exchange (metalation) at C-10 in 9-ethyl-9,10-DHA (**3**) should give a 50:50 mixture of **1a** and **2a**. The possibility that butyllithium would selectively abstract only one of the C-10 hydrogens so as to give exclusively **1a** (or **2a**), which then preserves its stereochemical integrity, would require a predominance of one of the two possible boat conformers (Chart I) together with atypical stereoselectivity during nucleophilic attack on the C-10 hydrogens. If **1a** and **2a** are not able to interconvert, quenching (D_2O, RX) of the intermediates produced *via* metalation of **3** would be expected to give different *cis*/*trans* product ratios than derivatization of intermediates obtained from the addition of ethyllithium to anthracene. In fact, derivatization of the intermediates produced either by metalation of **3** in THF or by alkylation (*i.e.*, addition) of anthracene in THF gave nearly identical *cis*/*trans* product ratios.

CHART I

THE CONFORMATIONAL AND CONFIGURATIONAL EQUILIBRIA OF 9-LITHIO-10-ETHYL-9,10-DIHYDROANTHRACENE[a]



[a] See E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, New York, N. Y., 1966, p 242.

Parallel butyllithium metalation experiments on 9-methyl-9,10-DHA (**4a**) followed by treatment with ethyl bromide and methyl iodide gave almost quantitative yields of **1c** and the known *cis*-9,10-dimethyl-9,10-DHA (**4b**).[11,12] Reaction of the metalation intermediate from **4a** with carbon dioxide gave a mixture of the known[11] *cis*-10-methyl-9,10-DHA-9-carboxylic acid (72% **5a**) and the *trans* isomer (9.0% **6**, detected by nmr).

These results indicated that both **1a** and **2a** probably are formed in the metalation of **3**. Further, they suggested that **1a** and **2a** are in equilibrium with each other and that the *cis*-lithioalkyl-DHA reacts faster than the *trans* isomer with alkyl halides and carbon dioxide.

It is not surprising that **1a** and **2a** should be capable of interconversion in ether solvents at temperatures of 25°. Only specialized organolithium[10] and secondary Grignard systems are capable of maintaining their stereochemical integrity.[13,14] Nevertheless, these data on product analysis do not unequivocally demonstrate the existence of an equilibrium between **1a** and **2a**. Nmr spectra at room temperature suggest either that a single species is present or that interconversion is fast. Present research efforts are directed at distinguishing between **1a** and **2a** at low temperatures in the nmr.

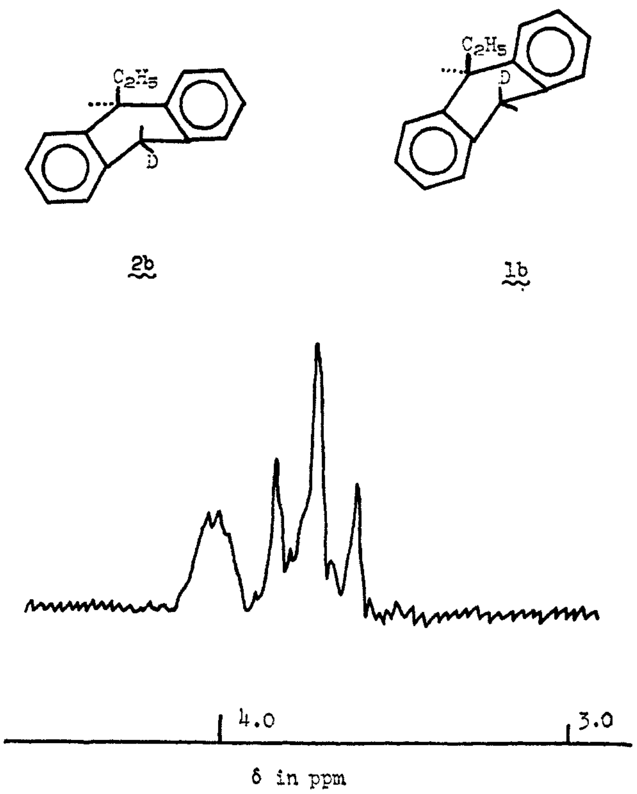
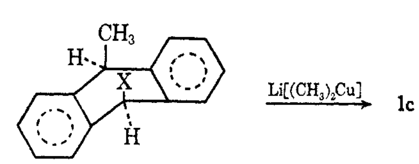


Figure 1.—Benzylic region of nmr spectra of *cis*- and *trans*-9-deuterio-10-ethyl-9,10-dihydroanthracene at 60 MHz in $CDCl_3$.

Stereospecific Synthesis of 1e.—In order to establish unambiguously the stereochemistry of the 9,10-dialkyl-9,10-DHAs,[3] a stereospecific synthesis of *cis*-9-methyl-10-ethyl-9,10-DHA was accomplished starting from the known tosylate of *cis*-9-(hydroxymethyl)-10-methyl-9,10-DHA (**5b**). Treatment of **5c** with lithium dimethylcopper afforded a quantitative yield of authentic *cis*-9-methyl-10-ethyl-9,10-DHA. This material proved to be identical in all of its physical and spectral properties with hydrocarbon obtained either by addition of methyl iodide to anthracene–ethyllithium adducts or by addition of ethyl bromide to the organolithium intermediates formed by metalation of **4a**.



5a, X = COOH
b, X = CH_2OH
c, X = $CH_2OSO_2C_6H_4CH_3$-*p*

Displacements of bromine with lithium dimethylcopper have been reported quite recently.[15] In this

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[11] A. H. Beckett and R. G. Lingard, *J. Chem. Soc.*, 2409 (1959).

[12] L. M. Jackman and J. W. Lown, *ibid.*, 3776 (1962).

[13] F. R. Jensen and K. L. Nakamaye, *J. Amer. Chem. Soc.*, **88**, 3437 (1966).

[14] G. M. Whitesides and J. D. Roberts, *ibid.*, **87**, 4878 (1965).

[15] E. J. Corey and G. N. Posner, *ibid.*, **89**, 3911 (1967).

TABLE I

NMR DATA FOR 9,10-DISUBSTITUTED 9,10-DIHYDROANTHRACENES (ArR_1R_2) IN $CDCl_3$[a]

				Benzylic			
	R_1	R_2	Aryl	C-9	C-10	CH_2	Methyl
cis	C_2H_5	D	428 (s)	225 (t, 7)	224.4 (t, 2.5)	99 (qu)	49 (t)
trans	C_2H_5	D	428 (s)	241 (br)		99 (qu, 7)	49 (t, 7)
cis	CH_3	C_2H_5	433 (s)	244 (q, 7)	226 (7)	108 (qu, 7)	92 (d, 7)
cis	C_2H_5	C_2H_5	427 (s)	223 (t, 7)		108 (qu)	58 (t, 7)
cis	CH_3	CH_3	435 (s)	244 (q, 7.5)			92 (d, 7.5)
cis[b]	CH_3	COOH	440	318.5 (s)	248 (q, 7.0)		104 (d)
	CH_3	H	435 (s)	244 (q, 7.5)			92 (d, 7.5)
cis	CH_3	CH_2OH	434 (s)	215–258 (m, 4 H, including CH_2OH)		110 (s, 1 H, OH)	90 (d, 7)
cis	CH_3	$CH_2OSO_2C_7H_7$	432 (m)	247 (m)		139 (s, 3 H, $RO_3SC_6H_4CH_3$)	75 (d, 7.5)

[a] In hertz (*J*, hertz). Multiplicity of signals is indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; qu, quintet; m, multiplet; br, broad. [b] In deuteriopyridine.

system, tosyl group displacement occurred more readily than displacement of bromine.[16]

Summary.—It has been shown that the 9-lithio-10-alkyl-9,10-DHA intermediates, which are formed either by metalation of **3** or **4** or by the addition of ethyllithium to anthracene, react with alkyl halides or carbon dioxide to give high yields of *cis*-9,10-disubstituted 9,10-DHAs. In contrast, reaction with deuterium oxide gives mixtures which depend upon the rate of mixing of the reactants. The reason for the discrepancy between these deuterolyses results and those reported earlier[6] has not been fully clarified.

Experimental Section

Standard cyclohexane solutions of ethyllithium were prepared by distillation *in vacuo* of the benzene in commercial ethyllithium (Foote Mineral). After the addition of two volumes of dry, olefin-free cyclohexane, titration was accomplished using a recently described procedure.[17] *n*-Butyllithium (Foote Mineral, in hexane) was titrated similarly prior to use. Methyllithium (Foote Mineral, in ether) was titrated with standard 0.1 *N* HCl.

Anthracene (Matheson Coleman and Bell, fluorescent grade) was dried at 110° for 24 hr before use. Cyclohexane was washed with aqueous potassium permanganate, sulfuric acid, and water, and dried over sodium ribbon. Gas chromatography was run with an F & M Model 500 instrument equipped with a 0.25-in. o.d., 2-ft. 25% Apiezon N column on Chromosorb P. The column temperature was held at 275° with a helium flow rate of 80 ml/min.

Mass spectra were run on a CEC Model 21-103 spectrometer in the Division of Chemistry at California Institute of Technology.

Addition of Ethyllithium–TMOPD Complex to Anthracene.—To a solution of ethyllithium (0.005 mol) and TMOPD (0.005 mol) in cyclohexane (40 ml) under a dry, oxygen-free argon atmosphere was added anthracene (0.005 mol) in one portion. The solution was magnetically stirred for 3 hr at room temperature, and reactions were terminated with deuterium oxide, methyl iodide, or ethyl bromide.

A. Deuterium Oxide.—A 1-ml portion of D_2O was added. The reaction mass was washed with aqueous HCl, 5% $NaHCO_3$, and brine, dried over sodium sulfate, and concentrated. Vpc and nmr analyses indicated an 88–95% yield of *cis*- and *trans*-9-deutero-10-ethyl-9,10-DHA (**1b** and **2b**) together with trace amounts of 9-ethylanthracene, 9,10-DHA, and anthracene. The *cis/trans* ratio (40 ± 3% *cis*) was determined from the integration traces of the benzylic hydrogens in the nmr spectrum. In the *trans* isomer, the hydrogen at C-9 appears as a broad (unresolvable) signal at much lower field (δ 241.0 Hz) than the proton at C-10 (δ 225.0 Hz) or the hydrogen at C-9 in the *cis* isomer (δ 224.4 Hz). See Figure 1 for the nmr spectrum in $CDCl_3$ and Table I for data.

An ir spectrum on a neat sample showed C–D stretching vibrations as a pair of doublets at 2110, 2088 (w), and 2160 (m) and 2145 cm^{-1} (m). These values show modest deviations from axial and equatorial C–D stretching vibrations reported for *cis*- and *trans*-4-deuterio-*t*-butylcyclohexane.[18]

The mass spectrum showed a molecular ion at *m/e* 209 and exhibited a fragmentation pattern in harmony with the loss of H, D, both H and D, and C_2H_5. When the *m/e* 209 peak was set equal to 100, the peaks at 210 and 211 had relative intensities of 20.1 and 2.45, in good agreement for a monodeuterio material. Absolutely no ions were observed at *m/e* 212–218, while a trace impurity could be detected at *m/e* 221.

Hydrolysis of a parallel run with water gave 9-ethyl-9,10-DHA, having mp 42–43° (low-temperature recrystallization from ethanol) and an nmr spectrum identical with the literature spectrum.[6]

B. Methyl Iodide.—Quenching with methyl iodide (3 ml) gave 85–93% yields of **1c**. After recrystallization from ethanol, white needles (70%), mp 105–106° (lit.[5] mp 108.0–108.5°), were secured. If any **2c** was present, it could not be detected either by vpc or by nmr (see Table I). A mass spectrum exhibited a characteristically small molecular ion peak at *m/e* 222. The nmr spectrum of the crude reaction mixture showed no sign of *trans*-9-methyl-10-ethyl-9,10-DHA (**2c**), which is reported to have a methyl doublet near 108 Hz from TMS.[19]

The uv spectrum in ethanol had values of 258.5 mμ (ϵ 708), 265.2 (1013), and 272.4 (1038), which compared well with values for the hydrocarbon obtained by reducing 9-methyl-10-ethylanthracene.[5]

C. Ethyl Bromide.—*cis*-9,10-Diethyl-9,10-DHA, mp 57.5–58.5° (lit.[20] mp 59–60°), was isolated in 80% yield after addition of ethyl bromide (3 ml) to 9-lithio-10-ethyl-9,10-DHA adducts (see Table I for the nmr spectrum). Nmr spectra on crude reaction mixtures indicated the presence of approximately 4% of the *trans* isomer, having a methyl group triplet at 51 Hz (J = 7 Hz). This material could not be isolated. The mass spectrum for the purified hydrocarbon exhibited a molecular ion at *m/e* 236 and a fragmentation pattern similar to spectra for **1b** and **1c**.

Preparation of 9-Methyl-10-ethylanthracene by Oxidation of 1c.—A mixture of **1c** (1.2 g) and sulfur (0.4 g) were heated at 250° for 3 hr. The crude product, analyzed by nmr, had a spectrum consistent with its formulation as 9-methyl-10-ethylanthracene: 500 and 499 (aromatic, 8 H, a pair of quartets, $J_{12} = 3.8$ Hz and $J_{23} = 3.0$ Hz), 216 (q, 2 H, $J = 7.5$ Hz, CH_2CH_3), 184 (s, 3 H, CH_3), and 79 Hz (t, 3 H, $J = 7.5$ Hz, CH_2CH_3). Recrystallization from ethanol afforded yellow needles (0.60 g,

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(16) Neither methylmagnesium chloride in THF nor methyllithium in ether could accomplish carbon–carbon bond formation. These experiments resulted in rupture of the O–S bond, affording *cis* alcohol **5b**. Treatment of **5b** with lithium dimethylcopper did not result in epimerization of the alcohol (See Experimental Section).

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

(18) W. H. Glaze and C. M. Selman, *ibid.*, **11**, P 3 (1968).

(19) Professor R. Harvey has kindly communicated chemical shift data for both *cis* and *trans* isomers of 9,10-diethyl-9,10-DHA, 9,10-dimethyl-9,10-DHA, and 9-methyl-10-ethyl-9,10-DHA in advance of publication.

(20) B. M. Milkailov and A. N. Bldkhina, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 164 (1949); *Chem. Abstr.*, **44**, 2963*b* (1950).

50.5% yield), mp 128–129° (lit.[21] mp 145.5°). Admixture with starting material depressed the melting point >20°.

Additions of Ethyllithium to Anthracene in THF.—To anthracene (0.005 mol) in dry THF (50 ml) maintained at 0–5° was added ethyllithium (0.005 mol) in cyclohexane. After magnetic stirring was performed for 30 min at room temperature, the reactions were terminated (a) with rapid addition of excess deuterium oxide (1 ml), (b) with rapid addition of excess methyliodide (2 ml), or (c) with rapid addition of excess ethylbromide (2 ml). After work-up as described above, the products obtained were (a) a 1:1 mixture of **1b** and **2b** in 98% yield, (b) a 98% yield of *cis*-9-methyl-10-ethyl-9,10-DHA (**1c**), and (c) a 96% yield of *cis*-9,10-diethyl-9,10-DHA. The melting points and nmr spectra of these compounds matched the melting points and spectral data for samples obtained by bisamine-catalyzed additions in cyclohexane.

Preparation and Reactions of 9-Lithio-10-alkyl-9,10-DHAs from Metalation of 9-Alkyl-9,10-DHA by Butyllithium in THF.—To a stirred solution of 9-alkyl-9,10-DHA (0.01 mol) (R = CH_3, C_2H_5) under dry argon at −60° was added, in one portion, *n*-butyllithium (0.01 mol, Foote Mineral) in hexane. After the mixture had warmed to 10° during 30 min, the deep red colored solution was cooled to −30° and reaction was terminated (a) with deuterium oxide, (b) with methyl iodide, or (c) with ethyl bromide.

A. **Metalation of 3 (R = C_2H_5).** 1.—The addition of D_2O (1 ml) in purified THF (3.5 ml) afforded a 1:1 mixture of **1b** and **2b** in 95–98% yield.

2. **Slow Addition of D_2O to 1a and 2a.**—To freshly prepared 9-lithio-10-ethyl-9,10-DHAs (0.005 mol from **3**) in THF (50 ml), deuterium oxide (0.10 ml in 40 ml of THF) was added dropwise during 1 hr at temperatures below −20°. Magnetic stirring for 1 additional hr with warming to 25° was followed by addition of deuterium oxide (0.1 ml). After product isolation, nmr analysis of the benzylic protons showed 64% **1b** and 36% **2b**. This analysis is less precise than earlier analyses because of the formation of **3** through reaction with the solvent.

3. **Inverse Addition.**—Rapid inverse addition of **1a** and **2a** (0.005 mol) to a solution of deuterium oxide (2 ml) in THF (15 ml) gave a 1:1 mixture of **1b** and **2b**. The addition of methyl iodide gave a 98% yield of **1b**. Addition of ethyl bromide afforded *cis*-9,10-diethyl-9,10-DHA in 96% (isolated) yield.

B. **Metalation of 4a (R = CH_3).**—The addition of methyl iodide to **1a** and **2a** (0.005 mol) gave known *cis*-9,10-dimethyl-9,10-DHA in 100% yield, mp 127–128° from ethanol (lit.[11] mp 130°). The nmr data are given in Table I.

Preparation of 9-Methyl-9,10-DHA (4).—9-Methyl-9,10-DHA (100 g) was prepared in 94% yield by metalation of 9,10-DHA (100 g, 0.55 mol) in dry THF with *n*-butyllithium (0.575 mol, 360 ml of 1.6 *N* Foote Mineral solution in *n*-hexane) and subsequent addition of excess methyl iodide. After isolation and purification using ethanol, the product had mp 54–55° (lit.[22] mp 61°). The nmr data are given in Table I.

10-Methyl-9,10-DHA-9-carboxylic Acid (5a). 1.—To a solution of 9-methyl-9,10-dihydroanthracene (29.1 g, 0.15 mol) in THF (500 ml), cooled to −50°, was added a 1.6 *M* (0.16 mol) solution of *n*-butyllithium in hexane (100 ml). The cold bath was removed and the solution was allowed to warm to 10° over 30 min, cooled to −22°, and poured into 500 ml of ether saturated with carbon dioxide at −70°. The reaction mass warmed to room temperature over 2 hr. It was transferred to a separatory funnel and thoroughly extracted with 10% aqueous sodium hydroxide (1 l.). The aqueous phases were combined, extracted with ether (200 ml), cooled in ice, and acidified to afford white crystals of crude acid. The acid was collected by filtration, washed with water, and recrystallized from glacial acetic acid (275 ml), affording 20.0 g (56%) of white, delicate plates: mp 226–227° (lit.[23] mp 225–226°); neut equiv 238 (calcd for $C_{16}H_{14}O_2$, 238). The nmr (deuteriopyridine) data appear in Table I.

Concentration of the acetic acid mother liquor to 25 ml gave 9.1 g (25.5%) of additional acid, mp 170–210°. Nmr spectra indicated the presence of 9% *trans*-10-methyl-9,10-DHA-9-carboxylic acid (**6**): δ 323 (H-9) and 96.5 Hz (doublet, J = 7.4 Hz, CH_3).

Evaporation of the neutral ether layers from extraction of the carboxylic acid salt solutions gave 3.14 g (12.5%) of recovered **4**.

2.—Acidification of lithium carboxylate salts with 1:1 HCl–water was used to avoid isomerization of *cis* and *trans* acids during basic work-up, and crude acids (31.4 g, 85%) were obtained from **4** (30 g). After recrystallization from acetic acid, 59.3% *cis* acid (21.84 g, mp 223–225°) was obtained. Nmr analysis of the acids remaining in the acetic acid mother liquor showed the presence of *cis* and *trans* (70:30) acids, or an overall yield of 77% *cis* and 8% *trans* isomer.

The *cis* acid **5a** (1.2 g, 0.005 mol) was dissolved in glacial acetic acid (23 ml). Concentrated hydrochloric acid (2 ml) was added and the solution was refluxed for 4 hr. The solution was cooled and the solvent was removed under reduced pressure, affording the starting acid (mp 227–228°) quantitatively. The nmr spectrum was identical with that of the starting *cis* acid, **5a**.

10-Methyl-9-hydroxymethyl-9,10-DHA (5b).—*cis*-10-Methyl-9,10-DHA-9-carboxylic acid (**5a**, 1.17 g, 0.0046 mol) was reduced with lithium aluminum hydride (0.8 g) in refluxing ether using a Soxhlet extraction apparatus for 6 hr. The reaction mixture was stirred at 25° for 15 hr, hydrolyzed with aqueous HCl, extracted with 5% sodium bicarbonate, and dried (sodium sulfate), and the ether was evaporated to dryness to afford the alcohol (1.03 g, 97%), mp 135–136° (lit.[11,12] mp 136–137°). The nmr data ($CDCl_3$) are given in Table I.

The *cis*-tosyl ester (86%) from **5b** and tosyl chloride in pyridine had mp 134–134.5 (lit.[11,12] mp 133.5–134.5°) after recrystallization from isopropyl ether. The nmr ($CDCl_3$) data are given in Table I.

***cis*-9-Ethyl-10-methyl-9,10-DHA from *cis*-Tosyl Ester 5c.**—The conversion of tosyl ester **5c** into **1c** was accomplished using lithium dimethylcopper.[15,24]

To a suspension of cuprous iodide (4.0 g, 0.021 ml, Fisher Scientific) in dry tetrahydrofuran (40 ml) was added methyllithium in ether (0.042 mol). Tosyl ester (1.5 g, 0.0039 mol) was added to the organocopper reagent. The solution was stirred for 24 hr at 25°, methyl iodide was added, and stirring was continued for 1.0 hr. Water was added and, after removal of copper salts, the product (0.69 g, 79% authentic **1c**, mp 103–104°) was isolated by crystallization from ethanol. Admixture of this material with a highly purified sample of **1c** obtained earlier showed no depression of the melting point. An nmr spectrum was identical with the spectrum obtained on samples prepared from intermediates **1a** and **2a**.

Anal. Calcd for $C_{17}H_{18}$ (mol wt, 222): C, 91.84; H, 8.16. Found: C, 91.58; H, 8.03.

The Reaction of 9-Lithio-10-ethyl-9,10-DHA with Triphenylmethane-*d*.—To a solution of 9-lithio-10-ethyl-9,10-DHA prepared from 0.005 mol each of anthracene, ethyllithium, and TMOPD in cyclohexane (50 ml) was added triphenylmethane-*d* (0.01 mol).[9] After 24 hr, deuterium oxide (1.0 ml) was added and the solution was allowed to stir for 1 additional hr before the product was isolated. Nmr of the isolated hydrocarbon indicated a 43:57 ratio of *trans*- to *cis*-9-deuterio-10-ethyl-9,10-DHA. This ratio is nearly the reverse of that obtained when hydrolysis with deuterium oxide alone is accomplished.

Attempted Isomerization of *cis* Alcohol.—The purpose of this experiment was to provide evidence that the tosyl ester did not undergo epimerization with cuprous iodide-methyllithium reagent.

To a solution of lithium dimethylcopper (0.005 mol) prepared as above in THF (20 ml) and ether (7 ml) was added *cis* alcohol (0.25 g, 0.001 mol) **5b**. After 7 hr, water was added and the product was isolated as above, using chloroform as the extractant. This afforded a pale yellow solid (0.25 g, 100% recovery), mp 130–132°. This material showed no depression on admixture with starting alcohol: mmp 134–135°.

Registry No.—**1b**, 20826-52-2; **1c**, 20826-53-3; **2b**, 20826-54-4; **4a**, 17239-99-5; **4b**, 13417-34-0; **5a**, 20826-57-7; **5b**, 20826-58-8; **5c**, 20826-59-9; *cis*-9,10-diethyl-9,10-DHA, 20826-55-5.

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Harvey (Ben May Laboratory, University of Chicago) and Professor William Closson (State University of New York at Albany, N. Y.). We are also indebted to the chemistry department of the California Institute of Technology for running the mass spectra.

Dipolar and Carbenic Reactions of *p*-Diazooxides

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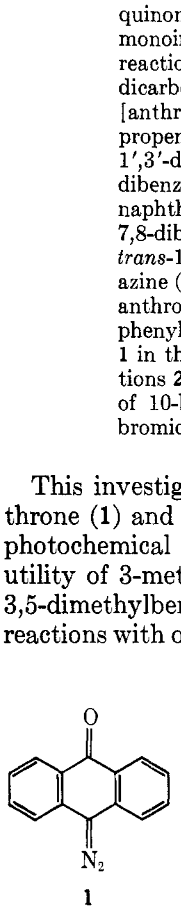
10-Diazoanthrone (**1**) has been prepared by base-catalyzed decomposition of 9,10-anthraquinone mono-*p*-tosylhydrazone (**8**), by oxidation of 9,10-anthraquinone monohydrazone (**7**), and by amination of 9,10-anthraquinone monoxime (**9**). Reactions of **1** with acrylonitrile, methyl vinyl ketone, methyl methacrylate, *trans*-1,2-dibenzoylethylene, and *p*-benzoquinone yield spiro[anthrone-10,1′-cyclopropanes] (**12–15, 18**); with *p*-benzoquinone, 4′,7′-dihydroxyspiro[anthrone-10,3′-indazole] (**17**) is also obtained. N-Phenyl-9,10-anthraquinone monoimine N-oxide (**19**) and N,N-dicarbethoxy-9,10-anthraquinone monohydrazone (**20**) are formed from reactions of **1** with nitrosobenzene and with diethyl azodicarboxylate. Additions of **1** to dimethyl acetylenedicarboxylate and to benzyne give 4′,5′-dicarbomethoxyspiro[anthrone-10,3′(3′H)-pyrazole] (**21**) and spiro[anthrone-10,3′-indazole] (**23**). Photolysis of **21** results in 1′,2′-dicarbomethoxyspiro[anthrone-10,3′-cyclopropene] (**22**). Thermolysis of **1** in 9,10-phenanthrenequinone yields spiro[anthrone-10,2′-(phenanthro[9.10]-1′,3′-dioxole)] (**24**) and $\Delta^{10,10'}$-bianthrone (**26**). 3-Methylnaphthalene 1,4-diazooxide (**2**) adds to *trans*-1,2-dibenzoylethylene and to benzyne to form *trans*-2,3-dibenzoyl-2′-methylspiro[cyclopropane-1,4′-(1′[1′H,4′H]-naphthalenone)] (**27**) and 2′-methylspiro[indazole-3,4′-(1′[1′H,4′H]-naphthalenone)](**28**). 3,5-Dimethyl-*trans*-7,8-dibenzoylspiro[2.5]octa-2,5-dien-4-one (**29**) is obtained from 3,5-dimethylbenzene 1,4-diazooxide (**3**) and *trans*-1,2-dibenzoylethylene. Thermolysis of **1** in benzene catalyzed by copper affords 9,10-anthraquinone azine (**30**) and **26**. Photolysis of **1** in benzene produces biphenyl (**35**), 10,10′-bianthrone (**36**), **30**, and 10-phenylanthrone (**37**). Decomposition of **1** in mesitylene yields **36** and 10,10-bis(3,5-dimethylbenzyl)anthrone. Triphenylphosphine reacts with **1**, yielding 9,10-anthraquinone monotriphenylphosphazine (**39**). Photolysis of **1** in the presence of triphenylphosphine leads to 10-triphenylphosphoranylanthrone (**38**); under similar conditions **2** and triphenylphosphine give 2-methyl-1,4-naphthoquinone 4-triphenylphosphazine (**40**). Displacement of 10-bromoanthrone by triphenylphosphine results predominantly in anthracene-9-oxytriphenylphosphonium bromide (**42**). Both *m*- and *p*-nitrobenzaldehyde react with **38** to give benzylideneanthrones (**44a** and **44b**).

This investigation involves synthesis of 10-diazoanthrone (**1**) and elaboration of its addition, thermal and photochemical reactions, and demonstration of the utility of 3-methylnaphthalene 1,4-diazooxide[2] (**2**) and 3,5-dimethylbenzene 1,4-diazooxide[2] (**3**) in 1,3-dipolar reactions with olefins and acetylenes.



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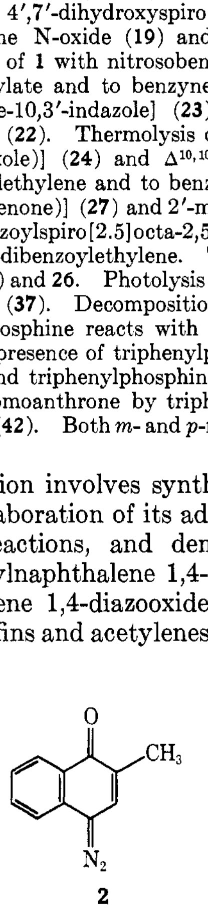

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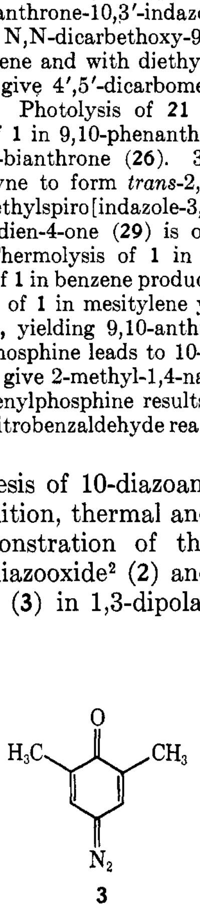

3

Presently **1** has been prepared from 9,10-anthraquinone monohydrazone (**7**), 9,10-anthraquinone mono-*p*-tosylhydrazone (**8**), and 9,10-anthraquinone monooxime (**9**), respectively. Neither **7** nor **8** is readily obtainable from 9,10-anthraquinone and hydrazine or *p*-tosylhydrazine in methanol containing hydrogen chloride. Monohydrazone **7** is formed (40%) along with 10-bromo-10,10′-bianthrone (**6**) from 10,10-dibromoanthrone (**4**) and hydrazine possibly as in eq 1 and 2[3] (Scheme I). Oxidation of **7** by mercuric oxide gives **1** (~100%). Mono-*p*-tosylhydrazone **8** is preparable from 10,10-dibromoanthrone (**4**) and *p*-tosylhydrazine and then converted (98%) by sodium hydroxide into **1** (eq 3).

9,10-Anthraquinone monooxime (**9**) and chloramine in basic solution yield **1**. Another principle product is 9,10-anthraquinone monoimine (**11**). Imines have not been reported in Forster reactions of oximes with chloramine.[4] Carbon amination of 9,10-anthraquinone monooxime anion to **10** and loss of water or nitroxyl (HNO; as nitrous oxide and water, eq 4) account for **1** and **11** though other mechanisms may be involved.[4b,5]

Diazooxides **2** and **3** were prepared[2] by reactions of 2-methyl-1,4-naphthoquinone and of 2,6-dimethyl-1,4-benzoquinone with *p*-tosylhydrazine and subsequent base-catalyzed decomposition.

Decomposition of **1** occurs slowly in refluxing benzene. The diazooxide functions as a 1,3-dipolar reagent with extrusion or retention of nitrogen upon addition to electron-deficient or strained olefins and acetylenes. Thus reactions of **1** with acrylonitrile, methyl vinyl ketone, methyl methacrylate, and *trans*-1,2-dibenzoylethylene take place in hot benzene with loss of nitrogen to give the spiro[anthrone-10,1′-cyclopropanes], **12–15** (56–91%).[6] The structures of the adducts as spiro-

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[1] (a) Abstracted in part from the Ph.D. dissertation of J. C. Fleming, The Ohio State University, Columbus, Ohio, 1964. (b) *Dissertation Abstr.*, **25**, 6958 (1965).

[2] W. Ried and R. Dietrich, *Ber.*, **94**, 387 (1961).

[3] (a) Reduction of positive halogen by hydrazine is well documented[3b] and 10-bromoanthrone (**5**) is converted into **6** by amines.[3c] (b) C. C. Clark, "Hydrazine," Mathieson Chemical Corp., Baltimore, Md., 1953, p 103. (c) E. B. Barnett, J. W. C. Cook, and H. H. Grainger, *J. Chem. Soc.*, **121**, 2059 (1922).

[4] (a) See B. Eistert, M. Regitz, G. Heck, and H. Schwall, "Methoden Der Organischen Chemie," E. Müller, Ed., G. Thieme Verlag, Stuttgart, Vol. X, part 4, 1968, pp 582–587 and references therein. (b) J. Meinwald, P. G. Gassman, and E. G. Miller, *J. Amer. Chem. Soc.*, **81**, 475 (1959).

[5] (a) M. Regitz, *Ber.*, **97**, 2742 (1964), prepared **1** (94%) from anthrone, *p*-tosyl azide, and piperidine. (b) For additional physical properties of **1**, see G. Cauquis, G. Reverdy, and R. M. Rastoldo, *Compt. Rend.*, **260**, 2259 (1965).

[6] Spiro[anthrone-10,1′-cyclopropanes] have been prepared from 10-methyleneanthrones and diazo compounds by A. Mustafa and M. K. Hilmy, *J. Chem. Soc.*, 1434 (1952).