Isolable Stereoisomeric Methylenedihydroanthracenes. Conformationally Isomeric 9-(Dichloromethylene)-10-ethyl-10-methyl-1,8-dichloro-9,10-dihydroanthracenes[1]

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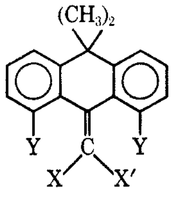
Two stereoisomeric 9-(dichloromethylene)-10-ethyl-10-methyl-1,8-dichloro-9,10-dihydroanthracenes (I) have been prepared and separated and found to be stable at room temperature owing to slow boat–boat inversion of the center ring. The isomers are interconverted at temperatures above 150°. The rates of interconversion (to an equilibrium mixture containing 12% *e*-ethyl I) of the two isomers in *sym*-tetrachloroethane have been found to be first order and with $k_1 + k_{-1} = 1.5 \times 10^{-5}$ sec^{-1} at 157°, $E_a = 42.8 \pm 0.6$ kcal/mol, and $\Delta S^{\ddagger} = 18 \pm 8$ eu. 9-(Bromomethylene)-10-ethyl-10-methyl-1,8-dichloro-9,10-dihydroanthracene (V) was prepared and preliminary work suggests that it can also be separated into *e*-ethyl and *a*-ethyl isomers. Syntheses and characterization are described for the three compounds 9-methylene-10,10-dimethyl-1,8-dichloro-9,10-dihydroanthracene (II), 9-(dichloromethylene)-10,10-dimethyl-9,10-dihydroanthracene (III), and 9-(bromomethylene)-10,10-dimethyl-1,8-dichloro-9,10-dihydroanthracene (IV), whose nmr temperature dependence has recently been reported.[3]

A number of disubstituted 9-methylene-10,10-dimethyl-9,10-dihydroanthracenes, A and B, have been

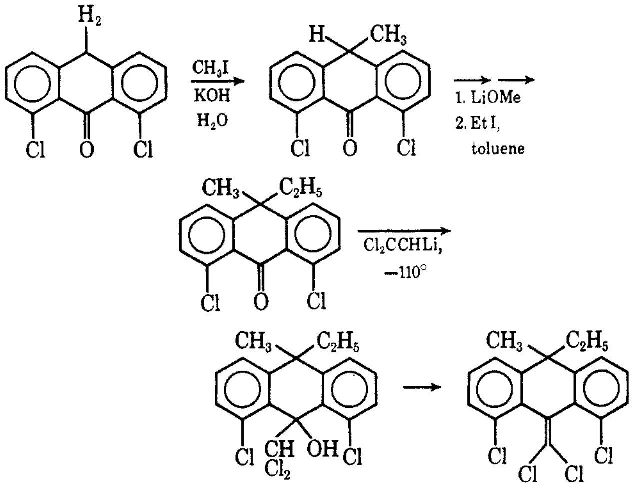


A, X,X′ = H
B, Y = H

shown to exist with the center ring in a boat conformation with a sufficient barrier for interconversion from one boat form to the other to permit observation of the inversion process by the use of nmr spectroscopy.[3,4] Inversion rate constants for all of these disubstituted compounds were greater than 1 sec^{-1}.

It was hoped that with an appropriate change of substituents it might be possible to synthesize molecules with barriers to ring inversion sufficiently large to permit isolation of stereoisomers. The tetrachloro compounds *a*-ethyl- and *e*-ethyl-I (Figure 1) have now been prepared and found to be separable and *conformationally* stable at room temperature.[5] Their synthesis, identification, and interconversion above 150° (Table I) are the subjects of this paper.

The synthesis of a mixture of *e*-ethyl-I and *a*-ethyl-I from 1,8-dichloroanthrone is outlined below. The *a*-ethyl isomer could be separated by crystallization. The *e*-ethyl isomer, however, was much more difficult



a-ethyl–I + *e*-ethyl–I
(87%) (13%)

to separate and was obtained (only after many unsuccessful attempts) by chromatography on alumina impregnated with silver nitrate. Configurational assignments to *a*-ethyl- and *e*-ethyl-I are based on the nmr spectra. The *equatorial methyl group* in the isomer assigned the *a*-ethyl-*e*-methyl configuration is 0.36 ppm downfield from the *axial methyl group* in the *e*-ethyl isomer; similarly, the *equatorial methylene group* in the *e*-ethyl isomer is 0.73 ppm downfield from the *axial methylene group* of the *a*-ethyl isomer. The axial and equatorial methyl proton positions in the 9,9-dimethyl-10-methylene-dihydroanthracenes A and B studied earlier were found to differ by 0.27–0.47 ppm, the lower field methyl group being assigned the protons in the equatorial position and the difference being ascribed primarily to the ring-current effect of the adjacent aromatic rings.[3,4,6]

The stereoisomers *a*-ethyl- and *e*-ethyl-I were found to be stable to prolonged treatment with refluxing

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[1] Taken from the Ph.D. Thesis of Z. M. Holubec, University of Illinois, 1968, available from University Microfilms, Ann Arbor, Mich. We are very much indebted to the Army Research Office, Durham, for partial support of this work.

[2] National Institutes of Health Predoctoral Fellow, 1966–1968

[3] Z. M. Holubec and J. Jonas, *J. Amer. Chem. Soc.*, **90**, 5986 (1968).

[4] D. Y. Curtin, C. G. Carlson, and C. G. McCarty, *Can. J. Chem.*, **42**, 565 (1964).

[5] An alkyl group more nearly "axial" is here designated "*a*," one more nearly equatorial is designated "*e*." As nomenclature of such compounds becomes standardized, it may be preferable to take advantage of the sequence rules [see E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962]. It will be seen that these compounds can be so named by extending the method applied to olefins [J. E. Blackwood, C. L. Gladys, K. L. Loening, A. E. Petrarca, and J. E. Rush, *J. Amer. Chem. Soc.*, **90**, 509 (1968)]. Thus, a reference plane through the 9 and 10 carbon atoms of the middle ring and parallel to the remaining four carbon atoms of that ring is employed. Then that isomer with the higher priority group (in this case, the ethyl group) on the same side of the plane as the methylene group at the opposite side of the ring is assigned a designation corresponding to the "Z" employed for olefins. The other isomer is of course analogous to that designated "E" in naming olefins. In the thesis of Z. M. H.[1] we have extended the Z-E nomenclature in this way. However, the editors of *Chemical Abstracts* have requested that these letters be reserved for the assignment of configurations to olefins only.

[6] A calculation of the expected effect of the ring current[8] by the method of Johnson and Bovey[7] gave a value of 0.6-ppm proton resonance for the difference in chemical shift between the axial and equatorial methyl proton resonance. It has been suggested,[8] however, that the method overestimates the magnitude of the ring-current effect.

[7] C. E. Johnson and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).

[8] K. G. Kidd, G. Kotowycz, and T. Schaeffer, *Can. J. Chem.*, **45**, 2155 (1967).

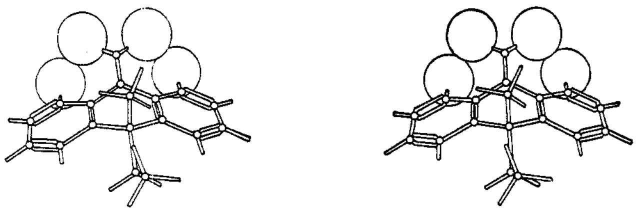


Figure 1.—Stereo view of 9-(dichloromethylene)-10-*e*-ethyl-10-*a*-methyl-1,8-dichloro-9,10-dihydroanthracene (*e*-ethyl-I). The *a*-ethyl isomer has the ethyl and methyl groups interchanged.

methanol. At temperatures above 150° it was found that either compound rearranges slowly to an equilibrium mixture which contained approximately 88% *a*-ethyl and 12% *e*-ethyl isomer. Rates of isomerization were conveniently followed in *sym*-tetrachloroethane by measuring the relative intensities of the 9-methyl absorptions of the two isomers. The data gave reasonable linear plots when a first-order approach to an equilibrium mixture was assumed. The value of the equilibrium constant, 7.5, did not vary significantly over the temperature range studied. Addition of hydrogen chloride or dimethylaniline (11%) gave an increase in the observed rate constant of only about 14%; the effect of added acid and base is clearly so small that it can be concluded that the isomerization under conditions when they have not been deliberately added is a reaction of neutral *e*- or *a*-ethyl-I, and is not being affected by traces of adventitious acid or base.

Table I

Rates of Interconversion of Stereoisomers *e*-Ethyl- and *a*-Ethyl-I in *sym*-Tetrachloroethane at 157–178°

Starting material	Concn, %	Temp, °C	Added acid or base	$k_{obsd} = k_1 + k_{-1}$ 10^6 sec^{-1} and standard deviation
e-Ethyl-I[a]	13.9	157.0	None	1.45 ± 0.01
	21	158		1.64 ± 0.01
e-Ethyl-I[a]	13.9	171.5	None	7.89 ± 0.09
e-Ethyl-I[a]	13.6	171.5	HCl[b]	8.98 ± 0.14
e-Ethyl-I[a]	15	171.5	Dimethyl-aniline[c]	8.96 ± 0.10
e-Ethyl-I[a]	13.9	178.5	None	16.54 ± 0.14
	16.1	178.5		15.90 ± 0.15
a-Ethyl-I	33	178.5	None	16.61 ± 0.86

[a] Although predominately *e*-ethyl-I the starting material contained 29–36% isomer *a*-ethyl-I. [b] Solution saturated with HCl gas. [c] 11% dimethylaniline.

The detailed geometry of the transition state for inversion cannot be described at present, but it is of interest to compare the activation parameters with those for the unimolecular *cis–trans* isomerization of olefins. These data[9–12] are presented in Table II. A question which arises immediately is to what extent does a rotation around the axis of the carbon–carbon double bond occur when the $Cl_2C=$ group passes the two aromatic chlorine atoms in the course of the *e*-ethyl to *a*-ethyl inversion? Such a rotation should lead to a loss of some or all of the π-bond energy of the exocyclic double bond, and, if the $Cl_2C=$ grouping became nearly perpendicular to its original position, the activation energy for the *e*-ethyl to *a*-ethyl inversion might be comparable in magnitude to that for the uncatalyzed *cis–trans* isomerization of olefins. The data in Table II suggest that the orders of magnitude of the rate and activation parameters are not different from what might have been expected if the ring inversion involved a good deal of twist of the exocyclic $Cl_2C=$. A mechanism somewhat analogous to the *cis–trans* isomerization of olefins appears then to be favored by the evidence.

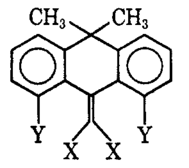
Table II

Activation Parameters for the Thermal Interconversion of *e*- Ethyl- and *a*-Ethyl-I and for *cis–trans* Isomerization of Olefins

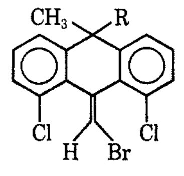
Compd	State	Temp, °C	E_a, kcal/mol	$\Delta S^{\ddagger}$, eu
e- and *a*-ethyl-I[a]	Liquid	157–179	42.8 ±0.6	18 ±8
CHD=CHD[b]	Vapor	504–550	61	−3
$CH_3CH{=}CHCH_3$[c]	Vapor	461–502	62	0
$C_6H_5CH{=}CHC_6H_5$[d]	Liquid	214–223	37	−13
		280–341	43	−2
$C_6H_5CCl{=}CHC_6H_5$[e]	Liquid	226–246	37	−8
$C_6H_5CCl{=}CClC_6H_5$[e]	Liquid	175–200	34	−10
p-$CH_3OC_6H_4CH{=}CHC_6H_5$[f]	Liquid	272–299	36	−14
p-$NO_2C_6H_4CH{=}CHC_6H_5$[f]	Liquid	172–210	34	−14

[a] Present work. The values and standard deviations reported were obtained from a least-squares plot of log k_{obsd} *vs.* I/*T*. [b] See ref 9. [c] See ref 10. [d] See ref 11. [e] See ref 11a. [f] See ref 12.

A further comparison which is of great interest is that of the ring inversion rate of *e*- and *a*-ethyl-I with the molecules II and III, whose rates of ring inversion at 41° are given below.[4] Extrapolation of the inversion rates of *e*-ethyl- and *a*-ethyl-I to 41° gives a value of approximately 10^{-13}. This means that replacement of a pair of chlorine atoms in I by hydrogens increases the inversion rate by a factor of 10^{13}–10^{14}.



II, X = H, Y = Cl; $k^{41°} = 83$ sec^{-1}
III, X = Cl, Y = H; $k^{41°} = 6.9$ sec^{-1}



IV, R = CH_3
V, R = C_2H_5

In the course of this work, the two bromomethylene compounds IV and V were synthesized. That the inversion rates of these compounds are much slower than those of II and III was shown by the fact that their nmr spectra did not change appreciably at 180°. *A preliminary experiment suggested that the methyl ethyl compound V can be separated into e-ethyl and a-ethyl isomers, and further work along these lines is being continued.* Since a study of the temperature dependence of the nmr spectra has been reported[4] but not the syntheses and characterization of II and III, they are described in the Experimental Section.

Experimental Section

Melting points were obtained with a Thomas-Hoover capillary melting point apparatus. Infrared spectra (10% solutions in carbon tetrachloride unless otherwise noted) were obtained with

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[9] J. E. Douglas, B. S. Rabinovitch, and F. S. Looney, *J. Chem. Phys.*, **23**, 315 (1955).

[10] B. S. Ravinovitch and K. W. Michel, *J. Amer. Chem. Soc.*, **81**, 5065 (1959).

[11] (a) T. W. J. Taylor and A. R. Murray, *J. Chem. Soc.*, 2078 (1938); (b) G. B. Kistiakowsky and W. R. Smith, *J. Amer. Chem. Soc.*, **56**, 638 (1934).

[12] M. Calvin and H. W. Alter, *J. Chem. Phys.*, **19**, 768 (1951).

a Perkin-Elmer Model 137 Infracord or by Mr. D. Johnson, Mr. G. Swafford, and Mr. R. Thrift and their associates with a Perkin-Elmer Model 521 spectrophotometer. A number of nmr spectra (10–20% solutions in carbon tetrachloride unless otherwise indicated) were measured by Mr. O. Norton, Mr. D. Johnson, Mr. G. Swafford, and Mr. R. Thrift and their associates with Varian Associates Model A-60, A-60A, or 56/60 instruments. Ultraviolet spectra were obtained with a Bausch and Lomb Spectronic 505 spectrophotometer. Microanalyses were carried out by Mr. J. Nemeth and his associates. Molecular weights were determined from the parent ion peak of mass spectra obtained by Mr. J. Wrona with an Atlas CH4 instrument.

1,8-Dichloroanthrone [mp 167.5–168.5° (lit.[13] mp 167°); ir 1675 cm^{-1}; uv λ_{max} 273 mμ (ϵ 14,800); nmr τ 2.67 (broad), 5.85 (broadened)] was prepared by reduction of 1,8-dichloroanthraquinone with aluminum in sulfuric acid.[13]

10-Methyl-1,8-dichloroanthrone, mp 204–205.5° (lit.[14] mp 204°) was best prepared by a modification of the mono-C-alkylation of anthrone,[15] which gave the desired product in 72% yield (50% after recrystallization from glacial acetic acid). The ir spectrum showed carbonyl absorption at 1685 cm^{-1}. The nmr spectrum ($CDCl_3$) showed aromatic proton absorption at τ 2.70, the methine proton at τ 5.84, and the methyl doublet at τ 8.53. The uv spectrum (95% in ethanol) showed a maximum at 275 mμ (ϵ 14,250).

10,10-Dimethyl-1,8-dichloroanthrone.—1,8-Dichloroanthrone (20 g, 0.076 mol) was alkylated by a procedure employed previously for anthrone[16] by treatment of its lithium salt [from reaction of the ketone with lithium methoxide prepared from 1.16 g (0.167 g-atom) of lithium and 60 ml of reagent grade methanol in dried glassware under an argon atmosphere and distillation of the solvent at 40° and 13 mm] with 110 g (0.76 mol) of methyl iodide and 8 drops of *t*-butyl alcohol in a combustion tube at 150° for 24 hr. After cooling, the reaction mixture was extracted with ether and water and the ether layer was repeatedly extracted with Claisen's alkali, washed with water, and dried, and cyclohexane was added to make the solvent composition 3:2 cyclohexane–ether. The solution was passed through a column of 150 g of neutral Merck alumina, and the product was eluted with cyclohexane–ether (3:2) to give 11.0 g (50%) of yellow crystals, mp 161–163.5°. Recrystallization from cyclohexane gave 8.8 g, mp 163–164°. Sublimation and a further crystallization gave mp 164–164.5°. The nmr spectrum showed a complex multiplet at τ 2.65 and a singlet at τ 8.32. The uv spectrum (95% ethanol) showed λ_{max} 277 mμ (ϵ 14,000).

Anal. Calcd for $C_{16}H_{12}Cl_2O$: C, 66.0; H, 4.2; Cl, 24.4. Found: C, 66.2; H, 4.2; Cl, 24.6.

10-Ethyl-10-methyl-1,8-dichloroanthrone was prepared by ethylation of the lithium salt of 10-methyl-1,8-dichloroanthrone (from lithium methoxide and 15 g of the anthrone, as in the preceding reaction) with 126 g of ethyl iodide and 0.3 ml of *t*-butyl alcohol in a sealed tube at 150° for 30 hr. The work-up described for the dimethyl compound above was employed, except that carbon tetrachloride was employed initially for the chromatography on 220 g of silica gel. Elution with carbon tetrachloride gave 2.2 g (13% yield) of O-alkylated product, mp 112–114°. Further elution with benzene–carbon tetrachloride (3:1) gave 8.0 g (49%) of 10-ethyl-10-methyl-1,8-dichloroanthrone, mp 144–147°. Recrystallization from hexane gave 6.8 g, and further recrystallization from 95% ethanol and from ligroin gave mp 149–150°. The ir spectrum ($CHCl_3$) showed broad carbonyl absorption at 1680 cm^{-1}. The nmr showed a complex multiplet at τ 2.63, a quartet at τ 8.16 partially superimposed upon a singlet at τ 8.29, and a triplet at τ 9.48.

Anal. Calcd for $C_{17}H_{14}Cl_2O$: C, 66.9; H, 4.6; Cl, 23.3. Found: C, 66.9; H, 4.6; Cl, 23.0.

***cis*- and *trans*-9-Dichloromethyl-10-ethyl-9-hydroxy-10-methyl-1,8-dichloro-9,10-dihydroanthracene.**—Dichloromethyllithium, prepared by the method of Köbrich, Trapp, Flory, and Drischell,[17] by the addition of 24.5 mmol of *n*-butyllithium in 45 ml of hexane–petroleum ether to 1.6 ml of methylene chloride in 100 ml of tetrahydrofuran, 12 ml of ether, and 12 ml of petroleum ether (bp 50–60°) at −110°, was treated with a solution of 6.79 g (22.3 mmol) of the ethylmethyldichloroanthrone in 100 ml of 1:1 tetrahydrofuran–ether over a period of 75 min at −110°. After 2 hr of additional stirring, the reaction mixture was poured on crushed ice containing 2 g of ammonium chloride. After extraction with ether, drying of the ether layer over magnesium sulfate, and distillation of the ether, there was obtained a mixture of 8.38 g (97%) of the *cis* and *trans* alcohols which solidified on standing and had mp 97–102°. An analytical sample prepared by three recrystallizations from ligroin had mp 109.5–110.5°. The nmr showed a multiplet at τ 2.61, singlets at τ 3.34 and 3.44 in a ratio of 6.8:1, singlets at τ 4.64 and 4.87 in a ratio of 5.8:1, a quartet at τ 7.95 partially superimposed upon a singlet at τ 8.16, a singlet at τ 8.44, and triplets at τ 9.35 and 9.90 in a ratio of 1:6.6.

Anal. Calcd for $C_{18}H_{16}Cl_4O$: C, 55.4; H, 4.1; Cl, 36.4. Found: C, 55.5; H, 3.9; Cl, 36.0.

9-(Dichloromethylene)-10-ethyl-10-methyl-1,8-dichloro-9,10-dihydroanthracenes (*e*-Ethyl- and *a*-Ethyl-I).—Dehydration of 8.38 g of the mixture of carbinols just described was carried out by triturating it with 20 ml of sulfuric acid.[17] After pouring on ice, extraction with ether, washing with water, drying over magnesium sulfate, and distillation of the solvent, there was obtained 7.58 g (95%) of a mixture of *e*- and *a*-ethyl-I, mp 128–140°. After chromatography on alumina (elution with cyclohexane), the yield was 6.1 g (76%) of a mixture of *e*- and *a*-ethyl-I, mp 133–140°, whose nmr spectrum showed (relative areas of quartet at τ 7.59 and singlet at τ 8.62 compared with the quartet–singlet combination at τ 8.28) the composition to be 87% *a*-ethyl- and 13% *e*-ethyl-I.

The Isomer *a*-ethyl-I, mp 144.5–145.5°, was separated by recrystallization of the mixture from methanol. Additional recrystallization failed to change the melting point. The uv spectrum (cyclohexane) showed λ_{max} 259 mμ (ϵ 15,200). The nmr peaks (and areas) were a complex multiplet at τ 2.80 (6.0), a quartet at τ 8.29, a singlet at τ 8.27 (4.9), and a triplet at τ 9.25 (3.0). The mass spectrum showed molecular ion peaks at *m/e* (rel intensity) 370 (100), 372 (131), 374 (62.5), and 376 (15.5).

Anal. Calcd for $C_{18}H_{14}Cl_4$: C, 58.1; H, 3.8; Cl, 38.1. Found: 58.1; H, 3.8; Cl, 37.9.

***e*-Ethyl-I** was separated from the mother liquors remaining from crystallization of *a*-ethyl-I by repeated crystallization from methanol (which failed to give complete separation) followed by chromatography on a column of alumina impregnated with 23% silver nitrate following the directions of Schroepfer, *et al.*[18] Elution with hexane–ether (10:1) gave *e*-ethyl-I, mp 129–132°, which, after two recrystallizations from methanol, had mp 131.5–132° and was shown by the nmr spectrum to be free from appreciable amounts of *a*-ethyl-I. The nmr spectrum (8% in CCl_4) had peaks (and areas) as follows: a multiplet at τ 2.78 (5.7), a quartet at τ 7.56 (2.0), a singlet at τ 8.63 (3.2), and a triplet at τ9.22 (3.2). The mass spectrum was indistinguishable from that of *a*-ethyl-I.

Anal. Calcd for $C_{18}H_{14}Cl_4$: C, 58.1; H, 3.8; Cl, 38.1. Found: C, 57.9; H, 3.8; Cl, 37.4.

9,10,10-Trimethyl-9-hydroxy-1,8-dichloro-9,10-dihydroanthracene was prepared by the reaction of 63 mmol of methyllithium (from 8.9 g of methyl iodide and 0.79 g of finely cut lithium in 27 ml of ether) with 3.3 g (11 mmol) of 10,10-dimethyl-1,8-dichloro-9,10-dihydroanthracene at 0° in 1:1 ether–benzene. After a reaction time of 3 hr, the mixture was poured onto crushed ice containing 2 g of NH_4Cl, and, after extraction, washing, drying, and distillation of solvent, there remained 3.3 g (93%) of the alcohol, mp 118–122°. Recrystallization from cyclohexane and from *n*-pentane gave a sample with mp 127–128°. The ir spectrum showed absorption at 3595 cm^{-1} and the nmr showed a complex multiplet at τ 2.77 and singlets at τ 6.42, 7.86, 8.25, and 8.50.

Anal. Calcd for $C_{17}H_{16}Cl_2O$: C, 66.5; H, 5.2; Cl, 23.1. Found: C, 66.5; H, 5.1; Cl, 23.7.

9-Methylene-10,10-dimethyl-1,8-dichloro-9,10-dihydroanthracene (II).—The carbinol (1.23 g), mp 124.5–126°, was dehydrated with concentrated sulfuric acid[17] as in the preparation of the dichloro analog I. Distillation of the solvent after drying gave 1.04 g (88%) of crude olefin, mp 134–135.5°. Chromatography on alumina (elution with cyclohexane) gave 0.89 g (77%) of II,

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[13] E. De B. Barnett and M. A. Matthews, *J. Chem. Soc.* **123**, 2549 (1923).

[14] E. De B. Barnett and J. L. Wiltshire, *Chem. Ber.*, **62**, 3063 (1929).

[15] K. H. Meyer and H. Schlosser, *Ann.*, **420**, 130 (1920).

[16] D. Y. Curtin, R. C. Tuites, and D. H. Dybvig, *J. Org. Chem.*, **25**, 155 (1960); C. G. Carlson, Ph.D. Thesis, University of Illinois, Urbana, Ill., 1963.

[17] G. Köbrich, H. Trapp, K. Flory, and W. Drischell, *Chem. Ber.*, **99**, 689 (1966).

[18] R. Kammerck, W.-H. Lee, A. Paliokas, and G. J. Schroepfer, Jr., *J. Lipid Res.*, **8**, 282 (1967).

mp 135.5–136.5°. Additional recrystallizations from methanol left the melting point unchanged. The ir spectrum had weak C=C absorption at 1630 cm^{-1} and the nmr spectrum showed a complex multiplet centered at τ 2.75, a singlet at τ 3.71, and a pair of broad peaks at τ 8.25 and 8.58.

10,10-Dimethyl-9-dichloromethyl-9-hydroxy-9,10-dihydroanthracene was prepared by the addition of dichloromethyllithium[17] to 10,10-dimethylanthrone,[16] following a procedure employed for the corresponding synthesis of the tetrachloro compound described earlier. The crude product, mp 135–138° (92%), isolated by evaporation of the solvent after work-up, was purified by two recrystallizations from ligroin, after which it had mp 137.5–138°. The ir spectrum showed absorption at 3200 and 3550 cm^{-1}. The nmr had a complex multiplet at τ 2.10, a multiplet at τ 2.66, and singlets at τ 4.21, 6.79 (disappeared when washed with D_2O), 8.22, and 8.38.

Anal. Calcd for $C_{17}H_{16}Cl_2O$: C, 66.5; H, 5.3. Found: C, 66.5; H, 5.2.

9-(Dichloromethylene)-10,10-dimethyl-9,10-dihydroanthracene (III) was prepared by dehydration of the carbinol in the preceding section by treating it with 20 ml of 20% sulfuric acid in glacial acetic acid by the method of Garbisch.[19] After pouring on ice, extraction with ether, neutralization with sodium bicarbonate, washing with water, drying over magnesium sulfate, and distillation of the solvent, there was obtained crude olefin which was purified by chromatography on alumina (cyclohexane eluent) to give a 76% yield of white solid, mp 134–136°. Further purification by two recrystallizations from methanol followed by sublimation gave mp 138–139°. The nmr spectrum had a complex multiplet centered at τ 2.25, a multiplet at τ 2.75, and a pair of slightly broadened singlets at τ 8.15 and 8.60. The uv spectrum (cyclohexane) showed λ_{max} 268 mμ (ϵ 16,800).

Anal. Calcd for $C_{17}H_{14}Cl_2$: C, 70.6; H, 4.9; Cl, 24.5; mol wt, 289. Found: C, 70.3; H, 4.9; Cl, 24.9; mol wt, 289.

9-(Bromomethylene)-10,10-dimethyl-1,8-dichloro-9,10-dihydroanthracene (IV) was prepared by bromination of the olefin II, a method analogous to that of Carlson[16] for the unchlorinated analog. Addition over a 2-hr period of 1.14 g (7.1 mmol) of bromine in 2 ml of CCl_4 to 2.05 g (7.1 mmol) of the olefin II in 30 ml of CCl_4 followed by standing at ambient temperature for 10 hr, 4 hr of refluxing, and distillation of the solvent (reduced pressure) gave a tan residue which was purified by chromatography on alumina (cyclohexane–ether 2:1). There was obtained 2.4 g (92%) of IV, mp 177–180°. Further crystallization from hexane and from ethanol gave mp 180.5–181.5°. The nmr showed a multiplet at τ 2.75 and singlets at τ 2.91, 8.16, and 8.62.

Anal. Calcd for $C_{17}H_{13}BrCl_2$: C, 55.5; H, 3.6; Br, 21.7. Found: C, 55.8; H, 3.7; Br, 21.7.

9,10-Dimethyl-10-ethyl-9-hydroxy-1,8-dichloro-9,10-dihydroanthracene was prepared by the addition of methyllithium to the ethylmethyldichloroanthrone following the procedure used for the addition to the dimethyldichloroanthrone described previously. Removal of the solvent after the preliminary work-up gave 1.40 g (95%) of carbinol, mp 107–113°. Several recrystallizations from hexane gave mp 116–117°. The ir spectrum showed hydroxyl absorption at 3597 cm^{-1}, and the nmr spectrum showed multiplets at τ 2.72 and 7.85, singlets at τ 6.41, 8.32, and 8.45, and a broad triplet at τ 9.66.

Anal. Calcd for $C_{18}H_{18}Cl_2O$: C, 67.3; H, 5.7. Found: C, 67.4; H, 5.8.

9-Methylene-10-ethyl-10-methyl-1,8-dichloro-9,10-dihydroanthracene was prepared by dehydration of the carbinol of the preceding section by the method of Garbisch[1] as described for the syntheses of olefin III. Evaporation of solvent gave crude olefin, mp 110–116°, which was purified by chromatography on alumina (elution with cyclohexane) to give an 89% yield of product, mp 119–122°. Two recrystallizations from methanol gave mp 122–123°. The nmr spectrum showed a multiplet at τ 2.77, singlets at τ 3.76 and 8.37, and a triplet at τ 9.37.

Anal. Calcd for $C_{18}H_{16}Cl_2$: C, 71.3; H, 5.3; Cl, 23.4. Found: C, 71.6; H, 5.5; Cl, 23.5.

9-(Bromomethylene)-10-ethyl-10-methyl-1,8-dichloro-9,10-dihydroanthracene (V) was prepared by bromination of the olefin in the preceding section, following the procedure employed for the preparation of IV. Chromatography of the crude product on Two recrystallizations from methanol gave mp 138–141°. The nmr spectrum (15% in $CDCl_3$) showed a multiplet at τ 2.70, a singlet at τ 2.90, a quartet at τ 7.59, a singlet superimposed upon alumina (cyclohexane eluent) gave 68% of V, mp 135–141°. a quartet at τ 8.26–8.31, a singlet at τ 8.69, and two triplets overlapping at τ 9.26–9.35.

Anal. Calcd for $C_{18}H_{15}BrCl_2$: C, 56.6; H, 4.0; Br, 20.9. Found: C, 56.9; H, 4.3; Br, 20.7.

Measurement of the Kinetics of Interconversion of *e*-Ethyl- and *a*-Ethyl-I.—Rate measurements were carried out with sample tubes prepared as for the nmr studies reported elsewhere,[4] except that before the tubes wre sealed the air was replaced by nitrogen. Solutions were 13–33% w/v in 1,1,2,2-tetrachloroethane with tetramethylsilane as an internal standard. The tubes were heated in a constant temperature bath (±0.5°) at the temperature indicated, and cooled rapidly to room temperature after the specified time. The nmr spectrum was measured with a Varian A56/60 spectrometer with a 100-Hz sweep width and a sweep time of 250–500 sec. Isomerizations of mixtures with excess *e*-ethyl-I were followed by measuring the disappearance of the methyl peak at τ 8.63; the reaction of the *a*-ethyl isomer was followed by measuring the disappearance of the methyl and methylene absorption at τ 8.27. Since the methyl absorption of the *a*-ethyl isomer was overlapped by the methylene quartet, the total area due to the five protons was measured and multiplied by a constant factor of 3/5. Infinity points were determined at a minimum of eight half-lives. The average value for the composition at infinite time corresponding to 11.79% of the *e*-ethyl isomer was employed throughout. The rate constants and standard deviations were calculated assuming the relationship[20]

$$\ln (A_0 - A_e)/(A - A_e) = k_{obsd}t$$

(where the A's are concentrations at $t = 0$, time t, and after equilibrium has been reached, and $k_{obsd} = k_1 + k_{-1}$) using an IBM 7094 computer and employing a weighted least-squares program.[21] Results are summarized in Table I. Detailed data are available in the Ph.D. Thesis cited in ref 1. The values of E_a and $\Delta S^{\ddagger}$ (Table II) were obtained from a least-squares plot of log k_{obsd} *vs.* $1/T$. Error limits were estimated[22] assuming a 5% error in the rate constants.

Registry No.—I, 20888-10-2; II, 20888-11-3; III, 20888-12-4; IV, 20888-13-5; V, 20888-14-6; 10,10-dimethyl-1,8-dichloroanthrone, 20888-15-7; 10-ethyl-10-methyl-1,8-dichloroanthrone, 20888-16-8; *cis*-9-dichloromethyl-10-ethyl-9-hydroxy-10-methyl-1,8-dichloro-9,10-dihydroanthracene, 20888-17-9; *trans*-9-dichloromethyl-10-ethyl-9-hydroxy-10-methyl-1,8-dichloro-9,10-dihydroanthracene, 20888-18-0; 9,10,10-trimethyl-9-hydroxy-1,8-dichloro-9,10-dihydroanthracene, 20888-19-1; 10,10-dimethyl-9-dichloromethyl-9-hydroxy-9,10-dihydroanthracene, 20888-20-4; 9,10-dimethyl-10-ethyl-9-hydroxy-1,8-dichloro-9,10-dihydroanthracene, 20930-48-7; 9-methylene-10-ethyl-10-methyl-1,8-dichloro-9,10-dihydroanthracene, 20888-21-5.

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