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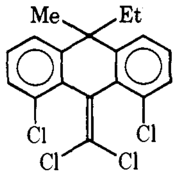
Isolable Stereoisomeric Methylenedihydroanthracenes. The Synthesis and Behavior toward Nucleophilic Displacement of Conformationally Isomeric 9-(Bromomethylene)-10-ethyl-1,8,10-trimethyl-9,10-dihydroanthracenes[1,2]

Pak-Tong Leung and David Y. Curtin*

Contribution from the Department of Chemistry, University of Illinois, Urbana, Illinois 61801. *Received December 5, 1974*

Abstract: Two stereoisomeric 9-(bromomethylene)-10-ethyl-1,8,10-trimethyl-9,10-dihydroanthracenes (**2**) have been prepared and separated and found to be stable at room temperature because of slow boat-boat inversion of the center ring. The rates of interconversion (to an equilibrium mixture containing 12% (e)-ethyl- and 88% (a)-ethyl-**2**) of the two isomers in tetrachloroethylene have been found to be first order with $k_1 + k_{-1} = 7 \times 10^{-4}$ sec^{-1} at 107° (ca. 4×10^4 times faster than 9-(dichloromethylene)-10-ethyl-10-methyl-1,8-dichloro-9,10-dihydroanthracene (**1**)). The free energy of activation was estimated to be 28.2 kcal/mol. A new type of reaction stereochemistry has been investigated, in which the original conformation of the 10-ethyl and 10-methyl groups in (a)-ethyl-**2** was retained during nucleophilic substitution by lithium diphenylphosphide at the vinyl carbon atom.

Earlier NMR studies[3-5] of restricted boat-boat interconversion for a number of substituted 9-methylene-10,10-dimethyl-9,10-dihydroanthracenes have been made. It has furthermore been demonstrated[6] that when four chlorine atoms, substituents of moderate steric size, were introduced onto the methylene carbon atom and the 1- and 8-aryl positions of 9-methylene-10-ethyl-10-methyl-9,10-dihydroanthracene, two stereoisomers, (a)-ethyl- and (e)-ethyl-**1**, could be separated and were found to be stable at room temperature. The introduction of a single substituent of sufficient bulk at the methylene position in the corresponding 1,8-dimethyl substituted compound, 9-methylene-1,8,10,10-tetramethyl-9,10-dihydroanthracene, should increase the barrier to ring inversion sufficiently to permit the isolation of stereoisomers. The present study was directed toward the synthesis of stereoisomeric 9-(bromomethylene)-10-ethyl-1,8,10-trimethyl-9,10-dihydroanthracene (**2**) to see whether it could be separated into (a)-ethyl- and (e)-ethyl isomers, and also in order to investigate replacement reactions at the vinyl carbon.[7] Thus, the presence of an intermediate with sufficiently reduced steric requirement would result in boat-boat interconversion concomitant with replacement. Compound **2** has the further potential interest that it could, in principle, be resolved into two pairs of optically active isomers interconvertible by a change of the configuration at the olefinic carbon atom.



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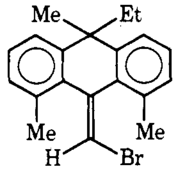
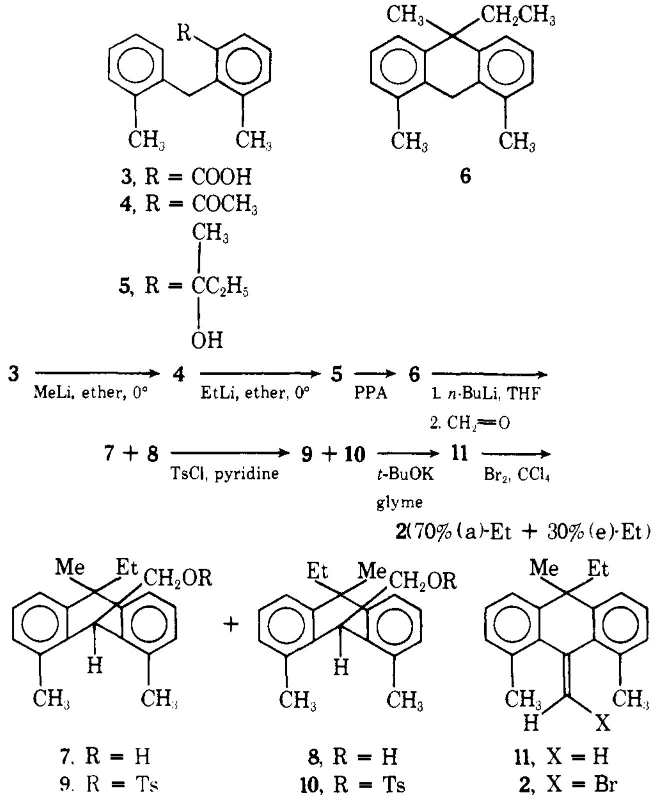


2

The synthetic sequence for the preparation of a mixture of (a)-ethyl-**2** and (e)-ethyl-**2** modeled after that employed for the synthesis of the 10,10-dimethyl homologs, is outlined in Scheme I. The structure assignments of compounds **7, 8, 9,** and **10** were established by NMR studies.[8] At ambient temperatures the NMR spectrum of methylene compound **11** indicated that the rate of interconversion of (a)-ethyl and (e)-ethyl isomers was fast on the NMR time scale, and only time-averaged signals could be seen. On the other hand, the NMR spectrum of compound **2** revealed the presence of a mixture of (a)-ethyl- and (e)-ethyl isomers. The (a)-ethyl isomer could be separated by crystallization from methanol. The (e)-ethyl isomer was very difficult to separate and was obtained by chromatography on alumina impregnated with 25% silver nitrate and elution with hexane. Configurational assignments to (a)-ethyl and (e)-ethyl isomers are based on comparison of the NMR spectra with the known spectra of the (e)-ethyl- and (a)-ethyl-**1**.[6]

The rates of isomerization of (a)-ethyl- and (e)-ethyl-**2**

Scheme I



3, R = COOH
4, R = COCH$_3$
5, R = C(CH$_3$)(OH)C$_2$H$_5$
6

$3 \xrightarrow[\text{MeLi, ether, 0°}]{} 4 \xrightarrow[\text{EtLi, ether, 0°}]{} 5 \xrightarrow[\text{PPA}]{} 6 \xrightarrow[\text{1. } n\text{-BuLi, THF; 2. CH}_2\text{=O}]{}$

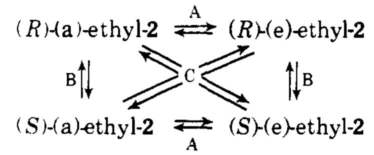
$7 + 8 \xrightarrow[\text{TsCl, pyridine}]{} 9 + 10 \xrightarrow[t\text{-BuOK, glyme}]{} 11 \xrightarrow[\text{Br}_2\text{, CCl}_4]{}$ 2(70% (a)-Et + 30% (e)-Et)

7, R = H
9, R = Ts

8, R = H
10, R = Ts

11, X = H
2, X = Br

Scheme II[a]

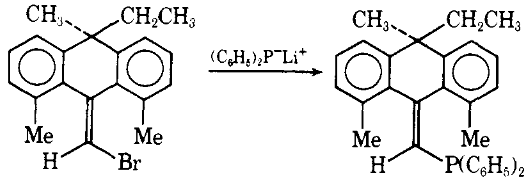


[a] Key: A = ring inversion process; B = inversion at vinyl carbon atom (or rotation of exocyclic double bond); C = simultaneous A plus B.

were conveniently followed in tetrachloroethylene by measuring the change with time of the relative integrated areas of the 9-methyl absorptions at δ 1.71 and 1.33, or of the vinyl protons at δ 6.43 and 6.33 of the two isomers. The data gave linear plots when a first-order approach to an equilibrium mixture was assumed. The rate of interconversion to an equilibrium mixture containing approximately 12% (e)-ethyl and 88% (a)-ethyl isomer was 7×10^{-4} sec^{-1} at 107°. The free energy of activation, $\Delta G^\ddagger$, was calculated to be 28.2 kcal/mol. This is in good agreement with that of the 10,10-dimethyl homolog whose free energy of activation was estimated to have a minimum value of 24 kcal/mol.[5] The equilibrium constant was estimated to be 7.6 which is in agreement with the value (7.5) obtained for the tetrachloro compound **1**.[6] The rate of isomerization of the monobromo compound **2** is thus about 4×10^4 times faster than that of the tetrachloro compound **1**, the rate constant of which was estimated[6] to be 1.7×10^{-8} sec^{-1} at 107°. This indicates that the major factor responsible for the differences in rates is due to the differences of the exocyclic groups, =CHBr and =CCl$_2$ since the effectiveness of the methyl groups and the chlorine atoms at the 1,8-aryl positions to interfere the ring inversion should be comparable.[5] Despite the fact that the size of the bromine atom is considerably larger than that of the chlorine atom, the effect of the =CHBr group in suppressing ring inversion is 4×10^4 times less than that of the =CCl$_2$. A plausible explanation is that in the course of the (e)-ethyl to (a)-ethyl inversion partial rotation around the exocyclic double bond (=CHBr or =CCl$_2$) occurs and allows first one of the smaller substituents to pass into its new conformation and then the second larger substituent. In other words, the nonbonded interaction between the aryl substituent and the H—C= is expected to be smaller than that with ClC= and the free energy of activation for the ring inversion process in compound **2** is much less.

Examination of the molecular structure of **2** reveals that the molecule lacks a plane of symmetry even if the central ring is in its average planar form. Four possible stereoisomers[9] of **2** can be distinguished and are interconvertible by the reaction network shown in Scheme II. A boat-boat ring inversion (process A) interconverts axial and equatorial conformers of the same configuration, whereas inversion at the vinyl carbon atom (process B) reverses the absolute configuration (*R* and *S*) leaving the conformation (axial and equatorial) unchanged. Of course, it is also possible that both processes can occur simultaneously (process C) changing both the absolute configuration (*R* and *S*) and the conformation (axial and equatorial) at the same time. As can be seen in the present system, conformational isomerism is superimposed on geometrical enantiomerism. Thus the present system would provide a very interesting model for the studies of replacement reactions at the vinyl carbon atom in view of the current interest in nucleophilic substitution reactions in vinyl halides.[7]

Preliminary studies were made on the stereochemical fate of the vinyl bromide **2** during a vinyl substitution reaction, bearing in mind that substitution reaction at the vinyl carbon atom might lead to geometrical enantiomerism which might in turn lead to boat-boat interconversion and thus alter the conformation at the 10-position. Although this study is incomplete, the initial results are reported here because no further work in this area is contemplated at present. Due to the difficulties in obtaining the less stable isomer, (e)-ethyl-**2**, in a reasonable amount, the question of stereospecificity was investigated only with optically inactive isomer (a)-ethyl-**2** in the reaction with lithium diphenylphosphide at room temperature. The substitution product, 9-(diphenylphosphoromethylene)-10-ethyl-1,8,10-trimethyl-9,10-dihydroanthracene (**12**), retained the original conformation at the 10-position ((a)-ethyl-(e)-methyl) of the starting bromide, (a)-ethyl-**2**.

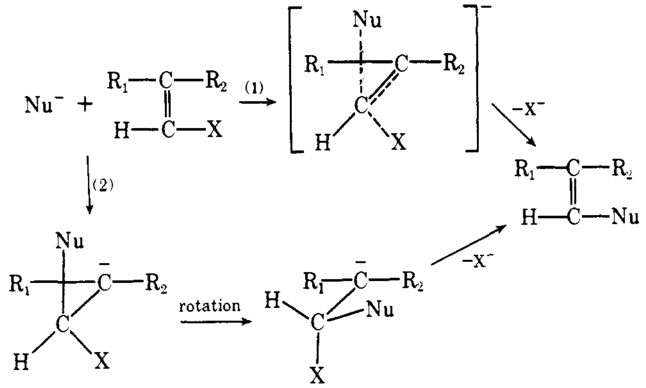


(a)-ethyl-**2**

(a)-ethyl-**12**

Two general mechanisms have been proposed to account for the replacement of vinyl halides with anionic groups.[7] In pathway (1), termed the "direct substitution mechanism", bond breaking and bond forming take place simultaneously. Pathway (2), termed an "addition-elimination reaction", proceeds via a carbanion. Path (1) proceeds with retention of configuration. Path (2) can proceed with retention only if X$^-$ leaves at a rate faster than C-C bond rotation. With a long-lived carbanion, products would form nonstereospecifically.

The result of this study is consistent with a concerted replacement at the vinyl carbon atom or at any rate with reaction by way of an intermediate whose ring inversion is inhibited during the replacement reaction. The direction of nucleophilic attack at the vinyl carbon presumably occurred from the front side of the double bond (the less hindered axial side of the central boat ring), as the rear side is



blocked by the methyl groups at the 1,8-aryl positions. However, there remain to be delineated the two possible pathways as well as the distinction between retention of configuration at the vinyl carbon atom in a direct displacement step vs. inversion. This distinction would be possible with optically active starting materials, e.g., (*R*)- or (*S*)-(e)-ethyl-**2**, since retention and inversion during replacement would also be accompanied by retention and inversion of configuration, respectively.

A related area of interest is the reaction of vinyl halides with lithium reagents at lower temperatures with regard to the existence of vinylidene carbene.[11]

Experimental Section

Melting points were obtained with a Thomas-Hoover capillary melting point apparatus and are corrected. Infrared (ir) spectra (10% solutions) were obtained with a Perkin-Elmer Model 137 infracord or by Mr. R. L. Thrift and his associates with a Perkin-Elmer Model 521 spectrophotometer. A number of proton magnetic resonance (NMR) spectra (7-20% solutions) were recorded by Mr. R. L. Thrift and his associates with Varian Associates Model A-60-A, 56/60, HA-100, or HR-220 instruments. Reported values are based on Me_4Si as an internal standard. Ultraviolet (uv) spectra were obtained with a Perkin-Elmer Model Coleman 124 spectrophotometer or a Cary Model 14M spectrophotometer. The mass spectra were run on an Atlas CH-4, MAT CH-5,[12] or MAT SM-1B[12] by Mr. J. Wrona and Dr. J. C. Cook and their associates. Elemental analyses were performed by Mr. J. Nemeth and his associates of the University of Illinois Microanalytical Laboratory. All compounds marked with an asterisk had elemental analysis within acceptable limits.

3-Methyl-2-(2-methylbenzyl)-*α*-ethyl-*α*-methylbenzyl Alcohol (5)*. A solution of 16.7 g (0.071 mol) of ketone **4**[5] in 100 ml of dry benzene was added dropwise to a well-stirred solution of ethyllithium (0.145 mol in 120 ml of benzene)[13] in 120 ml of anhydrous ether at 0° under a positive pressure of nitrogen over a period of 45 min. After stirring at 0° for 1 hr, the reaction mixture was quenched by adding dropwise a solution of 6.7 g (0.145 mol) of absolute ethanol in 30 ml of benzene over a period of 10 min. The red color gradually faded and the mixture was stirred at 0° for 0.5 hr. After a fresh solution of ethyllithium (0.16 mol in 140 ml of benzene) was added dropwise over a period of 45 min, the reaction mixture was stirred at 0° for 1 hr and quenched with a cold solution of ammonium chloride. After work up there remained an oily material which still contained 30% ketone, as analyzed by NMR. In order to get a complete conversion of alcohol, the above procedure was repeated twice. There was obtained 18.75 g (100% yield) of analytically pure oily product **5**: ir (CCl_4) 3610 cm^{-1} (OH): NMR (CCl_4) δ 0.73 (t, 3, J = 7 Hz, CH_3), 1.78 (q, 2, J = 7 Hz, CH_2), 1.39 (s, 1, OH), 1.45 (s, 3, CH_3), 2.06 (s, 3, CH_3), 2.35 (s, 3, CH_3), 4.22 (s, 2, CH_2), 6.15-6.50 (m, 1, aromatic), and 6.67-7.20 (m, 6, aromatic).

10-Ethyl-1,8,10-trimethyl-9,10-dihydroanthracene (6)*. A mixture of 18.5 g (0.069 mol) of the alcohol **5** and 282 g of PPA were stirred at room temperature for 0.5 hr and then heated at 120° for 6 hr. The brown mixture was decomposed with ice water and extracted thoroughly with 1300 ml of ether. After work-up, there remained 16.5 g (95.6%) of solid, mp 74-79°. Chromatography on 500 g of alumina, elution with 1.2 l. of pentane, and crystallization from ether-methanol gave 14.0 g (81%) of the desired product, mp 84.5-85.5°. Several recrystallizations from ether-methanol gave an analytical sample of **6**: mp 85.5-86.5°; ir (CCl_4) 1381 and 715 cm^{-1}; uv (cyclohexane) λ_{max} 263 (ϵ 439) and $\lambda_{shoulder}$ 269.5 nm (ϵ 347); NMR (CCl_4) δ 0.43 (t, 3, J = 7 Hz, CH_3), 1.98 (q, 2, J = 7 Hz, CH_2) 1.60 (s, 3, CH_3), 2.37 (s, 6, CH_3), 3.76 (s, 2, CH_2), and 6.8-7.3 (m, 6, aromatic); mass spectrum (70 eV) M^+ at *m/e* 250 ($C_{19}H_{22}$).

***cis*- and *trans*-10-Ethyl-9-hydroxymethyl-1,8,10-trimethyl-9,10-dihydroanthracene (7 and 8).** A solution of dihydroanthracene **6** (5.0 g, 0.02 mol) in 75 ml of anhydrous THF (freshly distilled over NaH) was prepared under a positive flow of nitrogen. Into the above solution, cooled in an ice bath, was added 15.5 ml (1.44 *N*,[13] 0.022 mol) of *n*-butyllithium in hexane over a period of 10 min. The solution assumed a deep red color after ca. 1 ml of *n*-butyllithium reagent was added. After stirring at 0° for 0.5 hr, powdered paraformaldehyde (1.35 g, 0.045 mol) was added. The red color disappeared gradually in a period of 10 min. Then the solution was warmed up to room temperature and stirred for 1 hr. After quenching with a saturated solution of sodium chloride, extraction thoroughly with ether, drying over $MgSO_4$, and evaporation of solvent, there remained 5.55 g (100%) of white solid, mp 100-122°. Examination of the NMR spectrum indicated the presence of a mixture of the two isomers **7** and **8** (1:1), with the one having an axial ethyl group (**7**) in slight excess. The above mixture (possibly with a trace of starting material) was subjected to the next synthetic step without purification.

Cis Alcohol 7 (ethyl and hydroxymethyl *cis*)*. Recrystallizations from hexane-ether gave **7**: mp 158-159°; ir ($CHCl_3$) 3600 (OH), 1465, 1382, and 1040 cm^{-1}; NMR ($CDCl_3$) δ 0.15 (t, 3, J = 7 Hz, CH_3), 1.27 (broad, 1. OH, disappeared after shaking with D_2O), 1.66 (s, 3, CH_3), 2.21 (q, 2, J = 7 Hz, CH_2), 2.50 (s, 6, CH_3), 3.58 (broad, sharpened to a doublet after shaking with D_2O, 2, J = 6 Hz, CH_2), 4.65 (t, 1, J = 6 Hz, CH), and 6.9-7.4 (m, 6, aromatic); uv ($CHCl_3$) λ_{max} 264 (ϵ 464) and $\lambda_{shoulder}$ 270 nm (ϵ 362).

Trans Alcohol 8 (ethyl and hydroxymethyl *trans*) was isolated as follows. A mixture of two isomers (9.6 g) was chromatographed onto 400 g of alumina and eluted first with 1350 ml of pentane-ether (7:1) to give 0.5 g of starting material, then further eluted with 600 ml of pentane-ether (5:1) to give 0.5 g of solid enriched with the desired isomer (**6**). The solid was redissolved in ether and the solvent was evaporated slowly to dryness to give some large colorless crystals which were picked out by hand. Further recrystallization from ether-hexane gave the desired isomer, **8**: mp 102.5-104°; ir ($CHCl_3$) 3600 (OH), 1465, 1385, 1040, and 910 cm^{-1}; NMR ($CDCl_3$) δ 0.70 (t, 3, J = 7 Hz, CH_3), 1.35 (s, 1, OH, disappeared after shaking with D_2O), 1.51 (s, 3, CH_3), 1.75 (q, 2, J = 7 Hz, CH_2), 2.38 (s, 6, CH_3), 3.52 (d, 2, J = 7 Hz, CH_2), 4.53 (t, 1, J = 7 Hz, CH), and 6.8-7.3 (m, 6, aromatic): uv ($CHCl_3$) λ_{max} 263.5 (ϵ 426) and $\lambda_{shoulder}$ 269 nm (ϵ 348).

Tosylates (9 and 10)* of *cis*- and *trans*-10-Ethyl-9-hydroxymethyl-1,8,10-trimethyl-9,10-dihydroanthracene. To an ice-salt-cooled solution of the above crude alcohols **7** and **8** (5.55 g, 0.02 mole) in 35 ml of dry pyridine was added portionwise 4.2 g (0.023 mol) of tosyl chloride (Eastman) over a period of 10 min with magnetic stirring. The mixture was stirred until solution was complete, and then placed in a refrigerator for 24 hr (−6°). The solution was diluted with ice and 20% hydrochloric acid. The ester was collected on a Buchner funnel, washed thoroughly with water, and sucked as dry as possible. There was obtained 7.4 g of solid which, after recrystallization once from ether-pentane, gave 5.15 g of tosylate, mp 150-153°. After evaporation of the solvent from the mother liquor portion, the residue (2 g) was redissolved in 16 ml of pyridine at 0° and 2 g of tosyl chloride was added. The solution was kept at room temperature for 24 hr. After work-up and recrystallization from ether-pentane, there was obtained another 1.2 g of the desired tosylate mixture, mp 150-152.5°. The total yield from **6** is 74%. An analytical sample, mp 154-155.5°, was prepared by recrystallization three times from ether-pentane and was shown by the NMR spectrum to be a mixture of **9** and **10** (1:1).

Tosylate (9)* of *cis*-10-Ethyl-9-hydroxymethyl-1,8,10-trimethyl-9,10-dihydroanthracene. To a solution of alcohol **7** (0.4663 g, 1.665 mmol) in 5 ml of pyridine, there was added portionwise 0.475 g (2.5 mmol) of tosyl chloride. The solution was kept at room temperature for 48 hr. After the usual work up, there was obtained 0.656 g (90.5%) of the desired product, mp 151-158°. One recrystallization from ether-pentane gave an analytical sample of **9**: mp 163.0-164.0°; ir (KBr) 1600, 1460, 1385, 1170, 1100, 960, 922, 880, 831, 790, and 760 cm^{-1}; uv (chloroform) λ_{max} 263 (ϵ 687), 273 nm (ϵ 513), $\lambda_{shoulder}$ 267 (ϵ 659); NMR ($CDCl_3$) δ 0.09 (t, 3, J = Hz), 1.34 (s, 2.5), 2.14 (d, J = 7 Hz) δ 2.33 (s, 5.0), 2.40 (s, 6.1), 3.77 (d, 2.1, J = 6 Hz), 4.39 (t, 0.7, J = 6 Hz), and δ 6.8-7.4 (m, 10.3); mass spectrum (70 eV) M^+ at *m/e* 434 ($C_{27}H_{30}O_3S$).

Tosylate (10)* of *trans*-10-Ethyl-9-hydroxymethyl-1,8,10-trimethyl-9,10-dihydroanthracene. To a solution of alcohol **8** (64 mg, 0.23 mmol) in 0.7 ml of pyridine, there was added 76 mg (0.4 mmol) of tosyl chloride. The solution was kept at room temperature for 48 hr. After the usual work-up, there was obtained 83 mg (83.5%) of the desired product, mp 153-155°. One recrystallization from ether-pentane gave an analytical sample, mp 155.5-156.5°: ir (KBr) 1600, 1482, 1465, 1389, 1380, 1365, 1195, 1180, 1100, 986, 962, 924, 900, 885, 832, 820, 795, 777, and 760 cm^{-1}; uv ($CHCl_3$) λ_{max} 262.5 (ϵ 1.07 × 10^3), $\lambda_{shoulder}$ 264.5 (ϵ 1.04 × 10^3), $\lambda_{shoulder}$ 267.5 (ϵ 1.01 × 10^3), and λ_{max} 273.5 nm (ϵ 795); NMR ($CDCl_3$) 0.48 (t, 2.9, J = 7 Hz), 1.44 (s), 1.46 (d, 5.0, J = 7 Hz), 2.21 (s, 2.9), 2.30 (s, 6.0), 3.77 (d, 1.8, J = 7 Hz), and 6.8-7.4 (m, 9.7); mass spectrum (70 eV) M^+ at *m/e* 434 ($C_{27}H_{30}O_3S$).

9-Methylene-10-ethyl-1,8,10-trimethyl-9,10-dihydroanthracene (11)*. A solution of tosylates **9** and **10** (4.4 g, 0.01 mol) in 60 ml of glyme (freshly distilled over sodium hydride) was prepared at 60° with magnetic stirring. There was added 2.25 g (0.02 mol) of potassium *tert*-butoxide. The heterogeneous mixture was stirred for 1 hr under a positive nitrogen flow. Then it was quenched with a saturated solution of sodium chloride and extracted thoroughly with pentane. After work up, there remained 2.65 g (100%) of white solid, mp 111-114°. Recrystallization thrice from methanol gave an analytical sample of **11**: mp 116-117°; ir spectrum (CCl_4) 1628, 1468, 1385, and 912 cm^{-1}; NMR ($CDCl_3$) δ 0.65 (t, 2.8), 1.81 (q, broad) 1.63 (s, somewhat broad, 4.6), 2.51 (s, 6.6), 5.51 (s, 1.9), and 6.9-7.3 (m, 6.0); uv (cyclohexane) λ_{max} 253.5 nm (ϵ 1.26 × 10^4); mass spectrum (70 eV) M^+ at *m/e* 262 ($C_{20}H_{22}$).

9-(Bromomethylene)-10-ethyl-1,8,10-trimethyl-9,10-dihydroanthracene ((a)-Ethyl- and (e)-Ethyl-2)*. To a stirred solution of the methylene compound **11** (2.60 g, 0.01 mol), in 30 ml of carbon tetrachloride, was added bromine (1.6 g, 0.01 mol) as a solution in 6 ml of carbon tetrachloride over an 8-min period. The solution was then stirred at room temperature for 9 hr and heated under reflux for 3 hr. Evaporation of solvent under reduced pressure gave a tan residue. Chromatography on 100 g of alumina and elution with 180 ml of hexane-ether (4:1) gave 3.40 g (100%) of a mixture of (a)-ethyl- and (e)-ethyl-**2**, mp 67-77°, whose NMR spectrum showed (relative areas of vinyl proton absorptions at δ 6.43 and 6.33) the composition to be 70% (a)-ethyl- and 30% (e)-ethyl-**2**. One recrystallization from methanol gave an analytical sample of **2**: mp 89-97°; NMR spectrum ($CDCl_3$) δ 0.69 (t), 0.76 (t, 2.9), 1.33 (s, 1.0), 1.70 (q), 1.71 (s, 3.5), 2.40 (q), 2.48 (s), 2.53 (s), 2.55 (s, 6.0), 6.33 (s, 0.2), 6.43 (s, 0.7), and 6.9-7.3 (m, 5.8).

9-(Bromomethylene)-10-ethyl-1,8,10-trimethyl-9,10-dihydroanthracene ((a)-Ethyl- and (e)-Ethyl-2)*. (a)-Ethyl-**2**, mp 93-94°, was separated by recrystallization of the mixture (vide supra) from methanol. Additional recrystallization failed to change the melting point of (a)-ethyl **2**: uv (cyclohexane) λ_{max} 257.5 nm (ϵ 1.54 × 10^4); ir (CCl_4) 1600, 1570, 1565, 1385, 1380, 1085, 1045, and 695 cm^{-1}; NMR ($CDCl_3$) δ 0.69 (t, 2.9, J = 7 Hz), 1.70 (q, J = 7 Hz), 1.71 (s, 4.8), 2.48-2.53 (s, 6.1), 6.43 (s, 0.9), and 6.9-7.2 (m, 6.2); mass spectrum (70 eV) M^+ at *m/e* 341.9 and 339.9 ($C_{20}H_{21}Br$).

(e)-Ethyl-**2***, mp 99-100°, was separated by chromatography on a column (4 ft, 12 mm o.d.) of alumina (70 g, Bio-Rad Neutral Alumina Ag 7, 100-200 mesh) impregnated with 25% silver nitrate.[14] A mixture of (a)-ethyl- and (e)-ethyl-**2** (1:1) (75 mg), obtained from the mother liquors remaining from crystallization of (a)-ethyl-**2** by repeated crystallization from methanol (which failed to give complete separation), was transferred into the column as a solution in 2 ml of hexane. Elution with 425 ml of hexane at a rate of 17 ml/12 min produced no olefin; further elution with 300 ml of hexane gave ca. 30 mg of the desired isomer: NMR ($CDCl_3$) (s) δ 0.76 (t, 3.0), 1.33 (s, 3.3), 2.40 (q), 2.48 (s) 2.55 (s, 7.8), 6.33 (s, 1.0), and 6.9-7.25 (m, 5.9); uv (cyclohexane) λ_{max} (256.5 nm (ϵ 1.78 × 10^4); ir (CCl_4) 1600, 1580, 1465, 1382, 1082, and 680 cm^{-1}; mass spectrum (70 eV) M^+ at *m/e* 342.0 and 340.0 ($C_{20}H_{21}Br$). It was shown by NMR spectrum to be free from appreciable amounts of (a)-ethyl isomer.

9-(Diphenylphosphoromethylene)-10-ethyl-1,8,10-trimethyl-9,10-dihydroanthracene (12). The method used was a modification of that reported by Aguiar et al.[15] A solution of lithium diphenylphosphide was prepared from 2.0 g (7.5 mmol) of triphenylphosphine and 0.1 g (0.015 g-atom) of lithium in 16.0 ml of tetrahydrofuran (Insta-Start-THF, Baker). Into 5.0 ml (2.5 mmol) of the above red solution was added, dropwise with stirring, a solution of 0.35 g (1 mmol) of (a)-ethyl-**2** in 3 ml of tetrahydrofuran. After stirring at room temperature under a positive pressure of nitrogen for 17.25 hr, the red reaction mixture was quenched with water and extracted with ether. Evaporation of the solvent gave 0.68 g of an oily material. A TLC test developed in hexane indicated the desired product **2** has an R_f value of 0.17 (for **2**: R_f = 0.51). Separation of the reaction mixture by preparative TLC (silica gel) developed four times in hexane gave 0.059 g (13%) of the crude product **2**. Further purification with preparative TLC recovered 28 mg (6%) of pure solid: mp 128-129° (corrected melting point taken on hot-stage); ir (KBr) 1480, 1460, 1435, 1375, 1090, 1030, 800, 775, 750, 740, 725, and 695 cm^{-1}; NMR ($CDCl_3$) δ 1.00 (t, 3, J = 7 Hz, CH_3), 1.40 (q, 2, J = 7 Hz, CH_2), 1.67 (s, 3, CH_3), 2.50 (s, 3, CH_3), 2.66 (s, 3, CH_3), 6.45 (d, 1, =CH, $J_{H,P}$ = 5 Hz), and 7.00-8.0 (m, 16, aromatic). Peak matching at high resolution identified the molecular ion as $C_{32}H_{31}P$ (calcd 446.2163; found, 446.2109).

Measurement of the Rates of Interconversion of (a)-Ethyl and (e)-Ethyl Isomers of 9-(Bromomethylene)-10-ethyl-1,8,10-trimethyl-9,10-dihydroanthracene (2). Rate measurements were carried out with sample tubes prepared as for the NMR studies and sealed under vacuum. Solutions were 16% w/v in tetrachloroethylene (bp 120°) with tetramethylsilane as an internal standard. The tubes were heated in a constant temperature bath (107.0 ± 0.5°), cooled rapidly to 0° by quickly immersing in ice water after the specified time, and stored at ice temperature before the spectra were measured. Although the rate of isomerization at probe temperature (41°) is negligible, care was taken to keep the measurement time short. The NMR spectrum was measured with a Varian A56/60 spectrometer with a 50-100 sweep width and a sweep time of 250 sec. Several integrations were performed for each spectrum at each time and at the same spectrum amplitude, rf field, and spinning rate. Isomerizations with a mixture of two isomers were followed by measuring the relative intensity of the vinyl proton signals at δ 6.43 and 6.33 and the methyl absorptions of the (a)-ethyl and (e)-ethyl isomers at δ 1.71 and 1.33, respectively. 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. The infinity point was determined at very long reaction time (ca. 3 days). The rate constants and standard deviations were calculated assuming the relationship:[16]

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

where A_0 = initial concentration of (e)-ethyl or (a)-ethyl isomer, A = concentration of (e)-ethyl or (a)-ethyl isomer at time t, A_e = equilibrium concentration of (e)-ethyl or (a)-ethyl isomer, and $k_{obsd} = k_1 + k_{-1}$.

References and Notes

(1) Taken from the Ph.D. Thesis of P.-T. Leung, University of Illinois, 1972, available from University Microfilms, Ann Arbor, Mich.

(2) We are very much indebted to the National Science Foundation for a grant partially supporting this work.

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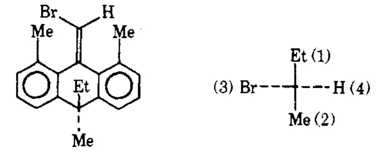
(8) The structural assignments to (a)-ethyl and (e)-ethyl isomers are based on the NMR observations. The triplet signal of the axial ethyl group in the assigned cis isomers (**7** and **9**) is 0.52-0.55 ppm upfield from that of the equatorial ethyl group in trans isomers (**8** and **10**). The preferred

axial configuration of the 9-substituent is inferred by the NOE studies of the corresponding 10,10-dimethyl compounds.[5]

(9) The configuration nomenclature of **2** resembles that of alkylidenecyclohexane.[10] The enantiomer shown is (*R*)-(a)-ethyl-**2** whose substituents 1, 2, 3, and 4 describe a right-handed screw.



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Stable Carbocations. CXCI.[1] Carbon-13 Nuclear Magnetic Resonance Spectroscopic Study of 7-Norbornenyl Cations Indicating Their "Nonclassical" Carbonium Ion Nature

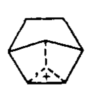
George A. Olah* and Gao Liang

Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. *Received January 6, 1975*

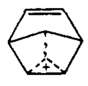
Abstract: A series of secondary and tertiary 7-norbornenyl cations were studied under stable ion conditions by carbon-13 NMR spectroscopy. The bridging carbon (C_7) in these ions is found substantially shielded. Substituents at C_7 do not greatly affect the carbon chemical shifts of the ions, except for C_7 itself which experiences a deshielding effect, by the attached substituent, indicating strong charge delocalization between C_2, C_3, and C_7. The carbon shift data and the characteristic and unusually large J_{C-H} coupling observed at C_7 in the parent 7-norbornenyl cation **1**-H (218 Hz) as well as at C_2 and C_3 in both secondary and tertiary ions (>190 Hz) suggest the nonclassical carbonium ion nature of these ions.

The structure of the 7-norbornenyl cations has been the subject of much interest[3] and controversy.[4] The high rate (10^{11} times that of related 7-norbornyl systems) and overall retention of configuration observed in the solvolysis of *anti*-7-norbornenyl *p*-toluenesulfonate were accounted for on the basis of a nonclassical 7-norbornenyl cation **1**-H[5] intermediate. Extensive solvolytic[6-10] and NMR spectroscopic studies[11] further confirmed the "bishomocyclopropenyl"[5a] type structure **1**-H. Delocalization and strain energy in the 7-norbornenyl cation also have been considered theoretically in agreement with the experimental results, favoring the nonclassical structure of the ion.[12]

Interested in the nature of carbocations,[2] we have previously reported both proton and carbon-13 NMR spectroscopic studies showing that the structure of the 7-norbornenyl cation **1** and the 7-norbornadienyl cation **2**, as well as that of the parent 2-norbornyl cation **3**, are those of typical nonclassical carbonium ions.[13]



1-H



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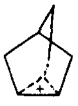

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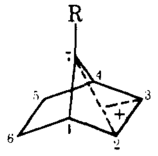
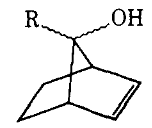
We now report our detailed ^{13}C NMR study of both secondary and tertiary 7-norbornenyl cations prepared under stable ion conditions to evaluate in full the structure of these ions.

Results and Discussion

Preparation of 7-Norbornenyl Cations. 7-Norbornenyl cations 1-R[14] (R = H, CH_3, CH_2CH_3, C_6H_5, and OH) were prepared by slow addition solutions of appropriate alcohols **4**-R[15] or ketone **5**[15] in SO_2ClF to FSO_3H-SO_2ClF at Dry-Ice-acetone temperature (ca. −78°). The 1,2,3,4-tetrachloro-7-methoxy-7-norbornenyl cation (**6**) was prepared from the corresponding 7,7-dimethoxy-2-norbornene (**7**) in a similar way.[16] Ions were stable under the reaction conditions, and their ^1H NMR spectra were identical with those previously reported.[11,14]



1-R



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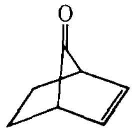

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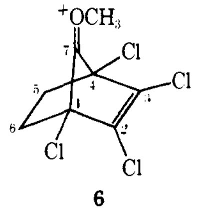

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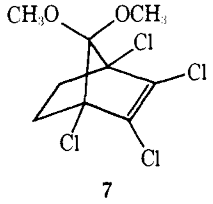

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Carbon-13 NMR Spectra. The proton-coupled FT ^{13}C NMR spectra and assignments of the 7-norbornenyl cations 1-R in FSO_3H-SO_2ClF solutions at −75° are summarized in Table I. Carbon shifts were obtained from their proton noise-decoupled ^{13}C NMR spectra. Multiplicities and coupling constants were obtained from the proton coupled ^{13}C NMR spectra. Typical are the spectra shown in Figure 1.