just prior to use, quickly weighed, and transferred directly to the nitrogen flushed reaction flask. Iodobenzene was distilled, and the colorless liquid stored in a foil wrapped brown bottle. The ketones were dried over molecular sieves and distilled through a Vigreux column. A sizeable forerun was discarded, and the main fraction distilled again. Purity was checked by GLC. The nitrogen was purified by passage through two Altech Oxytraps connected in series. The second trap was an indicating type.

GLC Analysis. GLC analysis of products was carried out on either a Varian 3760 or a Varian 400D flame-ionization instrument. A $^1/_8$ in. × 6 ft 5% Carbowax 20M on Chromsorb WHP or a $^1/_8$ in. × 4 ft 5% OV-101 column was used. Yields of products were determined by use of internal standards. In all cases, the area ratios were corrected for molar response determined from standard solutions of the products and the internal standard. Preparative GLC was carried out on an Aerograph A-90P instrument using a $^1/_4$ in. × 6 ft SE-30 column.

Reaction of Iodobenzene and Ketone Enolate in Me_2SO. General Procedure. Me_2SO (25 mL) was transferred by syringe into a N_2-purged 100-mL 3-neck flask fitted with two stoppers and a closed-end 12-mm tube with a 60° bend. The flask and tube were wrapped with black opaque tape. Freshly sublimed potassium *tert*-butoxide (1.22 g, 0.010 mol) was added, and the tube was charged with 1.00 g (0.010 mol) of pinacolone and 0.51 g (0.0025 mol) of iodobenzene. Stirring was employed to dissolve the base, and the tube containing the ketone and PhI was cooled with a dry ice–acetone bath. The system was evacuated and filled with nitrogen. This procedure was repeated 3–8 times. After the freeze–pump–thaw cycles were complete, the reactants were added to the flask by rotation of the bent tube. The solution was stirred and the flask placed in a 25 °C temperature bath. After 1 h, 6 N sulfuric acid (1.85 mL) was added. The solution was diluted with 50 mL of water and extracted 3× with ether. The combined ether extract was washed with water (3×) and dried ($MgSO_4$), and an internal standard (phenylacetone) added for GLC analysis. The aqueous layers were combined and an eliquot was used for iodide analysis. For each ketone studied, the product from at least one reaction was isolated by preparative GLC or by column chromatography on silica gel, and the IR and NMR spectra were compared with those of authentic compounds. Four identical experiments carried out as above with iodobenzene and pinacolone gave yields (I^-) of 67.2%, 60.0%, 66.5%, and 68.1%.

(17) (a) Matthews, W. S.; Bares, J. E.; Bartmess, J. E.; Bordwell, F. G.; Cornforth, F. J.; Drucker, G. E.; Margolin, Z.; McCallum, R. J.; McCollum, G. J.; Vanier, N. R. *J. Am. Chem. Soc.* **1975**, *97*, 7006. (b) Bordwell, F. G., private communication.

Competition Experiments. Typical Procedure. The competition experiments were carried out as described above except that equimolar amounts of two ketones were used; these were added by syringe and allowed to stir for several minutes prior to addition of the iodobenzene. In a typical experiment, acetone (0.29 g, 5.0 mmol) and pinacolone (0.50 g, 5.0 mmol) were added by syringe to 1.22 g (10.0 mmol) of potassium *tert*-butoxide in 25 mL of Me_2SO. After the pump cycles, iodobenzene (0.50 g, 2.5 mmol) was added. The organic products were analyzed by GLC. In one experiment, both ketones and the iodobenzene were added together. The results were the same as when the ketones were added separately.

Kinetic experiments were carried out as above except that aliquots were removed by syringe under a positive pressure of nitrogen, quenched with acid, and titrated for iodide ion.

Oxygen sensitivity was probed by injecting oxygen gas by syringe into the purged vessel, stirring for 15–20 min, and then adding reactants as described. Experiments with atmospheres containing 5, 10, 50, 100, and 1000 ppm oxygen were carried out as above. At these concentrations, there was little if any effect on the amount of reaction during 60 min.

Calculation of Relative Reactivities. The relative reactivities (Table II) from competition experiments were calculated from the equation $k_{R_1}/k_{R_2} = 1n\,[(R_1)_0/(R_1)_t]/1n\,[(R_2)_0/(R_2)_t]$ where R_0 and R_t are the initial and final enolate ion concentrations, respectively.[18]

Reaction Products. The products from these reactions have been previously reported from similar photochemical processes in Me_2SO[19] or NH_3.[20] Samples of 2-phenylcyclohexanone,[21] 3-phenyl-2-butonone,[22] and 2-phenyl-3-pentanone[23] used for GLC analysis were prepared by standard literature methods.

Acknowledgment. This research was supported by Research Corporation, an equipment grant from the National Science Foundation, and Ripon College faculty development funds.

(18) Bunnett, J. F. In "Investigation of Rates and Mechanisms of Reactions", 3rd ed.; Lewis, E. S., Ed.; Wiley-Interscience: New York, 1974; Part I, p 159.
(19) Scamehorn, R. G.; Bunnett, J. F. *J. Org. Chem.* **1977**, *42*, 1457.
(20) Bunnett, J. F.; Sundberg, J. E. *Chem. Pharm. Bull.* **1975**, *23*, 2620; *J Org. Chem.* **1976**, *42*, 1702.
(21) Newman, M. S.; Farbman, M. O. *J. Am. Chem. Soc.* **1944**, *66*, 1550.
(22) Sheirz, E. R. *Chem. Abstr.* **1954**, *48*, 1438.
(23) Leake, W. W.; Levine, R. *Chem. Ind. (London)* **1955**, 1160.

Reduction and Thermal Rearrangement of 9-Methylene-10-ethyl-10-phenyl-9,10-dihydroanthracene

H. M. Walborsky* and T. J. Bohnert

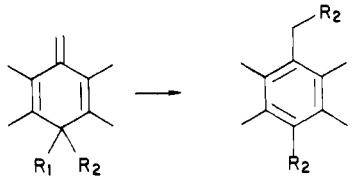
Department of Chemistry, Florida State University, Tallahassee, Florida 32306

Received June 15, 1984

The thermolysis of 9-methylene-10-ethyl-10-phenyl-9,10-dihydroanthracene (**2**) results in a 1,5-ethyl rearrangement to yield 9-propyl-10-phenylanthracene. The rearrangement is shown to occur by an intermolecular radical process. Thermolysis of **2** in thiophenol surpressed the rearrangement reaction and yielded instead the reduced product, a mixture of *cis*- and *trans*-9-methyl-10-ethyl-10-phenyl-9,10-dihydroanthracene (**8**). This unexpected result is discussed. The addition of hydrogen and tri-*n*-butyltin hydride to **2** is shown to be stereoselective whereas the addition of thiophenol is not. The geometric relationships of various substituents at C-9 and C-10 in 9,9,10-trisubstituted-9,10-dihydroanthracenes have been established.

The semibenzene rearrangement refers to the thermal rearrangement of cross conjugated methylenecyclohexadienes such as **1** to give aromatic compounds. This type of rearrangement was first reported by Auwers at the

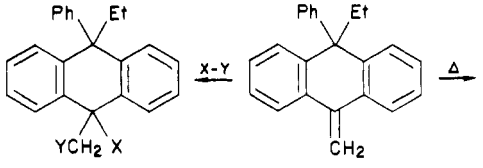
0022-3263/84/1949-4883$01.50/0



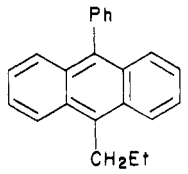
R_1 = CH_3; R_2 = $CHCl_2$

turn of the century.[1] It was also shown to proceed in the dihydronaphthalene series by Fuson.[2] Newman and Layton,[3] as well as Bird and Cookson[4] and Hart and DeVrieze[5] provided kinetic and chemical evidence that the reaction proceeded by a free radical chain mechanism.

This paper will concern itself not only with the thermal rearrangement of 9-methylene-10-ethyl-10-phenyl-9,10-dihydroanthracene (**2**) to yield the product of a semibenzene rearrangement **3** but also with the stereochemistry of the addition of a number of reagents to **2** to yield **4**.



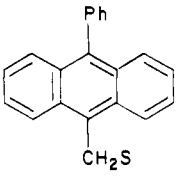
4 **2**



3

Thermal Rearrangement. It was of interest to ascertain whether **2**, which we have previously prepared,[6] would undergo a semibenzene type of rearrangement and if it did, to determine whether the rearrangement involved a radical chain process or was concerted. In a formal sense, the semibenzene rearrangement can be viewed as either a 1,5-migration or its equivalent, two 1,3-migrations, of the migrating group. The Woodward–Hoffman[7] sigmatropic rearrangements are unlikely to occur in the semibenzene type of rearrangements since 1,3-migrations are sterically not feasible and a 1,5-sigmatropic rearrangement is also not possible in this system since **2** does not contain the necessary all-cis polyolefin framework. Hence a concerted reaction for the semibenzene rearrangement is unlikely and the existing evidence[4,5] is in support of this conclusion as are our results on the thermolysis of **2**.

The thermolysis of **2** in triglyme at 200 °C for 60 h gave a 43% yield of 9-propyl-10-phenylanthracene (**3**) which is the product resulting from a 1,5-ethyl rearrangement. A 2% yield of 9-methyl-10-phenylanthracene (**5**) was also observed as was a 40% yield of **7**, a product resulting from a reaction with triglyme solvent (S–H). These observations are consistent with the radical chain mechanism postulated for the semibenzene rearrangement by Hart,[5] Newman,[3] and Bird and Cookson.[4] According to this mechanism, ethane should also be produced in the thermolysis of **2** and, indeed, ethane gas was trapped and identified by GC with a poropak Q column. However, no dimerization of the



S = $CH_3(-O-\underset{|}{C}HCH_2)_3OCH_3$

7

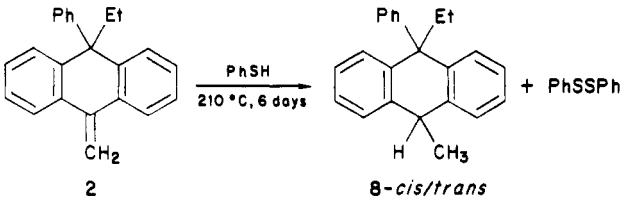
10-phenyl-9-anthracenylcarbinyl radical was observed.[8]

If the reaction is carried out in a solvent (SH) which produces a less reactive intermediate radical (S· = cumyl) one should observe a decrease in the yield of product resulting from solvent radical addition to the starting olefin **2**. When **2** was thermolyzed in cumene the 1,5-ethyl rearrangement product **3** was the major product (59%) of the reaction. The use of cumene also significantly increased the yield of **5** (27%) and decreased the yield of **7** (S = cumyl) to 10%.

Further evidence that the rearrangement was occurring though a radical chain process was obtained by the addition of a good radical trap, 1,1-diphenylethylene, to the reaction mixture. The addition of a radical trap to the reaction mixture should trap more of the ethyl radicals and result in a decrease in the yield of 9-propyl-10-phenylanthracene (**3**) and an increase in the yield of 9-methyl-10-phenylanthracene (**5**). If a radical chain mechanism is involved, the ratio of **3** to **5** which was 1:0.45 in cumene, should decrease when the reaction is carried out in the presence of the radical trap.

Heating a mixture of **2** in cumene at 240 °C for 72 h with a 50-fold excess of 1,1-diphenylethylene produced **3** and **5** in a ratio of 1:14. This ratio should be compared to the observed ratio of 1:0.45 when the thermolysis is carried out in cumene alone. A 31-fold decrease in the rearrangement product results when a reactive olefin is used as a radical trap, and therefore provides further evidence in support of a radical mechanism.

Before concluding the study of the 1,5-ethyl rearrangement, an attempt was made to trap all of the ethyl radicals with thiophenol, which is known to be an exceptionally effective radical trap.[9] When **2** was heated with thiophenol at 210 °C for 6 days a mixture of *cis*- and *trans*-9-methyl-10-ethyl-10-phenyl-9,10-dihydroanthracene (**8**) was obtained in better than a 80% yield along with diphenyl disulfide.



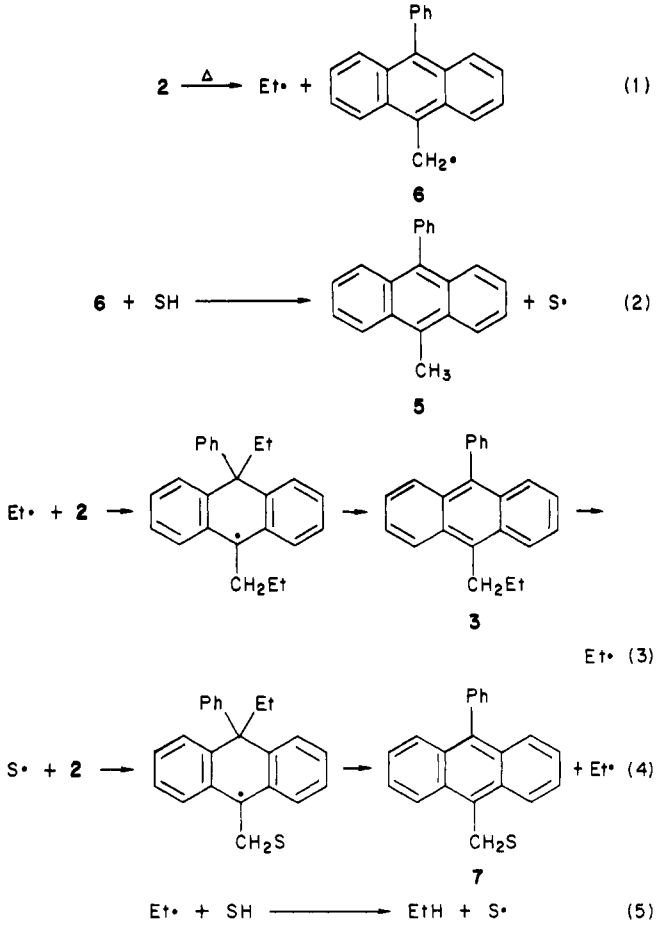
2 **8**-*cis*/*trans*

This apparent olefin reduction reaction with thiophenol was an unexpected and a previously unobserved result. A similar but not identical mixture of products was independently synthesized by catalytic reduction of **2** over platinum at room temperature and atmospheric pressure. Since a mixture of reduction products is obtained in both of the above reactions it became necessary to identify each

(1) Auwers, K.; Keil, G. *Chem. Ber.* **1903**, *36*, 1861. Auwers, K. *Leibigs Ann. Chem.* **1907**, *352*, 219.
(2) Fuson, R. C.; Miller, T. G. *J. Org. Chem.* **1952**, *17*, 316.
(3) Newman, M. S.; Layton, R. M. *J. Org. Chem.* **1968**, *33*, 2338.
(4) Bird, C. W.; Cookson, R. C. *J. Org. Chem.* **1959**, *24*, 441.
(5) Hart, H.; DeVrieze, J. D. *Tetrahedron Lett.* **1968**, 4259.
(6) Walborsky, H. M.; Bohnert, T. *J. Org. Chem.* **1968**, *33*, 3934.
(7) Woodward, R. B.; Hoffman, R. *J. Am. Chem. Soc.* **1965**, *87*, 2511.

(8) The (9-phenylanthracen-10-yl)carbinyl radical (**6**) may not be a planar π radical but rather a σ radical due to the steric interaction between the carbinyl hydrogen atoms and the perihydrogens of the anthracene. Only if the radical is a π radical would you expect the radical to be long-lived enough for dimerization.
(9) Hammond, G. S.; Sen, J. N.; Boozer, C. E. *J. Am. Chem. Soc.* **1955**, *77*, 3244.

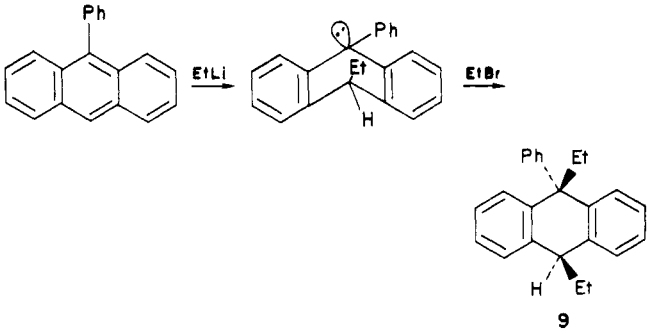
Scheme I. Radical Chain Mechanism for Thermolysis of 2



isomer in order to enable us to determine the stereochemistry of these reductions.

Establishing the Stereochemistry of *cis*- and *trans*-8. Harvey and co-workers[10] have shown that treatment of anthracene with ethyllithium followed by the addition of methyl iodide results in exclusive formation of *cis*-9-ethyl-10-methyldihydroanthracene. The specificity of this reaction has been rationalized by postulating that the ethyl group prefers to occupy the quasi-axial position in the 9,10-dihydroanthracene ring.

Using the procedure of Harvey,[10] ethyllithium was added to 9-phenylanthracene followed by the addition of ethyl bromide to give only one product which, based on the arguments of Harvey, and others[10] is designated *cis*-9,10-diethyl-10-phenyl-9,10-dihydroanthracene (**9**). One might expect the addition of ethyllithium to be regiospecific so as to produce the trityl anion since the pK_a of triphenylmethane is 32.5 as compared to 34.1 for diphenylmethane. Likewise, the pK_a of 9-phenylfluorene is 18.5 as compared to a value of 22.9 for fluorene.

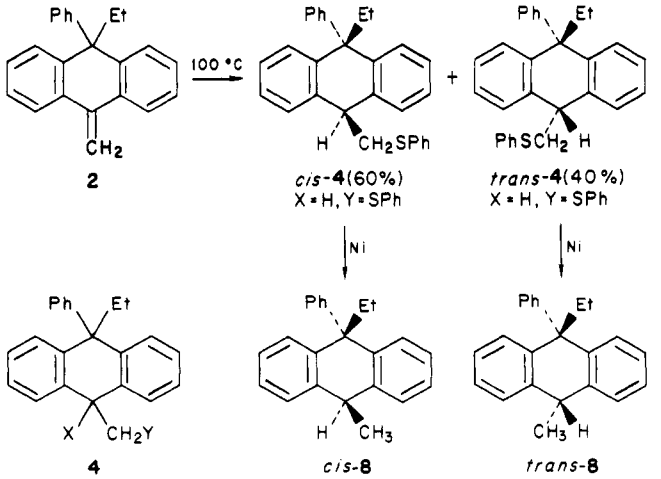


Direct verification of the cis relationship of the ethyl groups in the original sample of *cis*-9,10-diethyl-10-phenyl-9,10-dihydroanthracene (**9**) was obtained by observation of a nuclear Overhauser effect (NOE).

In the case of *cis*-9,10-diethyl-10-phenyl-9,10-dihydroanthracene (**9**) the methylene protons of the ethyl group at C_{10} were irradiated. The intensity of the methylene protons of the ethyl group at C_9 was determined with irradiation of the C_{10} methylene proton and with the irradiating signal offset from the methylene protons at C_{10}. The integrated intensity without irradiation was 224.8 ± 1.1 as compared to the integrated intensity with irradiation of 247.8 ± 7.8 (10% intensity increase). It can only be interpreted that the ethyl groups are cis to one another.

It was now only necessary to relate the configuration 9-methyl-10-ethyl-10-phenyl-9,10-dihydroanthracene (**8**) to 9,10-diethyl-10-phenyl-9,10-dihydroanthracene (**9**). This was accomplished by carrying out, under identical conditions, the hydrogenation of 9-methylene-10-ethyl-10-phenyl-9,10-dihydroanthracene and 9-ethylidene-10-ethyl-10-phenyl-9,10-dihydroanthracene. The isomeric ratio obtained from the reduction of each olefin was identical. The ratios were determined by NMR integration and the minor isomer in the hydrogenation product of 9-ethylidene-10-ethyl-10-phenyl-9,10-dihydroanthracene was shown to be *cis*-9,10-diethyl-10-phenyl-9,10-dihydroanthracene (**9**) by its NMR spectrum.

Reduction Reactions in Thiophenol. The transformation of **2** to **8** by thermolysis in thiophenol at 210 °C was unexpected. When the reaction was carried out at lower temperatures, 163 °C, both the reduced product **8** and 9-(thiophenoxymethyl)-10-ethyl-10-phenyldihydroanthracene (**4**, X = H, Y = SPh) were formed. At 100 °C for 3 h, the only product obtained was a mixture of *cis*- and *trans*-**4** (X = H, Y = SPh) shown by Raney nickel desulfurization to be in a cis–trans ratio of 59:41.



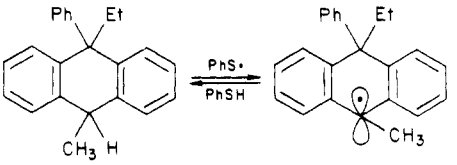
Free radical addition of thiols to olefins is a very facile reaction and the regiospecificity observed for the addition

(10) Harvey, R. G.; Arzadon, L.; Grant, J.; Urberg, K. *J. Am. Chem. Soc.* **1969**, *91*, 4535. For other relevant studies see: Curtin, D. Y.; et al. *J. Org. Chem.* **1969**, *34*, 3093; Panek, E. J. *J. Am. Chem. Soc.* **1974**, *96*, 7959. Leung, P-T.; Curtin, D. Y. *Ibid.* **1975**, *97*, 6799. Daney, M.; Lapouyade, R.; Mary, M.; Bonas-Laurent, H. *J. Organometal. Chem.* **1975**, *92*, 267. Cho, H.; Harvey, R. G.; Rabideau, P. W. *J. Am. Chem. Soc.* **1975**, *97*, 1140. Harvey, R. G.; Rabideau, P. W., et al. *Ibid.* **1975**, *97*, 1145. Bank, S.; Bank, J.; Daney, M.; Labrande, B.; Bonas-Laurent, H. *J. Org. Chem.* **1977**, *42*, 4058. Mallisard, M.; Mazaleyrat, J. P.; Welvart, Z. *J. Am. Chem. Soc.* **1977**, *99*, 6933. Rabideau, P.; Burkholder, E. G. *J. Org. Chem.* **1978**, *43*, 4283. Rabideau, P. W. *Acc. Chem. Res.* **1978**, *11*, 141. Rabideau, P. W. Burkholder, E. G. *J. Org. Chem.* **1979**, *44*, 2354. Daney, M.; Lapouyade, R. *J. Organometal. Chem.* **1979**, *172*, 385. Grant, D. M.; et al. *J. Am. Chem. Soc.* **1981**, *103*, 4817. Rabideau, P. W.; et al. *Tetrahedron Lett.* **1984**, *25*, 31. Rabideau, P. W.; Lipkowitz, K. B.; Nachbar, R. B., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 3119.

of thiophenol to 2 is consistent with a radical addition. No product resulting from an ionic addition was detected.

The mechanism of this reduction is thought to involve initial radical addition of thiophenol to the double bond followed by thermally induced homolysis of the carbon–sulfur bond to give an intermediate carbon radical. The carbon radical produced then reacts with thiophenol to give the product hydrocarbon and a thiophenoxy radical. From kinetic data[11] a similar mechanism was proposed for the quantitative conversion of trityl phenyl sulfide and thiophenol to triphenylmethane and diphenyl disulfide. If this mechanism is operating, reduction of the sulfide to the hydrocarbon should proceed without isomerization of the product. However, when pure *cis*-4 (X = H, Y = SPh) is heated with thiophenol, 8 is formed in a cis–trans ratio of 45:55. However, 8 is also shown to be configurationally unstable under the reaction conditions since a 91:9 ratio of *trans*-8–*cis*-8 isomerized to a ratio of 57:43.

The isomerization of 8 is thought to occur by the abstraction of the 9-H by a thiophenoxy radical since, when the reaction is carried out with thiophenol-*d*, the mass spectrum of 8 indicated 75% incorporation of one deuterium atom and the NMR spectrum showed that the 9-H was the exchanged atom. The source of the thiophenoxy radical is not known for certain but could have arisen from a trace of oxygen. It was subsequently found that isomerization during thermolysis of 4 (X = H, Y = SPh) could be prevented by employing tri-*n*-butyltin hydride, an exceptionally good radical trap, as a solvent.[12] Heating pure *cis*- and *trans*-4 (X = H, Y = SPh) at 163 °C in tri-*n*-butyltin hydride resulted in the formation of isomerically pure *cis*- and *trans*-8, respectively. Diphenyl disulfide was also observed as a product from this reaction.

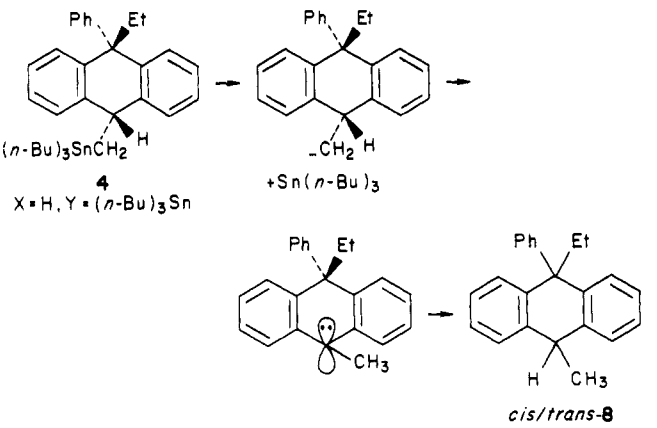


Reductions with Tri-*n*-butyltin Hydride. In a reaction analogous to the reduction of 2 with thiophenol it was also found that tri-*n*-butyltin hydride could reduce 2 to a 37:63 mixture of *cis*- and *trans*-8. Similar reductions of double bonds with organotin hydrides have been reported in the case of α,β-unsaturated nitriles, esters, and ketones.[13]

Heating 2 with tri-*n*-butyltin hydride at 100 °C for 18 h gave 4 (X = H, Y = Sn(*n*-butyl)$_3$) which is a result of the addition of tri-*n*-butyltin hydride to the starting olefin.[14] Upon standing at room temperature with exposure to air, surprisingly, 4 (X = H, Y = Sn(*n*-butyl)$_3$) slowly decomposed to 2 and a derivative of unknown structure.

Treatment of 4 (X = H, Y = Sn(*n*-butyl)$_3$) with trifluoroacetic acid gave 8 with a cis–trans ratio of 7:93. However, heating the same sample of 4 (X = H, Y = Sn(*n*-butyl)$_3$) with tri-*n*-butyltin hydride at 164 °C for 23 h yielded 8 with a cis–trans ratio of 37:63. This isomerization is puzzeling since the thermolysis of *cis*-4 (X = H, Y = SPh) in tri-*n*-butyltin hydride led to *cis*-8 without any isomerization.

The reason for the difference, we believe, is that in the case of 4 (X = H, Y = SPh) the thermolysis involves a homolytic fission of the carbon–sulfur bond. The carbon radical then reacts very rapidly with the excellent radical trap, tri-*n*-butyltin hydride, and therefore no isomerization occurs. On the other hand thermolysis of 4 (X = H, Y = Sn(*n*-butyl)$_3$) involves a heterolytic cleavage of the carbon–tin bond, due to the electropositive nature of the tin, to yield a carbanion and a tin cation. The primary carbanion formed will rearrange to the more stable diphenylcarbinyl type (planar or rapidly inverting tetrahedral) anion which on protonolysis leads to an isomeric mixture of 8.



Experimental Section

All melting points were determined with a Mel-Temp apparatus by using open capillaries. Melting points and boiling points are uncorrected. Infrared spectra were obtained with a Perkin-Elmer Model 237 spectrophotometer; band positions are reported in wave number (cm^{-1}). NMR spectra were obtained on a Varian A-60 spectrometer with tetramethylsilane (Me_4Si) as internal standard. The nuclear Overhauser effect studies were performed with a Bruker HFX-10 instrument with either Me_4Si or chloral as the internal lock and standard. Microanalyses were performed by Beller Laboratories, Göttingen, West Germany.

An F & M Model 500 temperature-programmed gas chromatograph with a thermal conductivity detector and a Bendix Chroma-lab series 2100 temperature-programmed gas chromatograph with a thermal conductivity detector were used in some product analyses. Most analyses were performed with a 6 ft × $^1/_4$ in. copper column packed with 15% SE-52 on acid washed chromosorb W at a column temperature between 200–280 °C.

Brinkman silica gel G was used for all the analytical thin-layer chromatography plates. Brinkman silica gel $PF_{366+254}$ was used for all preparative thin layer plates.

Thermolysis of 9-Methylene-10-ethyl-10-phenyl-9,10-dihydroanthracene (2) in Triglyme. A solution of 0.200 g (0.676 mmol) of 9-methylene-10-ethyl-10-phenyl-9,10-dihydroanthracene[6] (2) and 25 mL of triglyme was placed in a pressure tube, flushed with argon, sealed, and heated at 200 °C for 60 h. A second sample was prepared with the same procedure as for the first sample and was heated at 230 °C for 72 h. In both instances the workup procedure was the same. The crude solution was taken up in ether and washed repeatedly with water to remove the triglyme. The ether solution was dried over anhydrous sodium sulfate and the ether was removed. Product analysis was by GLC on a 6 ft SE-52 column programmed between 250–290 °C. The peaks due to 9-methyl-10-phenylanthracene[15] (5) and 9-propyl-10-phenylanthracene[16] (3) were identified by comparison with the retention time of authentic materials. By preparative GLC the two major products of the reaction were separated and identified. The NMR spectrum of the sample identified as 9-propyl-10-phenylanthracene

(11) Fava, F.; Iticeto, A.; Tasentelli, T. *Ric. Sci.* **1960**, *30*, 1607. Tasentelli, T. *Gazz. Chim. Ital.* **1960**, *90*, 1629, 1675.

(12) For the use of tri-*n*-butyltin hydride to cleave carbon–sulfur see: Barton, D. H. R.; Motherwell, W. B.; et al. *J. Chem. Soc., Chem. Commun.* **1980**, 732; *Pure Appl. Chem.* **1981**, *53*, 15.

(13) Pereyre, M.; Colin, C.; Valade, J. *Bull. Soc. Chim. Fr.* **1968**, 3358. Pereyre, M.; Valade, J. *Ibid.* **1967**, 1928.

(14) Kuivila, H. G. In "Advances in Organometallic Chemistry"; Stone, F. G. A., West R., Eds.; Academic Press: New York, 1964; Vol. 1.

(15) Barnett, E. B.; Mathews, M. A. *Chem. Ber.* **1926**, *59*, 1429.

(16) Barnett, E. B.; Cook, J. W.; Wiltshire, J. L. *J. Chem. Soc.* **1927**, 1724.

(43% yield) was identical with that of an authentic sample prepared by a previously reported procedure.[16] The second major component (40% yield) was collected and the structure assigned as 9-(triglymylmethyl)-10-phenylanthracene NMR and IR spectra: IR (CCl_4) 3070 (m), 2930 (s), 2880 (s), 1600 (m), 1465 (s), 1100 (s), 700 (m) cm^{-1}; ^1H NMR (CCl_4) δ 6.8–8.0 (multiplet, 13 H), 2.8–4.2 (multiplet, 18.6 H).

Thermolysis of 9-Methylene-10-ethyl-10-phenyl-9,10-dihydroanthracene (2) in Cumene. A solution of 0.200 g (0.676 mmol) of 9-methylene-10-ethyl-10-phenyl-9,10-dihydroanthracene (2) and 25 mL of cumene (distilled from sodium) was placed in a pressure tube, flushed with argon, sealed, and heated at 251 °C for 72 h. The tube was cooled, cumene was removed by distillation, and the crude product was analyzed by GLC and TLC. The GLC analysis was carried out with a 6 ft SE-52 column at a temperature of 250 °C. The crude product was chromatographed on a 20 × 20 TLC plate with (8/2) pentane/benzene as the eluent. Band I (highest R_f) weighed 0.115 g and by its NMR spectrum it was shown to be a mixture of starting material (13%), 9-phenyl-10-methylanthracene (27%), and 9-phenyl-10-propylanthracene (59%). Band II weighed 20 mg and by its NMR and IR spectra was identified as 9-phenyl-10-(2-phenyl-2-methylpropyl)anthracene (10%). Band II: IR (CCl_4) 3060 (s), 2960 (s), 1600 (m), 1450 (s), 1380 (m), 1370 (m), 1030 (s), 925 (m), 695 (s); ^1H NMR (CCl_4) δ 6.6–8.0 (multiplet, 17 H). Band III weighed 3 mg and was shown to be 10-ethyl-10-phenylanthrone by comparison of its IR spectrum with that of an authentic sample.[6]

Thermolysis of 9-Methylene-10-ethyl-10-phenyl-9,10-dihydroanthracene (2) in Cumene with 1,1-Diphenylethylene. A solution of 0.200 g (0.676 mmol) of 9-methylene-10-ethyl-10-phenyl-9,10-dihydroanthracene, 25 mL of distilled cumene, and 5.6 g (33.8 mmol) of distilled 1,1-diphenylethylene was placed in a pressure tube, flushed with argon, sealed, and heated at 251 °C for 72 h. The tube was cooled, the cumene and some 1,1-diphenylethylene were removed by distillation, and the crude product was analyzed by GLC with a 6 ft SE-52 column at a temperature of 250 °C. The ratio of 9-phenyl-10-propylanthracene to 9-phenyl-10-methylanthracene was shown by GC to be 1:14.

Thermolysis of 9-Methylene-10-ethyl-10-phenyl-9,10-dihydroanthracene in Thiophenol. A solution of 0.200 g (0.676 mmol) of 9-methylene-10-ethyl-10-phenyl-9,10-dihydroanthracene and 25 mL of thiophenol was placed in a pressure tube, flushed with nitrogen, sealed, and heated at 210 °C for 6 days. After the reaction had cooled, ether was added, the ethereal solution washed repeatedly with 0.5 N sodium hydroxide solution and saturated sodium chloride solution and dried over anhydrous sodium sulfate, and the solvent was evaporated. The crude product was chromatographed on a 20 × 20 TLC plate with (9:1) pentane/benzene and gave two components. Band I (highest R_f) contained diphenyl disulfide and band II (152 mg, 75%) had NMR and IR spectra that were identical with independently synthesized 9-methyl-10-ethyl-10-phenyl-9,10-dihydroanthracene. The cis–trans ratio was shown to be 40:60 (vide infra).

***cis*- and *trans*-9-Methyl-10-ethyl-10-phenyl-9,10-dihydroanthracene (8).** To a vigorously stirred slurry of 1 g of charcoal, 25 mL of anhydrous ethanol, and 1 mL of an 0.2 M chloroplatinic acid solution was added 5 mL of a 1 M sodium borohydride solution in ethanol. After stirring for about 1 min, 4 mL of glacial acetic acid was added, followed by a solution of 0.4 g (1.35 mmol) of 9-methylene-10-ethyl-10-phenyl-9,10-dihydroanthracene dissolved in 10 mL of ethanol. A Brown automatic hydrogen generator[17] was used and the sodium borohydride solution was added dropwise over a 45-min period. The solution was filtered, diluted with water, and extracted with ether, and the ether extract was washed with bicarbonate solution and saturated sodium chloride solution, dried over anhydrous sodium sulfate, and evaporated. The oil was crystallized from acetonitrile to obtain a quantitative yield of a 26:74 cis–trans ratio of isomers, mp 84–90 °C.

Anal. Calcd for $C_{23}H_{22}$: C, 92.57; H, 7.43. Found: C, 92.50; H, 7.45.

***cis*-9,10-Diethyl-10-phenyl-9,10-dihydroanthracene (9).** A solution containing 0.635 g (2.5 mmol) of 9-phenylanthracene and 25 mL of dry tetrahydrofuran was cooled to 0 °C, kept under a nitrogen atmosphere, and to it was added 9 mL (10.8 mmol) of a 1.2 M ethyllithium solution over a 15-min period. The deep red solution was stirred for 40 min, a 10-fold excess of ethyl bromide added, and the solution stirred for an additional 10 min. Water and ether were added and the ethereal layer was washed with water, saturated sodium chloride solution, dried over anhydrous sodium sulfate, and evaporated. The crude oil was crystallized from acetonitrile to give 0.460 g (60%) of the pure cis isomer: mp 110–112 °C; IR (CCl_4) 2960 (s), 1597 (m), 1445 (s), 1375 (m), 905 (s), and 690 (s) cm^{-1}; ^1H NMR (CCl_4) δ 0.51 (t, J = 7 Hz, 3 H), 0.67 (t, J = 7 Hz, 3 H), 1.59 (m, 2 H), 2.42 (q, J = 7 Hz, 2 H), 3.94 (t, J = 6 Hz, 1 H), 7.0–7.5 (m, 13 H). Anal. Calcd for $C_{24}H_{24}$: C, 92.26; H, 7.74. Found: C, 92.15; H, 7.83.

9-Ethylidene-10-ethyl-10-phenyl-9,10-dihydroanthracene. A solution of ethylmagnesium bromide was prepared from 1.4 g (0.06 mol) of magnesium and 6.5 g (0.06 mol) of ethyl bromide in 40 mL of dry ether, and to it was added dropwise a solution of 10 g (0.034 mol) of 10-ethyl-10-phenylanthrone dissolved in 150 mL of dry ether and 15 mL of dry tetrahydrofuran. The mixture was stirred 1 h at room temperature and hydrolyzed with ice and hydrochloric acid. The solution was washed with water and saturated sodium chloride solution and dried over anhydrous sodium sulfate, and the ether was evaporated. The oil was passed through an alumina column with pentane as the eluent and crystallized from acetonitrile: mp 73–76 °C; IR (CCl_4) 2970 (s), 2930 (s), 2880 (m), 2860 (m), 1600 (m), 1470 (s), 1445 (s), 1380 (m), 1365 (m), 1050 (m), 1030 (m), and 695 (m) cm^{-1}; ^1H NMR (CCl_4) δ 3.72 (t, J = 7 Hz, 3 H), 2.08 (d, J = 7 Hz, 3 H), 2.3 (q, J = 7 Hz, 2 H), 6.10 (q, J = 7 Hz, 1 H), 6.6–7.7 (m, 13 H). Anal. Calcd for $C_{24}H_{22}$: C, 92,86; H, 7.14. Found: C, 92.60; H, 7.26.

Hydrogenation of 9-Ethylidene-10-ethyl-10-phenyl-9,10-dihydroanthracene. To a vigorously stirred slurry of 0.25 g charcoal, 10 mL of anhydrous ethanol, and 0.25 mL of 0.2 M chloroplatinic acid solution was added 1 mL of a 1 M sodium borohydride solution in ethanol. After stirring for 1 min, 1 mL of glacial acetic acid was added, followed by a solution of 0.1 g of 9-ethylidene-10-ethyl-10-phenyl-9,10-dihydroanthracene dissolved in 4 mL of ethanol. Brown's automatic hydrogen generator[17] was then attached to the flask and the sodium borohydride solution slowly added in a dropwise manner over a 20-min period. The solution was filtered, diluted with water, and extracted with ether. The ether extract was washed with bicarbonate solution and saturated sodium chloride solution, dried over anhydrous sodium sulfate, and evaporated. The crude product was chromatographed on a 10 × 20 TLC plate with pentane/benzene (9/1) as the eluent to give 88 mg (87%) of *cis*- and *trans*-9,10-diethyl-10-phenyl-9,10-dihydroanthracene whose cis–trans isomer ratio was shown to be 24:76; ^1H NMR of *trans*-9,10-diethyl-10-phenyl-9,10-dihydroanthracene (CCl_4) 0.83 (t, J = 7 Hz, 3 H), 1.03 (t, J = 7 Hz, 3 H), 1.91 (m, 2 H), 2.36 (q, J = 7 Hz, 2 H), 3.98 (t, J = 7 Hz, 1 H), 6.6–7.5 (m, 13 H).

Synthesis of *cis*- and *trans*-9-(Thiophenoxymethyl)-10-ethyl-10-phenyl-9,10-dihydroanthracene. A solution containing 1 g (3.38 mmol) of 9-methylene-10-ethyl-10-phenyl-9,10-dihydroanthracene and 25 mL of thiophenol was heated on the steam bath for 3 h. The thiophenol was removed by distillation under vacuum (5 mmHg at 41 °C) and the oil was dissolved in acetonitrile from which the cis isomer crystallized, mp 145.5–146.5 °C. The remaining solution contained the trans isomer, which was purified by TLC using pentane/benzene (85/15) as the eluent. Total yield of product was 75% and the cis/trans ratio was determined by NMR of the crude mixture and shown to be 60:40.

Cis isomer: mp 145.5–146.5 °C; IR (CCl_4) 3060 (m), 2970 (m), 2890 (m), 2880 (m), 1600 (m), 1588 (m), 1485 (s), 1450 (s), 1030 (m), 695 (s), and 635 (m) cm^{-1}; ^1H NMR (CCl_4) δ 0.67 (t, J = 7 Hz, 2.7 H), 2.55 (q, J = 7 Hz), 2.68 (d, J = 7 Hz), 2.55 and 2.68 (4 H), 4.12 (t, J = 7 Hz, 1.1 H), 7.0–7.7 (m, 18.5 H). Anal. Calcd for $C_{29}H_{26}S$: C, 85.68; H, 6.45; S, 7.87. Found: C, 85.70; H, 6.46; S, 7.90.

Trans isomer (oil): IR (CCl_4) 3060 (m), 2970 (m), 2880 (m), 1600 (m), 1590 (s), 1482 (s), 1448 (s), 1330 (m), 1310 (m), 1030 (m), 695 (s), and 689 (s) cm^{-1}; ^1H NMR (CCl_4) δ 0.82 (t, J = 8 Hz, 2.8 H), 2.40 (q, J = 8 Hz, 0.9 H), 3.34 (d, J = 6.5 Hz, 1.9 H), 4.34 (t, J = 6.5 Hz, 0.9 H), 6.4–7.7 (m, 18 H).

(17) Brown, C. A.; Brown, H. C. *J. Am. Chem. Soc.* **1962**, *84*, 2829.

A sample of the 9-methylene compound was placed in an NMR tube with thiophenol as solvent. The temperature probe on the NMR was heated to 131 °C and the spectrum scanned at 5-min intervals for 45 min at which time the addition of thiophenol to the olefin was essentially complete.

Desulfurization of *cis*- and *trans*-9-(Thiophenoxymethyl)-10-ethyl-10-phenyl-9,10-dihydroanthracene. A mixture consisting of 50 mg of the thiophenol adduct, 10 mL of ethanol, and 500 mg of Raney nickel was refluxed for 30 min. The ethanol solution was filtered through a millipore filter and the ethanol evaporated to give crystalline hydrocarbon. *cis*-9-(Thiophenoxymethyl)-10-ethyl-10-phenyl-9,10-dihydroanthracene; mp 145.5–146.5 °C, gave *cis*-9-methyl-10-ethyl-10-phenyl-9,10-dihydroanthracene: mp 140–143 °C; IR (CCl_4) 3060 (s), 2970 (s), 1600 (m), 1490 (s), 1450 (s), 1305 (m), 1040 (s), and 690 (s) cm^{-1}; ^1H NMR (CCl_4) δ 0.43 (t, J = 7 Hz, 3 H), 1.45 (d, J = 7 Hz, 3 H), 2.48 (q, J = 7 Hz, 2 H), 4.2 (q, J = 7 Hz, 1 H), 7.2 (m, 13 H).

trans-9-(Thiophenoxymethyl)-10-ethyl-10-phenyl-9,10-dihydroanthracene (oil) gave *trans*-9-methyl-10-ethyl-10-phenyl-9,10-dihydroanthracene: mp 77–79 °C; IR (CCl_4) 3060 (s), 2970 (s), 1600 (m), 1490 (s), 1470 (m), 1450 (s), 1350 (w), 1330 (m), 1310 (m), 1040 (s), and 690 (s) cm^{-1}; ^1H NMR (CCl_4) δ 0.69 (t, J = 7 Hz, 3.1 H), 1.62 (d, J = 7 Hz, 2.9 H), 2.42 (q, J = 7 Hz, 1.9 H), 4.25 (q, J = 7 Hz, 1 H), 6.6–7.5 (m, 13 H).

Addition of Thiophenol to 9-Methylene-10-ethyl-10-phenyl-9,10-dihydroanthracene. A solution of 0.25 g of 9-methylene-10-ethyl-10-phenyl-9,10-dihydroanthracene, 20 mL of benzene, and 1 mL of thiophenol was allowed to stand at room temperature for 6 days under a nitrogen atmosphere. The solution was washed repeatedly with 1 N sodium hydroxide solution to remove the thiophenol, followed by washings with water and saturated sodium chloride solution. The benzene solution was dried over anhydrous sodium sulfate, the solvent was removed in vacuo, and the residue was chromatographed on a 10 × 20 TLC plate with pentane/benzene (85/15) as the eluent. Band V contained the thiophenol adduct in a 57:43 cis–trans ratio.

Thermolysis of 9-Methylene-10-ethyl-10-phenyl-9,10-dihydroanthracene in Thiophenol. A Pyrex tube containing a solution of 0.25 g (0.845 mmol) of 9-methylene-10-ethyl-10-phenyl-9,10-dihydroanthracene and 32 mL of thiophenol was flushed with nitrogen for 5 min and then sealed. The tube was heated at 163 °C for 18 h, cooled, and diluted with ether, the ether extract was washed successively with 0.1 N sodium hydroxide solution until all the thiophenol was removed and with saturated sodium chloride solution and dried over anhydrous sodium sulfate, and the solvent was evaporated. The crude product was chromatographed on a 20 × 40 TLC plate and eluted with pentane/benzene (85/15) to give five bands. Band I (highest R_f) weighed 3 mg and was shown by IR to be silicon grease. Band II weighed 0.167 g and was diphenyl disulfide. Band III weighed 0.184 g (0.617 mmol, 73% yield) and analyzed as 40:60 ratio of *cis*- and *trans*-9-methyl-10-ethyl-10-phenyl-9,10-dihydroanthracene. Band IV weighed 9 mg and could not be identified by its NMR and IR spectra. Band V (60 mg, 0.148 mmol, 18% yield) was shown by NMR and IR spectra to be the 9-(thiophenoxymethyl) compound in a cis–trans ratio of 59:41.

Thermolysis of *cis*-9-(Thiophenoxymethyl)-10-ethyl-10-phenyl-9,10-dihydroanthracene in Thiophenol. A sample (59 mg) of pure *cis*-9-(thiophenoxymethyl)-10-ethyl-10-phenyl-9,10-dihydroanthracene was placed in a tube on the vacuum manifold and 6 mL of distilled thiophenol which had been degassed by the freeze–thaw method was transferred under high vacuum to the tube containing the thiophenol adduct. The tube was sealed under a vacuum of 0.005 mmHg, heated at 164 °C for 14 h, and cooled, and the thiophenol was removed at room temperature under vacuum. The only product by NMR analysis was 9-methyl-10-ethyl-10-phenyl-9,10-dihydroanthracene in a cis–trans ratio of 45:55.

Isomerization of *trans*-9-Methyl-10-ethyl-10-phenyl-9,10-dihydroanthracene with Thiophenol. A sample (34 mg) of the 9-methyl compound with a cis–trans ratio of 9:91 was placed in a tube on the vacuum manifold and degassed thiophenol was transferred to the tube under high vacuum. The tube was sealed and heated at 164 °C for 17 h. Thiophenol was removed under vacuum at room temperature and an NMR spectrum was taken on the hydrocarbon product. The ratio was of *cis*- and *trans*-9-methyl-10-ethyl-10-phenyl-9,10-dihydroanthracene was found to be 43:57.

Isomerization of *trans*- and *cis*-9-Methyl-10-ethyl-10-phenyl-9,10-dihydroanthracene with Thiophenol-*d*. A sample (100 g) of 9-methyl-10-ethyl-10-phenyl-9,10-dihydroanthracene with a cis–trans ratio of 26:74 was placed in a tube on the vacuum manifold and degassed thiophenol-*d* was transferred to the tube under high vacuum. The tube was sealed and heated at 166 °C for 11 h. The thiophenol was removed under vacuum at room temperature and the crude product was chromatographed on a 10 × 20 TLC plate with pentane/benzene (9/1) to give 98.5 mg (98%) of 9-methyl-10-ethyl-10-phenyl-9,10-dihydroanthracene with a cis–trans ratio of 39:61: ^1H NMR (CCl_4) δ 0.43 and 0.69 (t, J = 7 Hz, 3 H), 1.45 (t, J = 3.5 Hz, 1.3 H), 1.62 (t, J = 3.5 Hz, 1.7 H), 2.5–2.6 (q, 2 H), 4.2 (m, 0.2 H), 6.6–7.5 (m, 13 H).

Isomerization of the Cis-Thiophenyl Adduct in Thiophenol. A solution of 0.095 g of *cis*-9-(thiophenoxymethyl)-10-ethyl-10-phenyl-9,10-dihydroanthracene and 1 mL of thiophenol was heated on the steam bath for 27.5 h and cooled, and the thiophenol was removed under vacuum at room temperature. An NMR spectrum of the product showed a 42/58 ratio of cis–trans 9-(thiophenoxymethyl)-10-ethyl-10-phenyl-9,10-dihydroanthracene.

Thermolysis of *cis*-9-(Thiophenoxymethyl)-10-ethyl-10-phenyl-9,10-dihydroanthracene with Tri-*n*-butyltin Hydride. A solution containing 60 mg (0.148 mmol) of the trans isomer of the thiophenol adduct and 190 mg (0.621 mmol) of tri-*n*-butyltin hydride was placed in a tube under a nitrogen atmosphere, sealed, and heated for 21 h at 164 °C. Some solid formed during the reaction. The excess solvent was distilled off in vacuo at 100 °C, and the crude product was placed on two 20 × 40 TLC plates and eluted with pentane/benzene (8/2). Band I (highest R_f) contained alkyl tin compounds, band II contained diphenyl disulfide, band III (39 mg, 66% yield) contained only *cis*-9-methyl-10-ethyl-10-phenyl-9,10-dihydroanthracene, and band V contained about 15 mg of unisomerized starting material, which represents about 10–15% recovery of starting material.

Thermolysis of *trans*-9-(Thiophenoxymethyl)-10-ethyl-10-phenyl-9,10-dihydroanthracene with Tri-*n*-butyltin Hydride. A solution containing 60 mg (0.148 mmol) of the trans isomer of the thiophenol adduct and 190 mg (0.621 mmol) of tri-*n*-butyltin hydride was placed in a tube under a nitrogen atmosphere, sealed, and heated for 21.5 h at 164 °C. The resulting solution was placed on a 20 × 20 TLC plate and eluted with pentane/benzene (9/1). Band IV (22 mg, 37% yield) contained only *trans*-9-methyl-10-ethyl-10-phenyl-9,10-dihydroanthracene and band V (18 mg, 30% yield) contained recovered unisomerized starting material.

Reduction of 9-Methylene-10-ethyl-10-phenyl-9,10-dihydroanthracene (2) with Tri-*n*-butyltin Hydride. A solution of 100 mg (0.338 mmol) of 9-methylene-10-ethyl-10-phenyl-9,10-dihydroanthracene and 5 mL of tri-*n*-butyltin hydride was placed in a tube under an atmosphere of nitrogen and heated at 164 °C for 23 h. Some solid was present in the bottom of the tube. The excess tin hydride was distilled off at 110 °C and the resulting crude oil was chromatographed on a 20 × 40 TLC plate and eluted with pentane/benzene (8/2) to give a band consisting of 9-methyl-10-ethyl-phenyl-9,10-dihydroanthracene and some alkyltin impurities. The rest of the bands on the plate contained only multiple alkyltin compounds. The band containing the reduced hydrocarbon was rechromatographed on another TLC plate with the same solvent mixture to give pure 9-methyl-10-ethyl-10-phenyl-9,10-dihydroanthracene in a cis–trans ratio of 37:63.

Tri-*n*-butyl[(10-ethyl-10-phenyl-9,10-dihydro-9-anthryl)-methyl]tin. A solution of 0.150 g (0.507 mmol) of 9-methylene-10-ethyl-10-phenyl-9,10-dihydroanthracene and 0.220 g (1.01 mmol) of tri-*n*-butyltin hydride was heated at 100 °C for 19 h. The excess tin hydride was removed at a vacuum of 0.2 mmHg and a temperature of 100 °C. The residue was chromatographed on a 20 × 40 TLC plate with pentane/benzene (9/1) and band I (highest R_f) was found to contain a trace amount of tri-*n*-butyltin hydride. Band II weighed 0.274 g (0.446 mmol, 92% yield) and was the desired tin hydride adduct. Band III weighed 9 mg and was shown to be starting olefin. The desired tin adduct was an oil which upon standing became cloudy and slowly de-

composed to starting olefin and some undetermined tin compound: IR (CCl_4) 3060 (m), 2960 (s), 2920 (s), 1600 (w), 1485 (m), 1470 (m), 1450 (m), 1380 (m), 1220 (w), 1070 (m), 860 (m), and 690 (m) cm^{-1}; ^1H NMR (CCl_4) δ 0.2-1.7 (m, 31.8 H), 2.45 (q, J = 7 Hz, 1.8 H), 4.28 (t, J = 7 Hz, 0.9 H), 6.5-7.5 (m, 13 H).

Anal. Calcd for $C_{35}H_{48}Sn$: C, 71.57; H, 9.23; Sn, 20.20. Found: C, 71.75; H, 8.16; Sn, 20.02.

Cleavage of the Tri-*n*-butyltin Hydride Adduct. To a solution of 100 mg (0.170 mmol) of the tri-*n*-butyltin hydride adduct and 5 mL of carbon tetrachloride was added 0.5 mL of trifluoroacetic acid, and the solution was allowed to stand at room temperature for 4 h. The solvent was removed on the rotary evaporator, and the product chromatographed on a 20 × 20 TLC plate with pentane/benzene (8/2) to give two bands. Band I (highest R_f) was shown by IR and NMR spectra to be a 7:93 ratio of *cis*- and *trans*-9-methyl-10-ethyl-10-phenyl-9,10-dihydroanthracene. Band II was the only other band present and the NMR and IR spectra indicated it to be tri-*n*-butylstannyl trifluoroacetate. No starting material was present on the thin-layer plate and no other products were observed.

Reduction of Tri-*n*-butyltin Hydride Adduct with Tri-*n*-butyltin Hydride. A solution of 80 mg (0.103 mmol) of tri-*n*-butyltin hydride adduct and 300 mg (1.03 mmol) of tri-*n*-butyltin hydride was placed in a tube under an atmosphere of nitrogen and heated for 23 h at 164 °C. The crude reaction product was chromatographed on a 20 × 40 TLC plate with pentane/benzene (92/8) as the eluent. Band III contained 9-methyl-10-ethyl-10-phenyl-9,10-dihydroanthracene in a cis-trans ratio of 39:61. No starting material was observed in any of the other bands.

The Addition and Reduction Reaction of 9-Methylene-10-ethyl-10-phenyl-9,10-dihydroanthracene with Tri-*n*-butyltin Hydride. A tube containing a solution of 300 mg (1.03 mmol) of tri-*n*-butyltin hydride and 200 mg (0.675 mmol) of 9-methylene-10-ethyl-10-phenyl-9,10-dihydroanthracene was placed under an atmosphere of nitrogen, sealed, and heated at 164 °C for 5 h. Some of the crude product (250 mg) was chromatographed on a 20 × 20 TLC plate with pentane/benzene (92/8). Band I (highest R_f) was tin hydride, band II was the tri-*n*-butyltin hydride adduct, and band III was a mixture of starting olefin and a 41:59 ratio of *cis*- and *trans*-9-methyl-10-ethyl-10-phenyl-9,10-dihydroanthracene. The *tri-n*-butyltin hydride adduct obtained in band II was dissolved in carbon tetrachloride and hydrolyzed with trifluoroacetic acid. After hydrolysis, the product was chromatographed with thin-layer techniques previously described. The hydrocarbon fraction was isolated and shown to be 93% *trans*-9-methyl-10-ethyl-10-phenyl-9,10-dihydroanthracene. Band II contained tri-*n*-butylstannyl fluoroacetate.

Procedure for Studying Nuclear Overhauser Effect. The spectra was recorded on a Bruker HFX-10 spectrometer in the frequency sweep mode. The sample was dissolved in carbon tetrachloride and contained chloral as the internal field frequency lock. It was degassed with the freeze-thaw method and sealed. The power requirement of the irradiating frequency was determined by increasing the power until the protons coupled to the irradiated protons were completely decoupled. The peak was then integrated four times with the same power level but with the irradiating frequency offset 30 Hz from the original irradiation.

Registry No. 2, 17407-18-0; 3, 92844-32-1; *trans*-4 (X = H; Y = PhS), 92844-39-8; *cis*-4 (X = H; Y = PhS), 92844-40-1; 4 (X = H; Y = Bu_3Sn), 92844-41-2; *trans*-8, 92844-34-3; *cis*-8, 92844-35-4; *trans*-9, 92844-36-5; *cis*-9, 92844-38-7; PhSH, 108-98-5; EtBr, 74-96-4; Bu_3SnH, 688-73-3; 9-phenyl-10-(2-phenyl-2-methylpropyl)anthracene, 92844-33-2; 9-phenylanthracene, 602-55-1; 10-ethyl-10-phenylanthrone, 17407-19-1; 9-ethylidene-10-ethyl-10-phenyl-9,10-dihydroanthracene, 92844-37-6.

Nucleophilic Ring Opening of 2-Oxazolines with Amines: A Convenient Synthesis for Unsymmetrically Substituted Ethylenediamines

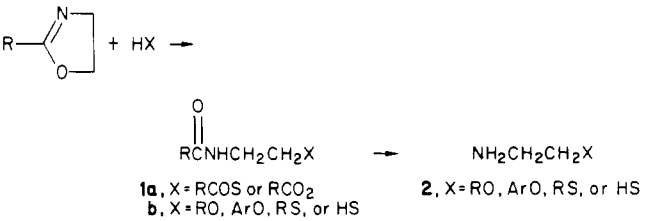
Michael J. Fazio

Designed Polymers and Chemicals Research Laboratory, The Dow Chemical Company, Midland, Michigan 48640

Received February 29, 1984

The reaction of 2-alkyl-2-oxazolines with alkyl- and arylamines was investigated. The acid-catalyzed nucleophilic ring opening of the 2-oxazolines yields *N*-(2-aminoethyl)carboxamides in good to excellent yields with secondary amines and hindered primary amines. The *N*-(2-aminoethyl)carboxamides were hydrolyzed under acidic or basic conditions to selectively yield unsymmetrically substituted ethylenediamines.

2-Oxazolines are versatile chemical intermediates.[1] The ring opening of oxazolines by nucleophiles was first reported in 1950 by Fry[2] and subsequently by several others.[3-6] The nucleophilic ring opening at the 5-position yields β-substituted ethylcarboxamides 1. Hydrolysis of the carboxamides **1b** yields 2-substituted ethylamines **2**. Oxazolines can, therefore, be viewed as an aminoethylation reagent or the synthetic equivalent of aziridine.



In our continuing study of oxazoline chemistry we have investigated the ring opening of oxazolines by primary and

(1) (a) Wiley, R. H.; Bennett, L. L. *Chem. Rev.* **1949**, *44*, 447. (b) Seeliger, W.; Aufderharr, R.; Diepers, W.; Feinauer, R.; Nearing, R.; Thier, W.; Hellman, H. *Angew. Chem.* **1966**, *78*, 917. (c) Frump, J. A.; *Chem. Rev.* **1971**, *71*, 483. (d) Collington, E. W. *Chem. Rev.* **1973**, 987. (e) Meyers, A. I.; Mihelich, E. D. *Angew. Chem.* **1976**, *88*, 321; *Angew Chem., Int. Ed. Engl.* **1976**, *15*, 270. (f) Meyers, A. I. *Acc. Chem. Res.* **1978**, *11*, 375.

(2) Fry, E. M. *J. Org. Chem.* **1950**, *15*, 802.

(3) (a) Wehrmeister, H. L. *J. Org. Chem.* **1962**, *28*, 2587. (b) Jaeger, A. German Patent 1 062 253, 1959. (c) Kaiser, M. E.; Smith, H. A. U.S. Patent 4 195 154, 1980.

(4) Berazosky, S.; Kaiser, M. E. U.S. Patent 4 086 273, 1978.

(5) (a) Goldberg, A. A.; Kelly, W. *J. Chem. Soc.* **1948**, 1919. (b) Fry, E. M. *J. Org. Chem.* **1950**, *15*, 802. (c) Kaiser, M. E.; Owen, P. W. U.S. Patent 4 086 274, 1978.

(6) Kaiser, M. E.; Owen, P. W. U.S. Patent 4 024 184, 1977.

0022-3263/84/1949-4889$01.50/0