Chemical Behavior of Charge-Transfer Complexes. IV. Phenanthrene Catalysis in Acetolysis of Some Dinitro-9-fluorenyl and Dinitrobenzhydryl *p*-Toluenesulfonates[1]

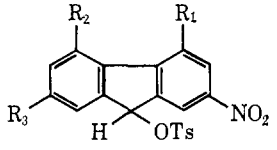
Allan K. Colter, Frederick F. Guzik, and Sai Hong Hui

Contribution from the Department of Chemistry, Carnegie Institute of Technology, Pittsburgh, Pennsylvania 15213. *Received September 9, 1966*

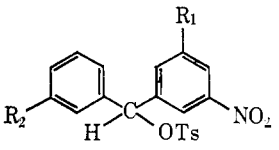
Abstract: As part of an investigation of the structural requirements for catalysis by charge-transfer complexing in acetolysis reactions, rates of acetolysis have been measured for 2,4- and 2,5-dinitro-9-fluorenyl *p*-toluenesulfonates at 50.17° and for 2,7-dinitro-9-fluorenyl *p*-toluenesulfonate at 50.17 and 70.07°, in the absence of phenanthrene and in the presence of a series of phenanthrene concentrations. The data were analyzed to obtain 1:1 substrate:phenanthrene complexation constants, K, and rate constants for acetolysis of the 1:1 complexes. For the 2,4-, 2,5-, and 2,7-dinitrofluorenyl esters at 50.17°, the 1:1 complexes are, respectively, 12, 14, and 11 times as reactive as uncomplexed substrates. Acetolysis of 2-nitro-9-fluorenyl *p*-toluenesulfonate is catalyzed to a smaller, but still significant, extent by added donors. In contrast, the rates of acetolysis of 3,3′- and 3,5-dinitrobenzhydryl *p*-toluenesulfonates are essentially unchanged by 0.05 M phenanthrene. The significance of these results is discussed.

In previous papers in this series[2] we have reported catalysis by aromatic donors in acetolysis of 2,4,7-trinitro-9-fluorenyl tosylate (I). In choosing for our initial studies a rigid coplanar substrate having strong acceptor properties our aim was to maximize catalytic effects due to charge-transfer complexing. In extending these studies, a logical starting point appeared to be an investigation of the structural requirements for such catalysis. Although we expect less extensive complexation in the more common types of arylmethyl systems, there is still the possibility of significant rate enhancement as a result of chance encounters.[2b,3] A second question of interest is how the chemical effects of a complexed donor molecule such as phenanthrene depend on substrate structure.

The compounds included in the present study were the closely related 2,4-, 2,5-, and 2,7-dinitro-9-fluorenyl tosylates (II, III, and IV), 3,3′- and 3,5-dinitrobenzhydryl tosylates (V and VI), and 2-nitro-9-fluorenyl tosylate (VII).



I, $R_1 = R_3 = NO_2$; $R_2 = H$
II, $R_1 = NO_2$; $R_2 = R_3 = H$
III, $R_1 = R_3 = H$; $R_2 = NO_2$
IV, $R_1 = R_2 = H$; $R_3 = NO_2$
VII, $R_1 = R_2 = R_3 = H$



V, $R_1 = H$; $R_2 = NO_2$
VI, $R_1 = NO_2$; $R_2 = H$

Results

The dinitrofluorenyl esters II, III, and IV were prepared as previously described.[4] The benzhydryl esters were prepared from the corresponding known benzhydrols[5,6] by treatment with *p*-toluenesulfonyl chloride and potassium hydroxide in anhydrous ether. The mononitrofluorenyl ester was prepared by treating 2-nitro-9-diazofluorene[7] with *p*-toluenesulfonic acid.

First-order rate constants for acetolysis of the dintrofluorenyl tosylates are listed in Table I. With all three esters, the only detectable product of acetolysis (in addition to *p*-toluenesulfonic acid) was the corresponding acetate, isolable[4] in yields up to 95%.

The mechanism proposed earlier[2] for phenanthrene catalysis is

$$\begin{array}{ccc} \mathrm{ROTs} + \mathrm{D} & \overset{K}{\rightleftharpoons} & \mathrm{ROTs \cdot D} \\ \mathrm{HOAc}\downarrow k_u & & \mathrm{HOAc}\downarrow k_c \\ \text{products} & & \text{products} \end{array}$$

ROTs, D, and ROTs·D represent substrate, donor, and 1:1 complex, respectively; K is the equilibrium constant for 1:1 complex formation; k_u and k_c are specific rates of acetolysis of uncomplexed and complexed substrate, respectively. This mechanism, together with the equilibrium condition for 1:1 complexation, leads to the equation[2]

$$1/(k_{obsd} - k_u) = 1/(k_c - k_u) + 1/[K[D]_0(k_c - k_u)] \quad (1)$$

where k_{obsd} is the observed first-order rate constant in the presence of a stoichiometric concentration of donor, $[D]_0$. Thus, assuming the correctness of this mechanism, the quantities k_c and K can be obtained from the slope and intercept of the straight line plot of $1/(k_{obsd} - k_u)$ *vs.* $1/[D]_0$. As pointed out previously,[2] the equilibrium constant so measured is a total equilibrium constant, $\sum_i K_i$, for all geometrically and/or electronically nonequivalent 1:1 complexes formed, while the k_c is a weighted average rate constant for all such complexes. Figure 1 shows a typical reciprocal plot (for acetolysis of II at 50.17°). The data were analyzed by means of a weighted least-squares procedure (see Experimental Section). Table II summarizes the derived data for the dinitrofluorenyl tosylates.

(1) (a) Abstracted in part from the Ph.D. thesis of Frederick F. Guzik, Carnegie Institute of Technology, Jan, 1966; (b) part III of this series, A. K. Colter and L. M. Clemens, *J. Am. Chem. Soc.*, 87, 847 (1965).
(2) (a) A. K. Colter and S. S. Wang, *ibid.*, 85, 114 (1963); (b) A. K. Colter, S. S. Wang, G. H. Megerle, and P. S. Ossip, *ibid.*, 86, 3106 (1964).
(3) L. E. Orgel and R. S. Mulliken, *ibid.*, 79, 4839 (1957).
(4) F. F. Guzik and A. K. Colter, *Can. J. Chem.*, 43, 1441 (1965).
(5) N. C. Deno and A. Schriesheim, *J. Am. Chem. Soc.*, 77, 3051 (1955).
(6) R. T. Puckowski and W. A. Ross, *J. Chem. Soc.*, 3555 (1959).
(7) K. D. Warren, *ibid.*, 1412 (1961).

Table I. Rates of Acetolysis of 2,4-, 2,5-, and 2,7-Dinitro-9-fluorenyl *p*-Toluenesulfonates[a] in the Presence of Phenanthrene

10^2[donor], M[b]	10^6k, sec^{-1}[c] II, 50.17°	III, 50.17°	IV, 50.17°	IV, 70.07°
0	6.31 ± 0.06[d]	1.88 ± 0.02[d]	0.558 ± 0.002[d]	5.59 ± 0.07[d]
5.00	13.9 ± 0.2	4.51 ± 0.03	1.28 ± 0.03	10.7 ± 0.1
6.00	15.0 ± 0.2	4.94 ± 0.10	1.41 ± 0.01	11.5 ± 0.1
7.00	16.3 ± 0.2	5.37 ± 0.13	1.52 ± 0.01	12.5 ± 0.1
8.00	17.6 ± 0.2	5.87 ± 0.12	1.63 ± 0.01	13.4 ± 0.2
9.00	18.6 ± 0.4	6.23 ± 0.10	1.76 ± 0.01	14.2 ± 0.2

[a] Concentration of ester, 0.002 *M*. [b] Measured at 25°. [c] Listed with average deviations for nine to ten measurements. [d] Reference 4.

Table II. Results of Analysis of Kinetic Data for the Dinitrofluorenyl *p*-Toluenesulfonates[a]

Substrate	Temp, °C	10^6k_c, sec^{-1}	K, l. mole^{-1}	k_c/k_u
II	50.17	77 ± 14	2.4 ± 0.5	12 ± 2
III	50.17	27 ± 3	2.4 ± 0.3	14 ± 2
IV	50.17	6.4 ± 0.5	2.9 ± 0.3	11 ± 1
IV	70.07	74 ± 13	1.7 ± 0.3	13 ± 2

[a] Uncertainties in k_c and K taken as standard deviations obtained from simple least-squares analysis.

Formal activation parameters for acetolysis of the 2,7-dinitro ester IV, calculated from the data in Table I, varied from $\Delta H^{\ddagger}$ = 24.9 ± 0.1 kcal mole^{-1}, $\Delta S^{\ddagger}$(50.17°) = −10.3 ± 0.5 eu mole^{-1}, in the absence of donor to $\Delta H^{\ddagger}$ = 22.5 ± 0.2 kcal mole^{-1}, $\Delta S^{\ddagger}$(50.17°) = −15.4 ± 0.8 eu mole^{-1} in the presence of 0.09 *M* (25°) phenanthrene. Thus, addition of donor produces a decrease in both formal enthalpy and formal entropy of activation. Exactly parallel results were obtained with the trinitro ester I.[2] From values of k_c at 50.17 and 70.07° (Table II) activation parameters for acetolysis of the 1:1 phenanthrene–2,7-dinitro-9-fluorenyl *p*-toluenesulfonate complex can be calculated. These are $\Delta H^{\ddagger}$ = 26.5 ± 2.1 kcal mole^{-1} and $\Delta S^{\ddagger}$(50.17°) = −0.5 ± 6 eu mole^{-1}. Again, as found earlier with the trinitro system, the 1:1 complex is more reactive than uncomplexed substrate because of a higher entropy of activation. Values of K at 50.17 and 70.07° (Table II) lead to the following thermodynamic quantities for 1:1 complexation between phenanthrene and IV at 50.17°: ΔG° = −0.69 ± 0.06 kcal mole^{-1}, ΔH° = −6.3 ± 3.1 kcal mole^{-1}, and ΔS° = −17.4 ± 9.7 eu mole^{-1}.

In order to define further the structural requirements for catalysis by organic donors, the catalytic effect of 0.05 *M* phenanthrene was measured in acetolysis of the two dinitrobenzhydryl tosylates V and VI and 2-nitrofluorenyl tosylate (VII). The results are shown in Table III. By comparison, the rate of acetolysis of trinitrofluorenyl tosylate (I) at 55.85° is increased 3.5-fold by 0.05 *M* phenanthrene,[2] and the rates of acetolysis of the dinitrofluorenyl tosylates (II, III, and IV) at 50.17° are increased by factors of 2.2, 2.4, and 2.3, respectively. Evidence that the small rate enhancement in acetolysis of the mononitrofluorenyl ester (VII) is a result of charge-transfer complexing was obtained by examining the effects of 0.02 *M* anthracene and 0.02 *M* hexaethylbenzene. The results were similar to those obtained earlier with the trinitro system, anthracene here giving roughly seven times the rate enhancement produced by phenanthrene at the same concentration and 0.02 *M* hexaethylbenzene producing no measurable change in rate.

Discussion

The observed rate enhancement by aromatic donors in acetolysis of 9-fluorenyl tosylates decreases with decreasing number of nitro groups.[8] A decrease in complexation constant with decreasing number of nitro groups is, of course, expected.[9] The more

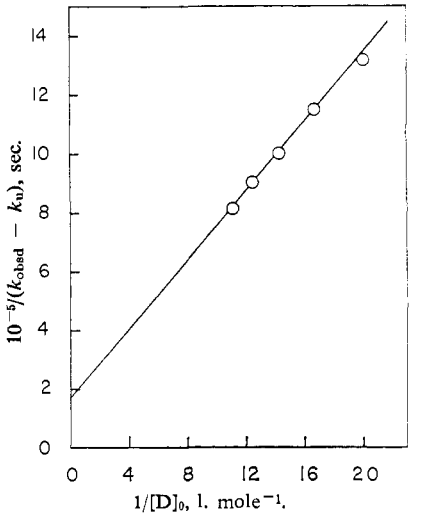


Figure 1. Plot of $1/(k_{obsd} - k_u)$ *vs.* $1/[D]_0$ for acetolysis of 2,4-dinitro-9-fluorenyl *p*-toluenesulfonate at 50.17°.

interesting result is that the actual chemical effect of complexation as measured by k_c/k_u is smaller for the three dinitro esters (Table II) than for the trinitro tosylate (I) (k_c/k_u = 21–27 between 56 and 85°). Since the dinitro and trinitro ground-state complexes are of comparable stability, it follows that the trinitro transition state forms a considerably stronger complex than the three dinitro transition states. The "virtual equilibrium constant,"[10] $K_{\ddagger}$, for 1:1 complex formation between the transition state and the donor measures the transition-state complex stability. This quantity may be calculated from the results in Table II by means of eq 2.[2,10] For acetolysis of II, III, and IV at 50.17°,

$$K_{\ddagger} = k_c K/k_u \qquad (2)$$

(8) Rates of reaction of 2,4,5,7-tetranitro-9-fluorenyl tosylate (as measured by titration of *p*-toluenesulfonic acid) in glacial acetic acid are increased to an even greater extent by phenanthrene (F. F. Guzik, Ph.D. Thesis, Carnegie Institute of Technology, 1966). The significance of this observation is in doubt, however, since the kinetics are not cleanly first order and the principal product is 2,4,5,7-tetranitrofluorenone. Further investigation of this reaction is planned.

(9) (a) B. Dale, R. Foster and D. L. Hammick, *J. Chem. Soc.*, 3986 (1954); (b) N. B. Jurinski and P. A. D. de Maine, *J. Am. Chem. Soc.*, 86, 3217 (1964).

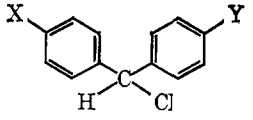
(10) J. L. Kurz, *ibid.*, 85, 987 (1963).

Table III. Structural Effects on Catalysis by Charge-Transfer Complexing

Substrate[a]	Temp, °C	Donor	[Donor], M[b]	10^6k, sec^{-1}[c]	k_{obsd}/k_u
V	30.1	None		9.26 ± 0.05	
V	30.1	Phenanthrene	0.05	9.69 ± 0.05	1.05 ± 0.01
VI	30.1	None		85.1 ± 0.8	
VI	30.1	Phenanthrene	0.05	87.1 ± 0.4	1.02 ± 0.01
VII	50.17	None		88.3 ± 0.8	
VII	50.17	Phenanthrene	0.05	118 ± 1	1.34 ± 0.02
VII	50.17	Anthracene	0.02	172 ± 2	1.95 ± 0.04
VII	50.17	Hexaethylbenzene	0.02	89.0 ± 0.5	1.01 ± 0.01

[a] Concentration of esters, 0.005 M for V and VI, 0.002 M for VII. [b] Measured at 25°. [c] Listed with average deviations for six to ten measurements.

$K_{\pm}$ is, respectively, 29, 34, and 33 l. $mole^{-1}$, compared to about 59 l. $mole^{-1}$ for the trinitro ester. Thus, in spite of changes in transition-state structure (in particular, the degree of carbonium ion character) as a result of having one fewer nitro group, the trinitro transition state is appreciably more electron deficient than the dinitro transition states. If it is correct to ascribe the chemical effect of complexation to electron supply by the donor, then charge-transfer theory[11] predicts greater electron supply and greater stabilization for the more electron-deficient transition state. Interestingly, these results appear to have a close analogy in the kinetic effect of an electron-supplying substituent in solvolysis reactions of arylmethyl compounds. Although few comparisons are available, it appears that, in solvolysis reactions in which bond breaking has occurred to a greater extent than bond making, the rate-enhancing effect of an electron-supplying substituent is increased by other substituents which are electron withdrawing. The clearest example is the kinetic effect of a 4′-methyl or 4′-methoxy group in solvolysis of 4-substituted benzhydryl chlorides (VIII) in 85% aqueous acetone at 0°.[12] The ratio of the rate



VIII, X = CH_3, CH_3O, H
Y = CH_3O, H, NO_2

of solvolysis of the p-methyl compound (X = CH_3) to that of the corresponding unsubstituted compound (X = H), $k(CH_3):k(H)$, varies with the substituent Y as follows: for Y = OCH_3, 7.33; for Y = H, 29.2; for Y = NO_2, 72.8. For X = OCH_3 and H, $k(OCH_3):k(H)$ shows a similar trend: for Y = OCH_3, 2.53×10^2; for Y = H, 3.88×10^4; for Y = NO_2, 5.30×10^5.

The complexation constants for the three dinitro esters at 50.17° differ by less than the estimated experimental uncertainty although that for the 2,7 isomer may be slightly larger than the other two. Steric interference between a nitro group in the 4 (or 5) position and the hydrogen in the 5 (or 4) position preventing coplanarity of one nitro group in compounds II and III[4] could account for small differences in stability. Similar arguments have been used to explain differences in complexation constants for the dinitronaphthalenes.[13]

The trends in apparent activation parameters parallel earlier results with the trinitro ester, as do differences between the activation parameters for acetolysis of uncomplexed 2,7-dinitrofluorenyl tosylate and those for acetolysis of its 1:1 phenanthrene complex. Both results have been discussed in an earlier paper.[2b]

The present results indicate that electron-withdrawing substituents are a necessary structural requirement for strong catalysis by hydrocarbon donors in acetolysis.[14] The almost complete absence of any catalysis by 0.05 M phenanthrene in acetolysis of the two dinitrobenzhydryl tosylates is most likely due to the absence of appreciable complex formation. Both the geometry of the benzhydryl system (specifically, noncoplanarity of the benzene rings) and its lack of rigidity make complex formation unfavorable. From the results of this work it is clear that a negligible fraction of the rate enhancements in acetolysis of the dinitro- and trinitrofluorenyl tosylates is a result of chance encounters between substrate and donor.

Experimental Section[15]

Phenanthrene was purified as previously described[2] and contained less than 0.0036% anthracene. Anthracene (mp 216–218°, Eastman Kodak blue-violet fluorescence) and hexaethylbenzene (mp 127–129°, Eastman White Label) were used without further purification. Anhydrous acetic acid and standard sodium acetate in glacial acetic acid were prepared as previously described.[2] The three dinitro-9-fluorenyl p-toluenesulfonates (II–IV, mp 164–166, 178–179, and 208–210°, respectively) were prepared as previously described.[4]

3,3′-Dinitrobenzhydryl p-Toluenesulfonate (V). A solution of 1.0 g of 3,3′-dinitrobenzhydrol[5] and 0.70 g of p-toluenesulfonyl chloride in 30 ml of anhydrous ether was stirred at −5° while 0.62 g of finely pulverized potassium hydroxide was added. After stirring for an additional 1.5 hr, 100 ml of water was added. Extraction with ether and evaporation led to 1.1 g (70%) of product, mp 140–141°, lit.[16] 134–135°.

3,5-Dinitrobenzhydryl p-Toluenesulfonate (VI). To a well-stirred solution of 0.50 g of 3,5-dinitrobenzhydrol[6] and 0.35 g of p-toluenesulfonyl chloride in 10 ml of anhydrous ether at 0° was slowly added 0.31 g of finely pulverized potassium hydroxide. Stirring was continued at this temperature for an additional hour, after which time 30 ml of water was added. Extraction with ether and evaporation led to 0.60 g (77%) of product, mp 148–151°. Crystallization from acetonitrile raised the melting point to 155–156°.

(11) R. S. Mulliken, *J. Am. Chem. Soc.*, 74, 811 (1952).
(12) J. R. Fox and G. Kohnstam, *Proc. Chem. Soc.*, 115 (1964).
(13) P. H. Emslie and R. Foster, *Tetrahedron*, 20, 1489 (1964).
(14) It is anticipated that this requirement will be less important in highly aqueous media, however. Several reports [*e.g.*, F. M. Menger and M. L. Bender, *J. Am. Chem. Soc.*, 88, 131 (1966); R. E. Moser and H. G. Cassidy, *ibid.*, 87, 3463 (1965)] as well as unpublished results in these laboratories indicate that complexation between large organic molecules is much more extensive in highly aqueous media. See also F. M. Richards, *Ann. Rev. Biochem.*, 32, 269 (1963); I. M. Klotz, *Brookhaven Symp. Biol.*, 13, 25 (1960); W. Kauzmann, *Advan. Protein Chem.*, 14, 1 (1959).
(15) Melting points are uncorrected. Microanalyses were performed by Galbraith Microanalytical Laboratories, Knoxville, Tenn. 37921.
(16) D. Bethell and J. Callister, *J. Chem. Soc.*, 3808 (1963).

Anal. Calcd for $C_{20}H_{16}N_2O_7S$: C, 56.09; H, 3.77; N, 6.54. Found: C, 55.98; H, 3.69; N, 6.32.

2-Nitro-9-fluorenyl *p*-Toluenesulfonate (VII). To a stirred solution of 17.3 g of 9-diazo-2-nitrofluorene[7] in 320 ml of acetonitrile was added 12.4 g of dried *p*-toluenesulfonic acid at room temperature. The mixture was stirred for an additional 30 min, after which time the product was isolated by filtration and washed with ether. The crude yield was 16.2 g (58.2%). After crystallization from acetone the product melted at 132.5–133.5 dec. The infrared spectrum showed absorption at 6.52 (s) and 7.54 μ (s), characteristic of aromatic nitro, and at 7.40 (s), 8.43 (m), and 8.52 μ (s), characteristic of the sulfonate ester group.[4]

Anal. Calcd for $C_{20}H_{15}NO_5S$: C, 62.98; H, 3.96. Found: C, 62.86; H, 3.78.

2-Nitro-9-fluorenyl Acetate. A solution of 3 g of VII in 100 ml of glacial acetic acid was gently refluxed for 1 hr. The solution was cooled and diluted with 100 ml of water, and the product was filtered and purified by crystallization from methanol; yield, 2.02 g (95.4%), mp 148–149.5°. The infrared spectrum showed absorption at 6.57 (s) and 7.48 μ (s), characteristic of aromatic nitro, and at 5.72 (s), 8.20 (s), and 9.65 μ (s), characteristic of the acetate group.

Anal. Calcd for $C_{15}H_{11}NO_4$: C, 66.91; H, 4.12; N, 5.20. Found: C, 66.65; H, 4.10; N, 5.30.

This compound was also prepared by stirring 3 g of 9-diazo-2-nitrofluorene in 80 ml of glacial acetic acid at room temperature for 30 min. The product was isolated by dilution with 80 ml of water followed by filtration. After crystallization from methanol the yield was 2.9 g (85.1%).

Kinetic Measurements. The kinetic procedures have been described previously[2] as has the calculation of activation parameters.

Analysis of Kinetic Data to Obtain K and k_e. The kinetic data were analyzed according to eq 1 using the weighted least-squares procedure previously described.[2,17] Uncertainties in k_e and K listed in Table II are standard deviations calculated by the simple least-squares procedure. Uncertainties in activation parameters and thermodynamic quantities were calculated using standard procedures.[17]

Acknowledgment. We are grateful to the National Science Foundation (Grants G-19842 and GP-3355) for support of this work.

(17) L. G. Parratt, "Probability and Experimental Errors in Science," John Wiley and Sons, Inc., New York, N. Y., 1961.

Structure of Some Carbanions as Deduced from Nuclear Magnetic Resonance Study of Their Protonation Products

D. Nicholls and M. Szwarc

Contribution from the Department of Chemistry, State University College of Forestry at Syracuse University, Syracuse, New York 13210. *Received August 1, 1966*

Abstract: The nmr spectra of 9,10-dihydroanthracene and its 9-ethyl derivative have been investigated. It has been shown that the former molecule undergoes a rapid oscillating motion through the planar configuration at temperatures as low as −55°. Introduction of the alkyl group either quenches this movement, or greatly favors one stereoisomer, even at 40°. These results and also those obtained from a study of the nmr spectrum of the 9-ethyl derivative monodeuterated in the 10 position have permitted a discussion of the structure of the carbanions derived from 9,10-dihydroanthracene. Thus, it has been shown that the anion is not planar. Its 9-ethyl derivative possesses the alkyl group preferentially in equatorial position and the Li^+ ion in the respective ion pair is located on the same side as the ethyl group.

In connection with our studies of the reactivity and structure of carbanions we investigated the negative ions derived from 9,10-dihydroanthracene and its derivatives. This work led us to study the nmr spectra of 9,10-dihydroanthracene and its 9-ethyl derivative. The results revealed that either a rapid "flapping" motion of the former molecule is quenched by substitution of one of the 9-hydrogens by the alkyl group or one stereoisomer of the alkyl-substituted compound is particularly favored. Moreover, collating all the evidence, we arrived at interesting conclusions about the structure of the respective carbanions.

Experimental Section

9,10-Dihydroanthracene was acquired commercially. The compound contained a small amount of anthracene which was removed by refluxing the impure material with maleic anhydride in xylene solution. After washing with water to remove the adduct and excess of maleic anhydride, the dihydroanthracene was isolated and recrystallized from methanol. The ultraviolet spectrum of the purified compound showed the presence of less than 0.1% of anthracene.

Commercial anthracene (chemically pure) was twice crystallized from toluene and sublimed under high vacuum before being used.

Ethyllithium in benzene solution (Foote Mineral Co.) was purified under high vacuum by repeated crystallization, using the procedure described elsewhere.[1] The purified solution, never exposed to air, was placed in ampoules equipped with breakseals and the solvent was removed by evacuation before sealing off the container.

Addition of ethyllithium to anthracene was accomplished by adding an equimolar amount of the lithium compound to a solution of anthracene in thoroughly purified tetrahydrofuran. The reaction was carried out in an evacuated ampoule at room temperature. The resulting lithium salt was converted into the hydrocarbon by adding an excess of deaerated water or isotopically pure D_2O. The ampoule was then opened to air and the hydrocarbon recovered. The resulting material contained a small amount of unreacted anthracene, but otherwise it was found pure.

The nmr spectra were taken on a A-60-A Varian spectrometer using deuterated chloroform or deuterated THF as solvent. The former compound was virtually free of any hydrogen-containing impurities, but the spectrum of the deuterated THF showed two single lines at 104 and 215 cps (δ 1.73 and 3.58, respectively) which were attributed to the partially hydrogenated ether. These lines did not interfere with the investigated spectra. All the reported chemical shifts are related to tetramethylsilane used as an internal standard and, unless otherwise stated, the spectra were taken at 40°.

(1) M. Van Beylen, D. N. Bhattacharyya, J. Smid, and M. Szwarc, in press.