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Acidity of Hydrocarbons. VII. Rates of Exchange of Polycyclic Methylarene-α-d's with Lithium Cyclohexylamide[1]

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Rates of exchange are reported for various deuteriomethyl derivatives of naphthalene, phenanthrene, anthracene, pyrene and fluoranthene with lithium cyclohexylamide in cyclohexylamine at 49.9°. The relative rates are discussed with reference to the stabilities of corresponding arylmethyl anions and are compared with those of related carbonium ion reactions.

Several studies are now available on the relative stabilities of polycyclic arylmethyl cations via rates of appropriate solvolysis reactions.[4,5] These studies have found important use in the development of theories in organic chemistry, particularly various molecular orbital theories.[5] No comparable studies have hitherto been available for the corresponding arylmethyl anions. We report in this paper the results of our studies of exchange rates of various polycyclic methylarene-α-d's with lithium cyclohexylamide in cyclohexylamine. The kinetics and mechanism of this reaction have been reported in previous papers in this series[6]; the reaction appears to involve the arylmethyllithium as an intermediate and the exchange rates appear to be valid measures of relative acidities.[7]

Details for the preparations of the methylarene-α-d's used are given in the Experimental section. The starting materials were generally the arenecarbinols which were prepared generally by lithium aluminum hydride reduction of the corresponding aldehydes or carboxylate esters; these starting materials are all known and available compounds. The arenecarbinols were converted to the chloromethyl compounds with thionyl chloride and subsequently reduced by Eliel's[8] method with lithium deuteride and lithium aluminum deuteride in tetrahydrofuran. Deuterium analyses showed that the final products were generally monodeuterated to the extent of 90% or better. The naphthalene compounds were prepared by treating the corresponding Grignard reagents with deuterium oxide.

For the conversion of the alcohols to the chloromethylarenes, we used initially the conventional technique of thionyl chloride and pyridine or refluxing with thionyl chloride alone. These techniques were found frequently to produce persistent colored impurities which could be removed only with substantial sacrifice of yield. We obtained better results by treating the solid carbinol with thionyl chloride in the cold for several minutes. Evacuation of the excess thionyl chloride left the crude chloromethyl compound which could be reduced without further purification to the hydrocarbon. Over-all yields by this method from carbinol to deuterated hydrocarbon ranged from 50 to 90%.

Attempts to prepare 9-methylphenanthrene by direct reduction of the carbinol with lithium aluminum hydride–aluminum chloride[9] proved unsuccessful even after prolonged refluxing. Unsuccessful attempts were also made to introduce deuterium via direct metalation of 3-methylphenanthrene and 2-methylanthracene using phenylsodium, butyllithium and ethyllithium in a variety of ether and hydrocarbon solvents. Either insufficient deuteration was accomplished or the conditions led to dideuteration and decomposition.

Experimental[10]

2-Methylnaphthalene-α-d.—The Grignard reagent was prepared from 24.6 g. of 2-chloromethylnaphthalene[11] and 7.0 g. of magnesium after an initial reaction with 5 ml. of n-butyl bromide. To the cooled mixture was added 10 ml. of deuterium oxide. Dilute hydrochloric acid was added and the washed and dried ether layer was distilled.[12] The product was distilled through a Podbielniak column; b.p. 95–96° (7 mm.). The resulting white crystals had m.p. 35.2–36.2° (lit.[13] m.p. 37–38°); picrate, m.p. 111–113° (lit.[13] m.p. 115°). The hydrocarbon showed a C–D band at 4.55 μ.

Anal. Calcd. for $C_{11}H_9D$: D, 10.0 atom %. Found: D, 8.3, 8.6 atom %.

1-Methylnaphthalene-α-d was prepared in a similar manner from the Grignard reagent of redistilled α-chloromethylnaphthalene and deuterium oxide.[12] The product was redistilled and the fraction b.p. 87.0–87.6° (4.0–4.5 mm.) was used for kinetics; $n^{25}D$ 1.6141 (lit.[14] $n^{25}D$ 1.6151); the C–D band showed a doublet at 4.58, 4.66 μ; picrate, m.p. 137–139° (lit.[15] m.p. 140°). The density, d^{25} 1.0235, corresponds to 0.998 atom of deuterium.[16]

3-Methylphenanthrene-α-d.—Commercial 3-methylphenanthrene was oxidized to the carboxylic acid by the method of Friedman, Fishel and Schechter.[17] A thick-walled glass tube was charged with 3.0 g. (0.015 mole) of 3-methylphenanthrene (K and K Laboratories) and 11.0 g. (0.036 mole) of sodium dichromate dihydrate. After addition of 20 ml. of water, the tube was

(1) This work was supported by the Directorate of Chemical Services, Air Force Office of Scientific Research, under grant no. 62-175 and contract No. AF 49(638)·105. Paper VI: A. Streitwieser, Jr., and R. A. Caldwell, J. Org. Chem., 27, 3360 (1962).

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sealed and heated at 250° for 72 hours. The tube was cooled to −78° and opened; the pressure released even at this low temperature probably resulted from thermal decarboxylation of the product acid. The contents were taken into aqueous potassium hydroxide and filtered. The filtrate was washed with benzene and acidified. The precipitate was dissolved again in base and reprecipitated with acid. Crystallization from acetic acid gave 3.2 g. (91%) of pale yellow crystals, m.p. 267–274° (lit.[18] m.p. 278.5–280°).

The carboxylic acid was converted to the ester in 75% yield in the usual way with ethanolic hydrogen chloride; m.p. 51–53° (lit.[19] m.p. 56–57°). Reduction of the ester with lithium aluminum hydride in ether gave 91% of white 3-phenanthrylcarbinol, m.p. 97–100.5° (lit.[20] m.p. 103–103.5°). The chloride was prepared with refluxing thionyl chloride.

A solution of 7.62 g. (0.037 mole) of 3-phenanthrylcarbinol in 50 ml. of dry benzene was refluxed for 10 min. with 60 ml. of freshly distilled thionyl chloride. The solvents were pumped off; the crystalline residue was taken up in a minimum of benzene and chromatographed repeatedly on neutral alumina to remove a persistent yellow oil. The product, 4.5 g. (45%), had m.p. 91.5° (lit.[21] m.p. 87.5°).

Anal. Calcd. for $C_{15}H_{11}Cl$: Cl, 15.54. Found: Cl, 15.62.

The reductions of the chloromethylarenes are exemplified by the following preparation: A solution of 4.25 g. (0.019 mole) of 3-chloromethylphenanthrene in 40 ml. of tetrahydrofuran, freshly distilled from lithium aluminum hydride, was added slowly to a slurry of 0.84 g. (0.02 mole) of lithium aluminum deuteride and 0.9 g. (0.1 mole) of lithium deuteride in tetrahydrofuran. After 5 hr. of reflux, an additional 0.4 g. (0.05 mole) of lithium deuteride was added and reflux was continued for 24 hr. The reaction mixture was quenched with water and extracted with benzene. The extract was washed with phosphoric acid and water and evaporated. The crude product was dissolved in hexane and chromatographed on neutral alumina to give 2.70 g. (77%) of white crystals which, on recrystallization from ethanol, had m.p. 67.2–68° (lit.[22] m.p. 65°); picrate, m.p. 140–141° (lit.[22] m.p. 141°). The infrared spectrum of the hydrocarbon showed a C–D stretching doublet, 4.50 and 4.55 μ.

Anal. Calcd. for $C_{15}H_{11}D$: D, 8.33 atom %. Found[23]: D, 8.33 atom %.

2-Methylpyrene-α-d.—Pyrene-2-carboxylic acid[24] was converted to the methyl ester with methanolic hydrogen chloride, reduced to the carbinol with lithium aluminum hydride and converted to 2-chloromethylpyrene with hydrogen chloride in benzene[25]; reduction with lithium deuteride and lithium aluminum deuteride in tetrahydrofuran gave 2-methylpyrene-α-d,[26] m.p. 143.5–144.5°. An authentic sample (Dr. Theodor Schuchardt, Munich) had m.p. 145–146° and a mixture m.p. showed no depression; picrate m.p. 195.4–195.6°. The infrared spectrum of 2-methylpyrene-α-d gave a C–D band at 4.57 μ.

9-Methylphenanthrene-α-d.—The conversion of 9-phenanthrylcarbinol to chloride using the "mild" conditions with thionyl chloride is typical of the procedure used with most of the compounds: To 3.12 g. (0.015 mole) of 9-phenanthrylcarbinol contained in a round-bottom flask was pipetted 30 ml. of redistilled thionyl chloride. Vigorous gas evolution occurred. With some compounds the mixture was contained in an ice-bath. After a reaction period of 3 min., the flask was attached to a rotary evaporator to remove excess thionyl chloride. Petroleum ether was added several times and evaporated to remove residual thionyl chloride. The addition of the initial petroleum ether caused crystallization of the oil. The crude product had m.p. 96–99°; one crystallization from heptane gave white crystals, m.p. 98–100° (lit.[27] m.p. 101–101.5°). The analysis of this sample was poor.

Anal. Calcd. for $C_{15}H_{11}Cl$: Cl, 15.64. Found: Cl, 14.31.

Reduction of the crude chloride with lithium deuteride–lithium aluminum deuteride gave 2.35 g. (81% from carbinol) of almost white crystals, m.p. 87.5–90°. Chromatography of a hexane solution on neutral alumina gave white crystals, m.p. 90–91° (lit.[28] m.p. 90–91°); picrate, m.p. 154.5–155.5° (lit.[28]

m.p. 152–153°). The infrared spectrum of the hydrocarbon showed a C–D doublet at 4.55 and 4.59 μ.

Anal. Calcd. for $C_{15}H_{11}D$: D, 8.33 atom %. Found: D, 7.8, 7.7, 8.0 atom %.

8-Methylfluoranthene-α-d.—8-Fluoranthenecarbinol,[26,29] 3.24 g., was converted to the chloride with 26 ml. of thionyl chloride at 0°. The crude product, m.p. 97–103° (lit.[4f] m.p. 102.7–103.7°), was reduced directly to the deuterated hydrocarbon, yielding 1.6 g. (53% from carbinol) of pale yellow crystals after chromatography on neutral alumina, m.p. 88–89° (lit.[29] m.p. 93–94°); picrate, m.p. 155–156° (lit.[29] m.p. 156–157°). The C–D band occurred at 4.56 μ.

Anal. Calcd. for $C_{17}H_{11}D$: D, 8.33 atom %. Found: D, 7.2, 7.1, 7.3 atom %.

1-Methylpyrene-α-d.—Five grams (0.0215 mole) of 1-pyrenecarbinol (from reduction of pyrene-1-aldehyde[24] with lithium aluminum hydride)[12] was treated with cold thionyl chloride, and the product was reduced with lithium deuteride–lithium aluminum deuteride to give 4.15 g. (89%) of 1-methylpyrene-α-d which was chromatographed twice in benzene on neutral alumina; m.p. 69.5–70.5° (lit.[24] m.p. 71–72°); picrate, m.p. 213–214° (lit.[24] m.p. 211–212°). The infrared spectrum showed a C–D doublet, 4.52, 4.61 μ.

Anal. Calcd. for $C_{17}H_{11}D$: D, 8.33 atom %. Found: D, 7.9, 8.1, 8.2 atom %.

2-Methylanthracene-α-d.—Commerical 2-methylanthraquinone was oxidized with chromic acid[30] and reduced with zinc dust and ammonia[31] to anthracene-2-carboxylic acid. Ethanolic hydrogen chloride gave the ester which was reduced with lithium aluminum hydride in ether to 2-anthracenylcarbinol, m.p. 221–222°. Treatment of 3.75 g. (0.018 mole) of carbinol with cold thionyl chloride and reduction with lithium deuteride–lithium aluminum deuteride gave 2.01 g. (58%) of fine white crystals of 2-methylanthracene-α-d, which, after crystallization from ethanol, had m.p. 205–205.8° (lit.[32] m.p. 207°); 2-methylanthracene does not form a stable picrate—the red-brown crystalline complex with 2,4,7-trinitrofluorenone has m.p. 179.2–180.2°; that formed with an authentic sample of 2-methylanthracene (prepared by zinc and aqueous ammonia reduction of 2-methylanthraquinone) had m.p. 178–180°. The infrared spectrum shows a C–D doublet, 4.51, 4.55 μ.

Anal. Calcd. for $C_{15}H_{11}D$: D, 8.33 atom %. Found: D, 8.0, 8.2 atom %.

4-Methylpyrene-α-d.—Pyrene-4-carboxylic acid was synthesized by the method of Berg[33] and converted to the methyl ester, m.p. 97–98° from methanol (lit.[33] m.p. 107–108°).[26] Lithium aluminum hydride gave 90% of the carbinol, m.p. 152–154° (lit.[33] m.p. 155–155.5°). Treatment of 1.80 g. (0.0077 mole) with cold thionyl chloride followed by lithium deuteride–lithium aluminum deuteride gave 0.79 g. (49%) of fine white crystals of 4-methylpyrene-α-d, m.p. 141–142° (lit.[34] m.p. 148.8–149.4°); picrate, m.p. 228–229° (lit.[34] m.p. 229–232° dec.). The infrared spectrum showed a C–D doublet, 4.49, 4.59 μ.

Anal. Calcd. for $C_{17}H_{11}D$: D, 8.33 atom %. Found: D, 7.75 atom %.

3-Methylfluoranthene-α-d.—The preparation of fluoranthene-3-carboxylic acid by metalation of fluoranthene with sodium in dimethoxyethane followed by carbonation[35] was found to be less convenient than the preparation from 3-bromofluoranthene. To a flask containing 125 ml. of 1.5 M butyllithium in heptane (Lithium Corp. of America) and 100 ml. of refluxing ether was injected a solution of 8.7 g. (0.031 mole) of 3-bromofluoranthene[36,37] in 700 ml. of ether. The mixture was refluxed for 1 hr. and poured onto Dry Ice. The precipitate was dissolved in ammonia, washed with methylene chloride and acidified to give 4.9 g. (64%) of crude carboxylic acid which was converted with refluxing ethanolic hydrogen chloride to ethyl fluoranthene-3-carboxylate, reduced to carbinol with lithium aluminum hydride, converted to chloride with thionyl chloride and finally reduced with lithium deuteride–lithium aluminum deuteride. The product was purified by chromatography on neutral alumina and *via* the picrate, m.p. 170.5–172° (lit.[38] m.p. 172°). The regenerated hydrocarbon gave yellow crystals from ethanol;

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TABLE I

EXCHANGE RATES OF DEUTERIOMETHYLARENES WITH LITHIUM CYCLOHEXYLAMIDE IN CYCLOHEXYLAMINE AT 49.9°

Ar in ArCH$_2$D	Concn. of hydrocarbon, M	Formal concn. of lithium cyclo-hexylamide, M	$10^5 k_{exp}$, sec.$^{-1}$	$10^5 k_1$, sec.$^{-1}$	$10^3 k_2$, 1. mole^{-1} sec.$^{-1}$	Weighted average[a] $10^3 k_2$, 1. mole^{-1} sec.$^{-1}$
1-Naphthyl	0.29	0.048	102	95.6	70.4	69
	.28	.062	108	100	67.9	
2-Naphthyl	.28	.051	74.5	69.0	49.8	50
	.26	.046	70.7	65.7	49.7	
3-Phenanthryl	.14	.088	193	185	114	94
	.14	.050	106	101	75	
9-Phenanthryl	.070	.096	223	218	131	129
	.072	.044	170	167	128	
2-Anthracenyl	.031	.046	260	260	197	210
	.023	.055	320	320	226	
1-Pyrenyl	.071	.011	640	630	(960)[b]	1300
	.069	.053	2080	2030	1450	
2-Pyrenyl	.096	.054	140	137	97	102
	.072	.047	144	141	106	
4-Pyrenyl	.033	.073	381	377	247	270
	.031	.044	385	380	288	
3-Fluoranthyl	.031	.062	(5000)	(5000)	(3000)[c]	(1400)
	.029	.036	(1630)	(1610)	(1360)	
8-Fluoranthyl	.071	.069	138	135	89	94
	.071	.052	143	139	100	

[a] For comparison, toluene-α-d has $k_2 = 6.70 \times 10^{-3}$ 1. mole^{-1} sec.$^{-1}$ (ref. 6a).   [b] Points in this run were spaced over an insufficient length of time, and this run is given less weight.   [c] This run went faster than expected; the result has low precision.

m.p. 62–63° (lit.[38] m.p. 66°). The C–D absorption in the infrared spectrum occurred at 4.58 μ.

Anal. Calcd. for C$_{17}$H$_{11}$D: D, 8.33 atom %. Found: D, 6.0, 6.3 atom %.

Kinetics.—The rates of exchange for some of the compounds were followed using modifications of exchange procedure (B) described earlier.[6a,39] For some compounds, particularly the relatively reactive hydrocarbons, the following improved procedure was used: weighed methylarene was dissolved in spectral grade 2,2,4-trimethylpentane (in some cases, reagent grade chloroform was added to produce solution) and syringed into one side of the reaction vessel in Fig. 1 which had first been baked overnight at 150° and flamed out with a nitrogen purge. The solvent was pumped out on the vacuum line and the reaction vessel was filled with nitrogen. A known amount of butyllithium (Foote) in pentane–heptane was injected into the other arm and the solvent was pumped off. Cyclohexylamine was vacuum transferred in and the liberated butane was pumped off in the cold. The hydrocarbon was allowed to dissolve completely in its half. In all cases, solubility was sufficient for kinetic study. While the reaction vessel was maintained at −80°, purified nitrogen was admitted and the reaction vessel was placed in the thermostat. At equilibrium, the solutions were mixed and the first aliquot was taken by allowing the nitrogen pressure to force 4 ml. of reaction solution through the capillary side-arm into 1 ml. of water. For the fast reactions (half-lives < 1 min.) the operation was dictated into a tape recorder registering the start and end of an aliquot (∼1 sec.). The middle time was taken to represent the elapsed time for the aliquot.

Lithium cyclohexylamide concentrations were determined by titration of aliquots quenched with water and evaporated as described earlier.[6a]

The deuterium contents of methylarene aliquots were determined by infrared spectra of 5–10 mole per cent solutions in carbon tetrachloride using 1-mm. cells. The intensity of a C–D band at about 4.5 μ was used in conjunction with a band at about 5.1 μ used to normalize the concentration of hydrocarbon. The latter band is generally accurately constant for hydrogen and deuterium compounds. In a few cases, Beer's law was confirmed by calibration spectra. In others, Beer's law was implied by the first-order behavior observed. Pseudo-first-order rate constants were obtained from semi-log plots of the deuterium content minus infinity values *vs.* time.

2-Methylanthracene was insufficiently soluble to permit use of infrared spectra for accurate analyses. Loss of deuterium from this compound was followed by observing the increase of methyl-hydrogen resonance in the n.m.r. spectrum using a Varian Associates model A60 analytical n.m.r. spectrometer. A number of spectra were run for each point, but the precision by this method is lower than in infrared analysis.

The experimental rate constants, k_{exp}, were corrected for the back reaction and converted to the true pseudo-first-order rate

constants, k, by equation 8 of reference 6a. The experimental lithium cyclohexylamide concentrations were used with equation 16 of reference 6a to derive the corresponding second-order rate constants, k_2. The experimental results and the derived kinetic constants are summarized in Table I.

Several hydrocarbons gave colored solutions during a kinetic run. These colors may be due to significant concentrations of arylmethyllithium derivatives, but the change in color during the course of a run in some cases indicates some side reactions. Because of the satisfactory and reproducible kinetics obtained, such side reactions are apparently unimportant except for the case of 3-methylfluoranthene. This compound gives a kinetic solution which is momentarily an intense blue-green, but the color changes rapidly to an intense brown-black which is nearly opaque. After 50 seconds, about 90% of the hydrocarbon is destroyed. A second kinetic run used methylfluoranthene aliquots from early reaction times and gave reasonable kinetic behavior; however, the significance of the derived rate constants is doubtful and they are enclosed in parentheses in Table I. The main product isolated by chromatography of material salvaged from these runs was a pale yellow amorphous powder with blue-green fluorescence, m.p. 272–278° (s. 235°). The infrared spectrum (KBr pellet) showed only poorly resolved aromatic bands. The product appears to be dimeric and was not studied further.

Anal. Calcd. for (C$_{17}$H$_{12}$)$_2$: C, 94.40; H, 5.60; mol. wt., 432. Found: C, 94.53; H, 5.47; mol. wt., 412.

Results and Discussion

The kinetic results summarized in Table I cover a variation of reactivity of 200-fold and a reproducibility generally better than 10%. The colors produced by some of the hydrocarbons in the lithium cyclohexyl-amide–cyclohexylamine solution (3-methylphenanthrene, red; 1-methylpyrene, violet; 2-methylanthracene, yellow; 8-methylfluoranthene, yellow-brown) deserve comment. These colors may represent the spectra of the corresponding arylmethyllithium derivatives present in small concentration. Although in most cases the colors seemed relatively stable, in a few cases they changed with time (2-methylanthracene changed from yellow to green over a several-hour period). Electron spin resonance measurements were made on some of the infinity solutions. Samples from both runs with 3-methylfluoranthene-α-d gave an apparent septuplet with a g-value of 2.0026. A sample from an 8-methylfluoranthene-α-d run gave a sextuplet spectrum. No detectable signal was obtained from a 2-methylanthracene-α-d run.[40] These phenomena are

(39) For further details, see W. C. Langworthy, Ph.D. Dissertation, University of California, 1961.

(40) We are indebted to Professor R. J. Myers for these e.s.r. determinations.

currently under detailed study; subsequent results indicate, for example, that the e.s.r. signals are due to radical anions formed by reduction of the hydrocarbons by lithium cyclohexylamide.[41] The radical anion was shown also not to be important for 2-methylpyrene, which, with lithium metal in cyclohexylamine, gives a red-orange solution[41] differing substantially from the intense blue-green color of a kinetic run.
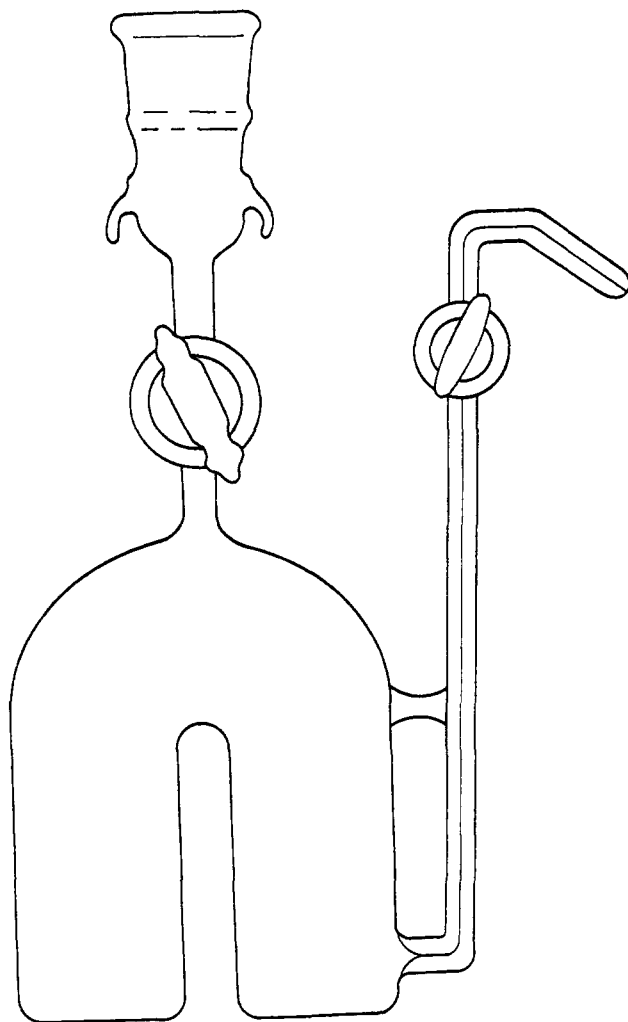

Fig. 1.—Reaction flask used for fast reactions.

For the most part, these phenomena apparently do not affect the interpretation of the kinetics; the infrared spectra of the kinetic aliquots corresponded to those expected for the partially deuterated hydrocarbons. Only in the case of 3-methylfluoranthene was anomalous behavior observed (see Experimental). The rate constant for 3-methylfluoranthene-α-d must be treated with reservations.

For the other compounds, however, the rate constants would appear to be valid measures of the base-catalyzed exchange rate, and, consequently, to be related closely to the acidities of the hydrocarbons. As expected, the polycyclic hydrocarbons with their more extensive π-systems are more reactive than toluene. These reactivities are compared with the theoretical predictions of simple molecular orbital theory in the following paper. At this point, it is instructive to compare the present reactivities with analogous carbonium ion reactions. Consider the following reactions in the gas phase
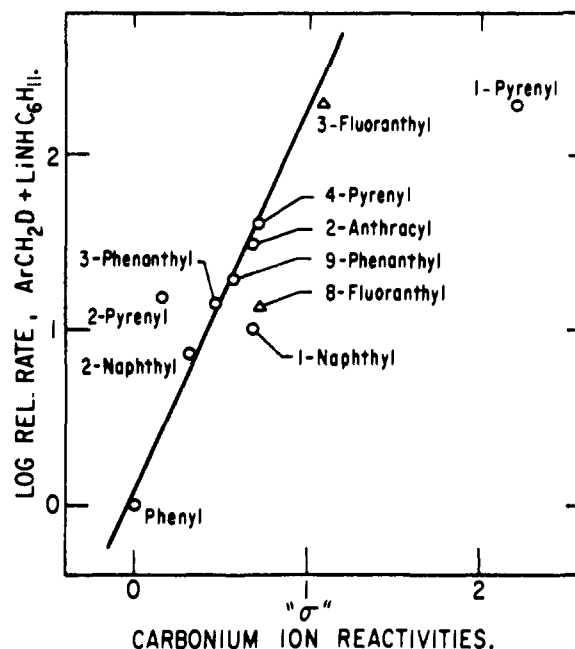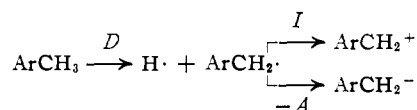
(41) R. G. Lawler, unpublished results.

Fig. 2.—Comparison of base-catalyzed exchange rates with rates of related carbonium ion solvolyses.

$$\mathrm{ArCH_3} \xrightarrow{D} \mathrm{H\cdot + ArCH_2\cdot} \begin{array}{c} \xrightarrow{I} \mathrm{ArCH_2^+} \\ \xrightarrow{} \mathrm{ArCH_2^-} \\ {\scriptstyle -A} \end{array}$$

D is the bond dissociation energy, I is the ionization potential and A is the electron affinity. Relative to a standard, the energy difference for formation of the arylmethyl anion, $\Delta E_i^- = \Delta D_i - \Delta A_i$, whereas for the arylmethyl cation, $\Delta E_i^+ = \Delta D_i + \Delta I_i$. Hush and Pople[42] have proposed and justified by a molecular orbital method which included specific incorporation of electron repulsion terms, that for alternant hydrocarbon systems, $A + I =$ a constant. If this assumption is correct, it follows that $\Delta E_i^- = \Delta E_i^+$.

The relative rates of solvolysis of many polycyclic arylmethyl systems in various solvents[4] are interrelated and seem clearly to be proportional to ΔE_i^+. These interrelationships have been developed in the form of a typical Hammett type of $\sigma\rho$ treatment in which each arylmethyl structure has an associated "σ" value and in which "ρ" is characteristic of the solvolysis system.[5] "ρ" has been defined as 1.00 for $\mathrm{ArCH_2Cl}$ in 80% aqueous ethanol and ranges up to 4.5 for solvolyses of $\mathrm{ArCH_2Cl}$ in formic acid. A proportionality between solvolysis rates and gas phase ΔE^+ values has been established for substituted benzyl systems.[43,44] A related proportionality is implied by the success of various molecular orbital correlations of carbonium ion reactions in which solvation energies are also neglected. This argument leads to the conclusion that our relative rates for base-catalyzed exchange should be proportional to the carbonium ion "σ" values. These values are summarized in Table II and are compared in Fig. 2. Most of the compounds define a remarkably good line, but there are serious deviations. The non-alternant fluoranthyl systems were included for interest, although the theory does not encompass these compounds; it is interesting that the 3-fluoranthylmethyl system whose exchange rate is in question

(42) N. S. Hush and J. A. Pople, *Trans. Faraday Soc.*, **51**, 600 (1955)

(43) A. G. Harrison, P. Kebarle and F. P. Lossing, *J. Am. Chem. Soc.*, **83**, 777 (1961).

(44) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 179.

TABLE II

COMPARISON OF ARYLMETHYL CARBONIUM ION AND CARBANION
REACTIVITIES

Ar of ArCH₂D or ArCH₂X	ArCH₂D + LiNHC₆H₁₁ 49.9° rel. rate	"σ"ᵃ
Phenyl	1	0.00
1-Naphthyl	10.3	.68 ± 0.10
2-Naphthyl	7.4	.31 ± .03
3-Phenanthryl	14	.46 ± .05
9-Phenanthryl	19	.56 ± .03
2-Anthracenyl	31	.67 ± .03
1-Pyrenyl	190	~2.2
2-Pyrenyl	15	0.15 ± 0.06
4-Pyrenyl	40	0.70 ± 0.06
3-Fluoranthyl	(200)	~1.08
8-Fluoranthyl	14	~0.73

ᵃ From ref. 5.

fits rather well, whereas the point for the 1-pyrenyl-methyl system deviates beyond hope. The deviations of 1-naphthylmethyl and 2-pyrenylmethyl are also far outside of combined experimental errors and emphasize the basic limitations of this sort of correlation. These deviations may result from a breakdown of Pople and Hush's proposal that $I + A$ = constant. It is interesting in this regard that the 1-pyrenylmethyl cation and 2-pyrenylmethyl anion are apparently more stable than expected on molecular orbital grounds.[5,45]

The slope of the line in Fig. 2 corresponds to "ρ" = 2.2, a value that shows substantially less variation of rate with structure than that shown by some solvolytic reactions, for example, the acetolyses of arylmethyl p-toluenesulfonates ("ρ" = 4.5).[5] This may be a reflection of differences in charge in the hydrocarbon moiety of the various transition states.

(45) A. Streitwieser, Jr., W. C. Langworthy and J. I. Brauman, following paper.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY 4, CALIF.]

Acidity of Hydrocarbons. VIII. An HMO Examination of Exchange Rates of Methylarene-α-d's with Lithium Cyclohexylamide[1,2]

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The HMO method is shown to provide a fair correlation of the experimental results reported in the preceding paper. Application of MO theory suggests that the McEwen scale of hydrocarbon acidities is seriously compressed and new values are tentatively assigned.

In the preceding paper[1] in this series, the rates of exchange were determined for a number of polycyclic methylarene-α-d's with lithium cyclohexylamide in cyclohexylamine. In previous studies of the mechanism of this exchange reaction, it has been shown to high probability that in the rate-determining step the hydrocarbon reacts with monomeric lithium cyclohexylamide to form the corresponding arylmethyllithium intermediate via a transition state that has substantial carbanionic character.[4] The present series is ideally suited to an attempted correlation of relative reactivity with molecular orbital theory.

The approach used is that which has been found to be successful in other applications of molecular orbital theory to the general problem of the effect of structure on reactivity.[5] The effect of structure is put entirely into the π-electronic change; π-energies are calculated in the usual Hückel molecular orbital (HMO) method with the reactant taken as the parent unsubstituted hydrocarbon and the transition state calculated as the corresponding arylmethyl anion

$$\Delta E_\pi(\text{ArCH}_2\text{D}) = E_\pi(\text{ArCH}_2^-) - E_\pi(\text{ArH}) \quad (1)$$

$$= 2\alpha + \Delta M_i\beta \quad (2)$$

A successful correlation presumes a linear relation between the experimental relative rates and the calculated ΔM values of the form

$$\log k_i/k_0 = a + b\Delta M_i \quad (3)$$

(1) Paper VII: A. Streitwieser, Jr., and W. C. Langworthy, J. Am. Chem. Soc., 85, 1757 (1963).

(2) This work was supported in part by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under grant no. 62-175 and contract no. AF-49(638)-105.

(3) (a) Alfred P. Sloan Fellow, 1958-1962; (b) National Science Foundation Coöperative Fellow, 1959-1960; (c) National Science Foundation Predoctoral Fellow, 1959-1962.

(4) A. Streitwieser, Jr., et al., J. Am. Chem. Soc., 84, 244, 249, 251, 254, 258 (1962).

(5) Examples are summarized in A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," J. Wiley and Sons, Inc., New York, N. Y., 1961.

The relative exchange rates from ref. 1 and the corresponding calculated ΔM values are summarized in Table I and are plotted in Fig. 1. Methyl groups at

TABLE I

ANIONIC REACTIVITIES OF METHYLARENES

Ar in ArCH₂D	Rel. exch. rate with LiNHC₆H₁₁, 50° (ref. 1)	ΔM_iᵇ
Phenyl	1.0	0.721
1-Naphthyl	10.3	.812
2-Naphthyl	7.4	.744
3-Phenanthryl	14	.754
9-Phenanthryl	19	.813
2-Anthracyl	31	.769
1-Pyrenyl	190	.868
2-Pyrenyl	15	.717
4-Pyrenyl	40	.828
3-Fluoranthyl	(200)ᵃ	.943
8-Fluoranthyl	14	.764

ᵃ This number is unreliable because of side reactions during kinetic runs; see ref. 1. ᵇ These values were calculated with programs written by us and using standard library routines on the IBM 704 computer of the Computer Center, University of California.

the unhindered positions, phenyl, 2-naphthyl, 3-phenanthryl and 2-anthracyl, provide an excellent linear correlation between theory and experiment. Methyl groups at the more hindered "α-naphthyl"-type positions form a separate correlation in common with related carbonium ion examples.[6] The steric argument used for solvolysis reactions of arylmethyl halides would appear to apply equally well in the present case; that is, in anions of the α-naphthylmethyl type, steric interference with the neighboring peri-hydrogen opposes complete coplanarity of the exocyclic methylene group with the aromatic ring and reduces conjugation with

(6) P. J. C. Fierens, H. Hannaert, J. V. Rysselberge and R. H. Martin, Helv. Chim. Acta, 38, 2009 (1955); M. J. S. Dewar and R. J. Sampson, J. Chem. Soc., 2789 (1956).