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.

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

BY A. STREITWIESER, JR.,[3a] W. C. LANGWORTHY[3b] AND J. I. BRAUMAN[3c]

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

$$\Delta E_\pi(ArCH_2D) = E_\pi(ArCH_2^-) - E_\pi(ArH) \quad (1)$$

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

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

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

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_i[b]
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

(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.

(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).
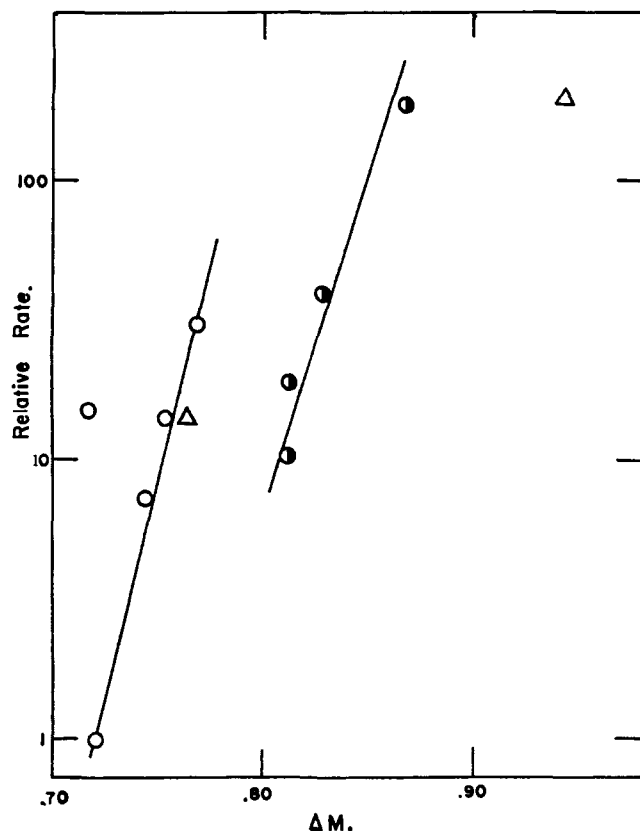
Fig. 1.—Correlation of exchange reactions of methylarene-α-d's with lithium cyclohexylamide with HMO calculations: open circles, toluene type methyls; Half-closed circles, α-naphthyl type; triangles, fluoranthene compounds.

the ring below that calculated—coplanarity is assumed in HMO calculations. The α-naphthyl compounds form a fair linear correlation of their own in which the correlation line is drawn parallel to that of the unhindered compounds in Fig. 1 and displaced by 0.06β. A correction to the conjugation energy can be applied using the usual equation for the effect of angle on β[7]

$$\beta = \beta_0 \cos \theta \tag{4}$$

To a first approximation, the effect of a small change in β on E_π is given by eq. 5 in which p is the bond order of the bond to the methylene group[8]

$$\delta E_\pi \cong 2p\delta\beta_{rs} \tag{5}$$

$$\cong 2p(1 - \cos \theta) \tag{6}$$

The displacement of the α-naphthyl correlation corresponds to an average twist of 17° for the exocyclic methylene group in these cases.[9] This effect can be used as the basis for a correction to the calculated ΔE_π that would put these compounds on the same basic correlation as the unhindered benzylic systems.

Some of the methylarenes included in the kinetic survey were chosen because of special properties. The derivatives of the non-alternant hydrocarbon fluoranthene were included in this study because such non-alternant systems frequently deviate from correlations obeyed by alternant systems. In the present case, however, 8-methylfluoranthene has reactivity close to that expected for other non-hindered compounds. The experimental reactivity of the 3-methylfluoran-

(7) R. G. Parr and B. L. Crawford, Jr., J. Chem. Phys., 16, 526 (1948); M. J. S. Dewar, J. Am. Chem. Soc., 74, 3345 (1952); ref. 5, p. 105.

(8) C. A. Coulson and H. C. Longuet-Higgins, Proc. Roy. Soc. (London), A191, 39 (1947).

(9) p for the exocyclic bonds has the values: 1-naphthylmethyl, 0.688; 9-phenanthrylmethyl, 0.689; 1-pyrenylmethyl, 0.714; 4-pyrenylmethyl, 0.694.

thene system is uncertain because of the side reactions mentioned in ref. 1. Accordingly, the wide divergence from theoretical reactivity of this system suggested by the present results does not have a sound experimental basis.

The 2-pyrenylmethyl system is an unhindered odd alternant system and was included because in solvolytic reactions 2-pyrenylmethyl compounds often react faster than expected on the basis of simple HMO theory.[10] In the present exchange reaction, 2-methyl-pyrene is over fifteen times more reactive than predicted. No satisfactory explanation for this large deviation is available in the simple theory. The effects of electronic repulsion which are not taken into explicit account in the HMO method may provide an explanation; the similar deviations of 2-pyrenylmethyl systems in carbonium ion reactions are apparently the result of this neglect and are interpretable by application of the ω-technique.[11]

In this treatment, the Coulomb integral of each carbon is altered in proportion to the π-charge density on the carbon. The effect on the π-energy may be given in terms of a power series expansion[12]

$$\delta E_\pi/\beta = \omega\Sigma q_r(1 - q_r) + \frac{\omega^2}{2}\Sigma\Sigma\pi_{rs}(1 - q_r)(1 - q_s) + \ldots \tag{7}$$

q_r is the electron density, ω is the additional parameter of the ω-technique and π_{rs} is the atom–atom polarizability. The first term on the right implies a correlation with the sum of the squares of the charge densities of the type discussed by Mason[13] for carbonium ion reactions. In the present case of carbanion exchange reactions, such a correlation is mediocre and shows much scatter. Inclusion of the second term on the right of eq. 7 requires a value for ω. For carbonium ions, a value close to 1.4 seems to be well established[14]; however, for carbanions, a value of 3.8 has been suggested recently to correlate better the electron affinities of hydrocarbons.[15] In the present application, the use of $\omega = 1.4$ gives a correlation no better than that in Fig. 1, whereas the use of $\omega = 3.8$ gives a different but also mediocre correlation in which 2-methylpyrene is predicted to be 10^{11} more reactive than it is! We believe that a more detailed discussion of the application of the ω-technique to carbanions is not warranted at this time but should await additional experimental and theoretical results.

Up to now we have viewed the exchange reaction as a base-catalyzed proton exchange of hydrocarbons; however, we may also view the reaction as a rate-determining proton transfer to a base. In this interpretation the hydrocarbons serve as general acids. This approach suggests the application of the Brönsted relationship, eq. 8, in which the logarithm of the relative exchange rate is proportional to the relative equilibrium acidity of the hydrocarbon.[16] The parameter α can vary between 0 and 1 and is a measure of the extent of proton transfer at the transition state; that is, α is a measure of the degree to which the hydro-

$$-\log k_i/k_0 = \alpha\Delta pK_i \tag{8}$$

(10) M. Planchon, P. J. C. Fierens and R. H. Martin, Helv. Chim. Acta, 42, 517 (1959); A. Streitwieser, Jr., R. H. Jagow and R. M. Williams, unpublished results; see ref. 5, p. 371.

(11) Reference 5, p. 376.

(12) A. Streitwieser, Jr., J. B. Bush and J. I. Brauman, Tetrahedron, in press.

(13) S. F. Mason, J. Chem. Soc., 808 (1958).

(14) Reference 5, sec. 4.5.

(15) S. Ehrenson, J. Phys. Chem., 66, 706, 712 (1962).

(16) For modern discussions, see A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1961, p. 218, and S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, sec. 16.3.

carbon moiety in the transition state resembles the free carbanion. Because the carbanion was also used as the model of the transition state in the HMO treatment of our exchange reaction, we expect that the value of α should also be reflected in the effective value of β for the HMO correlation in the same way that this effective value of β reflects the carbonium ion character of the transition state in HMO correlations of solvolysis reactions.[6,17] The correlation of Fig. 1 corresponds to an effective value of β for our exchange reaction of -49 kcal.[18]

Several decades ago, McEwen[19] presented a list of pK's of some hydrocarbons based on his experiments and those of Conant and Wheland.[20] These pK's have been found[21] to provide a satisfactory correlation with the HMO method and the same theoretical model used in this paper; however, the effective value of β for that correlation is only -22 kcal. At face value, these results imply that α for the exchange rates has the impossible value of 2.2! Analysis suggests strongly that the trouble lies in McEwen's pK assignments. These values were assigned on the basis of exchange reactions of hydrocarbons with alkali metal salts of hydrocarbons. With the less acidic hydrocarbons, no measurement of equilibrium constant was possible, the direction of the equilibrium (by color or by carbonation) being used to assign arbitrarily a ΔpK of 2 units between adjacent hydrocarbons in a series. It seems probable that McEwen's scale is seriously com-

(17) M. J. S. Dewar and R. J. Sampson, J. Chem. Soc., 2946, 2952 (1957); ref. 5, sec. 12.3.

(18) Effective values of β of this magnitude are given by several types of HMO correlations. Pertinent to the present discussion is the value -55 kcal., given by correlations of polarographic reduction potentials of hydrocarbons in which carbanions are also involved.[5]

(19) W. K. McEwen, J. Am. Chem. Soc., 58, 1124 (1936).

(20) J. B. Conant and G. W. Wheland, ibid., 54, 1212 (1932).

(21) A. Streitwieser, Jr., Tetrahedron Letters, No. 6, 23 (1960).

pressed for pK's of hydrocarbons above the early twenties. In the intervening years since McEwen's paper, his pK's have been widely quoted and used, and few serious attempts have been reported to obtain more quantitatively reliable equilibrium constants for hydrocarbons.[22] Such experiments are now in progress in our laboratory, but a report of results at this time would be premature. Meanwhile, however, a revised scale of acidities can be established *tentatively* on the basis of the MO correlations, the more soundly established pK's of comparatively acidic hydrocarbons and the assumption that the Brönsted α equals unity for our exchange reaction. This treatment leads to eq. 9, from which the pK's in Table II are derived. Note that the use of a smaller value for the Brönsted α would result in further spreading of the acidity scale.

$$pK = 84 - 35\Delta M_i \qquad (9)$$

TABLE II

REVISED ACIDITIES OF HYDROCARBONS

Hydrocarbon	pK, eq. 9	pK, exptl.
Fluoradene	10	11–12[a]
Cyclopentadiene	14	14–15[b]
Indene	23	~21[c]
Fluorene	31	
4,5-Methylenephenanthrene	31	
Cycloheptatriene	45	
2-Methylanthracene	57	
Toluene	59	
Methane	84	

[a] In water; H. Rapoport and G. Smolinsky, J. Am. Chem. Soc., 82, 934 (1960). [b] R. E. Dessy, Y. Okuzumi and A. Chen, ibid., 84, 2899 (1962). [c] Ref. 19.

(22) As one noteworthy exception, the equilibrium acidity of 9-phenylfluorene is apparently well established (pK = 18.49) in aqueous sulfolane: C. H. Langford and R. L. Burwell, Jr., J. Am. Chem. Soc., 82, 1503 (1960).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE 39, MASS.]

Application of Mass Spectrometry to Structure Problems. XIII.[1] Acetates of Pentoses and Hexoses[2]

BY K. BIEMANN, D. C. DEJONGH AND H. K. SCHNOES

RECEIVED DECEMBER 31, 1962

The mass spectra of a number of monosaccharide polyacetates (aldohexoses, ketohexoses, deoxyhexoses, pentoses, pyranoses and furanoses) are discussed and a detailed interpretation of the fragmentation processes which these molecules undergo is presented. The various types mentioned above can be differentiated on the basis of their characteristic fragmentation, but it is more difficult to distinguish epimers. The proposed fragmentation processes are supported by the spectra of isotopically labeled compounds, mainly trideuterioacetates.

During the last few years the usefulness of mass spectrometry as a technique for the determination of the structure of complex organic molecules has been demonstrated, and the method has been applied successfully to a wide variety of compounds.[3] Areas having received more detailed attention encompass lipids,[4a] steroids,[4a,b,c] amino acids,[4d,e] peptides[4d,e] and alkaloids[4f];

(1) Part XII: K. Biemann, H. K. Schnoes and J. A. McCloskey, Chem. Ind. (London), 448 (1963).

(2) Presented in part at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., September, 1962. For a preliminary communication see ref. 1.

(3) For a summary see K. Biemann, "Mass Spectrometry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

(4) For recent reviews see (a) R. Ryhage and E. Stenhagen, J. Lipid Research, 1, 361 (1960); (b) S. Bergström, R. Ryhage and E. Stenhagen, Svensk Kem. Tidskr., 73, 11 (1961); (c) C. Djerassi, H. Budzikiewicz and J. M. Wilson, "Proc. Intern. Congress Hormonol Steroids, Milano, May, 1962, Academic Press, Inc., New York, N. Y., in press; (d) K. Biemann, Chimia, 14, 393 (1960); (e) E. Stenhagen, Z. anal. Chem., 181, 462 (1961); (f) ref. 3, Chapter 8.

the number of compounds whose structure was elucidated, in part or entirely, by mass spectrometry is already considerable.[3]

Very little has been done in the area of carbohydrate chemistry, and only a few sporadic notes have been published by Reed and collaborators. Their first note[5] reports the results of appearance-potential measurements on the $C_6H_{11}O_5{}^+$ ion derived from α- and β-methylglucopyranosides and four disaccharides. The result, namely, a slightly lower appearance potential for the ion derived from α-glycosides, is interpreted as being due to a weakening of the bond as compared with β-glycosides. In view of the small differences reported and the difficulties inherent in the determination of accurate appearance potentials with conventional instruments, the technique seems to be of little practical

(5) P. A. Finan, R. I. Reed and W. Snedden, Chem. Ind. (London), 1172 (1958).