is indicated by the coefficient of about 0.4 kcal/mol in the free energy of activation[14] per part per million shift on ionization in magic acid.

Acknowledgment. We are pleased to acknowledge the assistance of Miss Karin Schneider in part of the experimental work. Helpful discussions with Dr. Stanton Ehrenson and Professors H. C. Brown, G. A. Olah, V. J. Shiner, Jr., and M. Wolfsberg are gratefully acknowledged.

(14) V. J. Shiner, Jr., W. E. Buddenbaum, B. L. Murr, and G. Lamaty, *J. Amer. Chem. Soc.*, **90**, 418 (1968).

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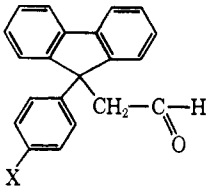
Substituent Effects at a Radical Migration Origin

Sir:

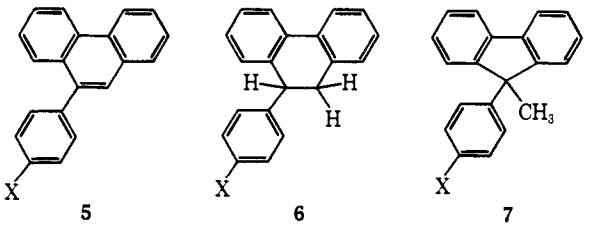
Free-radical aryl migrations have been under investigation by organic chemists for over two decades, but, except for the illuminating work of Rüchardt and coworkers[1] on the migratory aptitudes of substituted phenyl groups, little is known concerning the nature of the rearrangement transition state and the effects of substituents upon its stability. The interesting observation[2] that (9-phenyl-9-fluorenyl)acetaldehyde (**1**), upon peroxide-induced decarbonylation, gives a radical which undergoes 100% rearrangement with the exclusive migration of the phenylene ring prompted us to investigate the reaction further. Clearly, this system presents a unique opportunity to study the effects of various substituted phenyl groups at the migration origin of free-radical rearrangement reactions and avoids the possibility that such a group would compete in the rearrangement.

Accordingly, compounds, **1**, **2**, **3**, and **4** were synthesized for this purpose.



1, X = H
2, X = OCH_3
3, X = CH_3
4, X = Cl

These particular substituents were chosen because they correlated well in Rüchardt's work. All of the decarbonylation reactions were carried out under the same experimental conditions in the presence of benzyl mercaptan. In each case, 20 mol % of the mercaptan was added to a 0.5 *M* solution of the aldehyde in 1,2-dichlorobenzene. The solution was first degassed to remove oxygen and then it was maintained at 140 ± 0.01° and two quantities of di-*tert*-butyl peroxide consisting of 20 mol % each were added initially and after 120 min (40 mol % total amount), the total reaction time being 330 minutes. The rates of carbon monoxide evolution were measured and from these it was found that all four aldehydes undergo decarbonylation at the same rate, to the same extent, and presumably, therefore, by the same mechanism. The products, isolated by preparative tlc and column chromatography and characterized by elemental analysis and ir and nmr spectroscopy, were found to be 9-(*p*-X-phenyl)phenanthrenes **5**, 9,10-dihydro-9-(*p*-X-phenyl)phenanthrenes **6**, and 9-methyl-9-(*p*-X-phenyl)-fluorenes **7** (X = OCH_3, CH_3, H, or Cl).



5 **6** **7**

The product percentages were determined by nmr, and the results are shown in Table I.

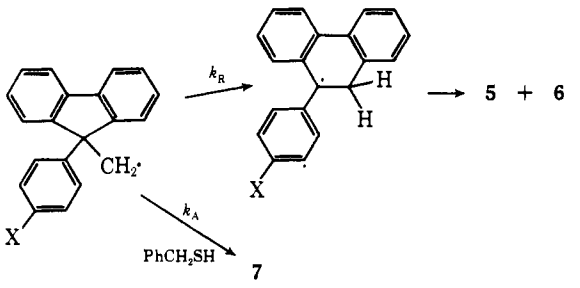
Table I. Product Percentages[a]

Substituent	% 5	% 6	% 7
OCH_3	54	23	23
CH_3	54	26	20
H	53	28	19
Cl	54	31	15

[a] Error is ±1%.

When the reaction was run in the absence of the mercaptan no **7** could be isolated. The presence of the benzyl mercaptan thus has the effect of trapping the unrearranged radical to produce **7**. In the presence of mercaptan the initial radical formed by decarbonylation is involved in a competition between rearrangement and hydrogen atom abstraction as shown in Scheme I.

Scheme I



Assuming that the rate constant for hydrogen-atom abstraction, k_A, is independent of the substituent X (a reasonable assumption when one considers the distance of the substituent from the radical center), an equation can be developed which allows the calculation of the relative rate constants for the rearrangement steps.

$$\frac{\text{rearranged product}}{\text{unrearranged product}} = \frac{k_R}{k_A[PhCH_2SH]} = \frac{\%\,5 + \%\,6}{\%\,7}$$

(1) C. Rüchardt and R. Hecht, *Chem. Ber.*, **98**, 2471 (1965), and preceding papers.
(2) B. M. Vittimberga, *Tetrahedron Lett.*, 2383 (1965).

$$\text{rel } k_R = \frac{\left(\frac{\text{rearranged}}{\text{unrearranged}}\right)_X}{\left(\frac{\text{rearranged}}{\text{unrearranged}}\right)_H} = \frac{(k_R)_X}{(k_R)_H}$$

The product ratios and relative rearrangement rate constants are shown in Table II.

Table II. Product Ratios and Relative Rate Constants

Substituent	Rearranged / Unrearranged	Relative k_R rearrangement aptitude	Rüchardt[a] migration aptitude
OCH_3	3.35	0.785	0.35
CH_3	4.00	0.938	0.65
H	4.26	1.000	1.00
Cl	5.67	1.329	1.82

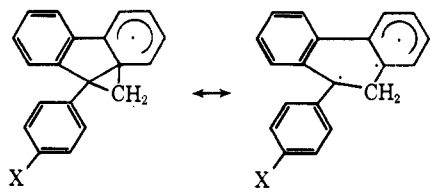
[a] See ref 1.

A good Hammett correlation was obtained by plotting log relative k_R *vs.* σ, and the value of the reaction constant was calculated by the method of least squares to be +0.426. This rearrangement is, therefore, facilitated to a small degree by electron-withdrawing substituents on a benzene ring attached to the migration origin.

Rüchardt's picture of the rearrangement transition state as a semipolar hybrid with partial positive character at the migration origin is, however, incompatible with these results. Based on our data, such a semipolar transition state for our system would require the migration origin to have a partial negative charge. Results on the analogous rearrangement of the 2,2-diphenyl-2-(*p*-nitrophenyl)ethyl radical[3] indicate, however, that no charge reversal is involved.

Interestingly, the present results on the effects of substituents at the migration origin (rearrangement aptitudes) and Rüchardt's results on the effects of substituents attached to the migrating aromatic nucleus (migration aptitudes) are of different magnitudes *but in the same direction* (Table II). This is clearly demonstrated by the linear relationship which is obtained by plotting the logarithms of the relative rearrangement rate constants obtained in the present study against those obtained by Rüchardt. The slope of this line (+3.11) shows that the effect of a substituent on an aromatic ring at the migration origin is approximately one-third the effect of the same substituent on the aromatic ring which is migrating. This could simply be due to the greater distance of the substituent from the radical center in the fluorenyl system.

We have concluded from these results that for the substituents studied the transition state for a free-radical aryl migration is purely radical in character,



8

(3) D. Y. Curtin and J. C. Kauer, *J. Org. Chem.*, **25**, 880 (1960).

with contributing structures such as shown in **8** for this study.

Rüchardt found that some substituents such as the nitro and cyano groups increased the migration aptitude by a very large extent and consequently did not lie on the straight line. It is likely with very strong election-withdrawing groups that ionic contributions are important.

Further work is in progress with these systems and a complete report is forthcoming.

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Nuclear Magnetic Resonance Determination of Syn and Anti Conformations in Pyrimidine Nucleosides

Sir:

Recently considerable study has been directed toward determination of the relative positions of sugar and base moieties about the glycosidic bond in nucleosides and nucleotide derivatives. Crystallographic data[1] have shown that in most cases the anti conformational range for the torsion angle, ϕ_{CN}, is preferred.[2] However, for purine nucleosides substituted in the 8 position with bulky groups, both X-ray data on the crystals[3] and CD spectra in aqueous solution[4] indicated predominantly syn conformers. In terms of biological significance, it has been shown that certain enzymes catalyzing polynucleotide synthesis will not function with purine and pyrimidine nucleoside di- or triphosphate substrates not having normal anti conformations, including the di- or triphosphate of 6-methylcytidine.[5,6]

We wish to report a facile determination of syn and anti conformation in various substituted pyrimidine nucleosides in solution using nuclear magnetic resonance. Nmr techniques have previously been successful in determination of conformation about the glycosidic bond in some nucleosides, nucleotides, and dinucleoside monophosphates.[7-10] In this communication we make use of the 2-keto anisotropic effect upon ribose proton chemical shifts to determine syn and anti nucleoside conformation.

Chemical shifts for several pyrimidine nucleosides are presented in Table I. Comparison of 5- and 6-methylcytidine and 5- and 6-methyluridine reveals a significant deshielding at H-2′ (0.5–0.6 ppm) and at H-3′ (0.15–0.2 ppm) in the 6-methyl derivatives. Concomitant with

(1) M. Sundaralingam, *Biopolymers*, 7, 821 (1969).
(2) J. Donohue and K. N. Trueblood, *J. Mol. Biol.*, **2**, 363 (1960).
(3) S. S. Tavale and H. M. Sobell, *ibid.*, **48**, 109 (1970).
(4) D. W. Miles, L. B. Townsend, M. J. Robins, R. K. Robins, W. H. Inskeep, and H. Eyring, *J. Amer. Chem. Soc.*, in press.
(5) A. M. Kapuler, C. Monny, and A. M. Michelson, *Biochim. Biophys. Acta*, **217**, 18 (1970).
(6) A. M. Kapuler and S. Spiegelman, *Proc. Nat. Acad. Sci.*, **66**, 539 (1970).
(7) F. E. Hruska, A. A. Grey, and I. C. P. Smith, *J. Amer. Chem. Soc.*, **92**, 4088 (1970).
(8) M. P. Schweizer, A. D. Broom, P. O. P. Ts'o, and D. P. Hollis, *ibid.*, **90**, 1042 (1968).
(9) S. I. Chan and J. H. Nelson, *ibid.*, **91**, 168 (1969).
(10) P. O. P. Ts'o, N. S. Kondo, M. P. Schweizer, and D. P. Hollis, *Biochemistry*, **8**, 997 (1969).