

AN UNUSUAL AROMATIC SUBSTITUTION REACTION

Barry M. Trost

Department of Chemistry, University of Wisconsin

Madison, Wisconsin 53706

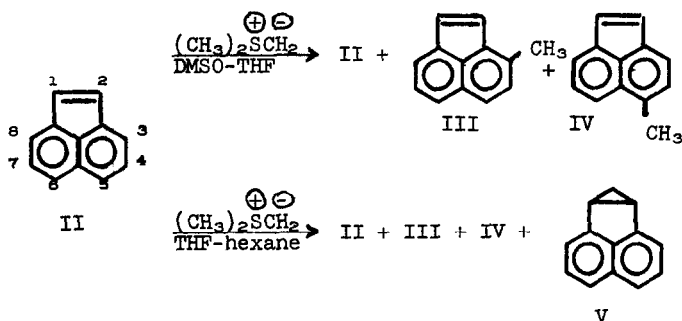
(Received 27 August 1966)

The nucleophilic addition of sulfur ylides to the carbonyl group (1) and to olefins (1) and aromatics substituted with electron withdrawing groups (2) is well known. The condensation of these intermediates with simple olefins (3) and aromatics (2,4,5) has been studied to a much less extent; in some instances, carbenes were suggested as intermediates. We wish to report the first example of a nucleophilic reaction of dimethylsulfonium-methylide (I) with unsubstituted aromatic hydrocarbons. Such nucleophilic aromatic substitution reactions on unsubstituted aromatics are virtually unknown. Correlation of chemical reactivity with molecular orbital theory give such reactions special significance.

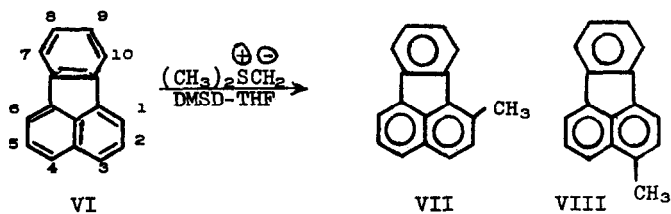
Treatment of acenaphthylene with I in dimethylsulfoxide-tetrahydrofuran leads to a mixture of II (10.5%), 3-methylacenaphthylene (III, 71.0%), and 5-methylacenaphthylene (IV, 3.0%). If the reaction is performed in tetrahydrofuran-hexane, in addition to 25.2% II, 52.6%

III, and 2.3% IV, there is produced 8.4% 1,2-methano-acenaphthylene (V) (6). These results are summarized in Scheme I. The products were identified by comparison to authentic samples prepared in completely independent manners (7).

Scheme I



Similarly, treatment of fluoranthene (VI) with I leads to a mixture of 1-methylfluoranthene (VII, 24.7%) and 3-methylfluoranthene (VIII, 5.3%) in addition to recovered starting material (65.3%) as illustrated in Scheme II (6). Again, the products were identified by comparison to authentic samples prepared independently (7).



The nucleophilic nature of this reaction is reflected by the product distribution and by the reaction in dimethylsulfoxide. Electrophilic and free radical reactions occur at position 1 in acenaphthylene and at positions 3 and 8 in fluoranthene (8). The orientations observed in the present cases are quite different and agree well with molecular orbital calculations for nucleophilic attack summarized in Chart I. It is interesting to note that,

CHART I

Reactivity Indices for Nucleophilic Attack

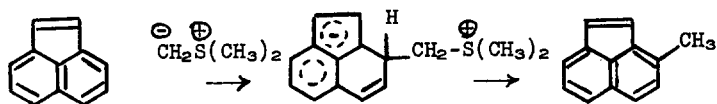
	Position						
	1	2	3	4	5	6	7
Acenaphthylene							
π Electron densities	1.066		0.909	1.008	0.926		
Localization energies	2.124		1.999	2.513	1.969		
Fluoranthene							
π Electron densities	0.927	1.005	0.958			0.997	1.008
Localization energies	1.46	1.82	1.41			1.71	1.76

of the two methods, π electron densities better predict the observed orientations. This fact indicates that the transition state more closely resembles starting materials than intermediates or products. These calculations also

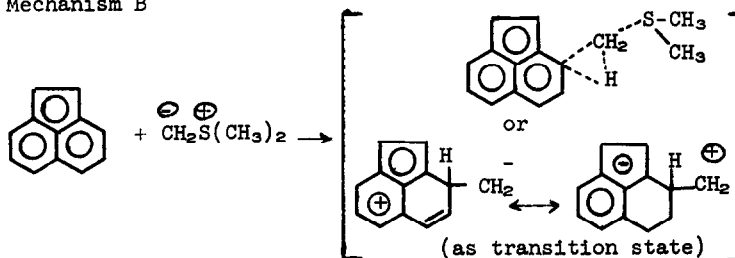
indicate that acenaphthylene should show a higher positional selectivity than fluoranthene--i.e. the ratio of III/IV should be greater than the ratio of VII/VIII. This prediction is borne out--III/IV = 23.3 whereas VII/VIII = 7.7.

The use of DMSO as solvent eliminates the reaction of a highly electrophilic species with II or VI (9). Thus, the formation of III and IV was unaffected by changing from THF-hexane to THF-DMSO. However, no cyclopropane V was formed in this latter solvent mixture. These observations further confirm the nucleophilic nature of the methylation reaction and suggest that V arises from the electrophilic carbene intermediate. There are two likely mechanisms that must be considered for this unusual nucleophilic substitution reaction. The first is simple nucleophilic addition to the aromatic to form a sigma complex intermediate followed by elimination of dimethylsulfide concomitant with hydrogen shift (Mechanism A). The second involves carbon-sulfur bond cleavage simultaneous with carbon-carbon bond formation (Mechanism B). The present data do not allow a distinction between the two.

Mechanism A



Mechanism B



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REFERENCES

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2. (a) H. Metzger, H. König and K. Seelert, Tetrahedron Letters, No. 15, 867 (1964); (b) H. König, H. Metzger, and K. Seelert, Aus. Forsch., 49 (1965); Chem. Abstr., **64**, 17409f (1966).
3. B. M. Trost, J. Am. Chem. Soc., **88**, 1587 (1966) and references therein.

4. Johnson and coworkers (5) report the formation of cyclopropanes in the reaction of acenaphthylene with diphenylsulfoniumbenzylide and diphenylsulfoniumbutylide. However, lack of satisfactory analytical data, incomplete characterization of products and, in one case, a high melting point for the product make his structural assignments tenuous. It also appears unlikely that intermolecular reaction of the carbene generated from the butylide would compete successfully with intramolecular hydride shift (see W. Kirmse, "Carbene Chemistry," Academic Press, New York, 1964, pp. 47-66).
5. A. W. Johnson, V. J. Hinby, and J. L. Williams, J. Am. Chem. Soc., 86, 918 (1964).
6. Analyses were performed by vapor phase chromatographic analysis on silicon oil 710 column. The ratios of methylated products could also be determined by integration of the methyl singlet absorption in the nmr spectra.
7. Satisfactory analyses were obtained for all new compounds. Nmr, ir, uv, and mass spectra also support the assignments.
8. For a discussion of these orientations and their correlation with molecular orbital theory, see (a) R. D. Brown, J. Chem. Soc., 2232 (1959); (b) K. Fukui, T. Yonezawa and C. Nagata, Bull. Soc. Chem. Japan, 34, 37 (1961); (c) C. Sandorfy, Compt. Rend., 227, 198 (1963); (d) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, 1962, pp. 307-356 and 392-412.
9. Unpublished observations in these laboratories.