dine (III, mp[7] 133–136°) was obtained in 49% yield from I, and the tris(cyanoethyl) derivative of 5′-O-monomethoxytritylthymidylylthymidylylthymidylylthymidine (mp[7] 144–146°) was obtained in 57% yield from III. These compounds were characterized by elemental analysis, by isolation of the de(methoxytrityl) derivatives, and by conversion to TpTpT and TpTpTpT, respectively.

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Bimolecular Substitution–Fragmentation. The Reaction of Phenylmethanesulfonyl Halides with Halide Ion

Sir:

While studying the action of nucleophilic reagents on sulfonyl halides,[1] we have encountered a new reaction of alkanesulfonyl halides exemplified by eq 1. We wish

$$\mathrm{PhCH_2SO_2Br} \xrightarrow{\mathrm{Br^-}} \mathrm{PhCH_2Br} + \mathrm{SO_2} \tag{1}$$

to present evidence which indicates that the reaction is simultaneously a bimolecular nucleophilic displacement on carbon and a concerted fragmentation reaction, and thereby displays mechanistic features which have not hitherto been demonstrated to exist in the same process.

Reaction 1 proceeds readily and quantitatively at room temperature in inert solvents such as methylene chloride or acetonitrile, using alkylammonium bromides as the source of bromide ion. Methanesulfonyl bromide reacts similarly but roughly $^1/_{1000}$ as fast. The analogous reaction of phenylmethanesulfonyl chloride with chloride ion also occurs, but again more slowly (see Table I).

Table I. Reaction of Sulfonyl Halides with Alkylammonium Halides in Dichloromethane at 25.0 ± 0.1°

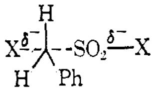
Sulfonyl halide	Salt (concn, *M*)	*k*, l. mole^{-1} sec^{-1}
$PhCH_2SO_2Br$	$Et_4N^+Br^-$ (0.00012)	3.10×10^{-2}
$PhCH_2SO_2Br$	$Et_4N^+Br^-$ (0.001)	2.45×10^{-2}
$PhCH_2SO_2Br$	$Et_4N^+Br^-$ (0.0123)	2.35×10^{-2}
$PhCH_2SO_2Br$	$Bu_4N^+Br^-$ (0.00082)	2.6×10^{-2}
$PhCH_2SO_2Br$	$Et_3NH^+Br^-$ (0.0098)	1.53×10^{-4}
p-$NO_2C_6H_4CH_2SO_2Br$	$Et_4N^+Br^-$ (0.001)	3.85×10^{-2}
m-$NO_2C_6H_4CH_2SO_2Br$	$Et_4N^+Br^-$ (0.001)	3.50×10^{-2}
p-$ClC_6H_4CH_2SO_2Br$	$Et_4N^+Br^-$ (0.001)	3.15×10^{-2}
m-$ClC_6H_4CH_2SO_2Br$	$Et_4N^+Br^-$ (0.001)	1.72×10^{-2}
p-$MeC_6H_4CH_2SO_2Br$	$Et_4N^+Br^-$ (0.001)	5.26×10^{-2}
$PhCH_2SO_2Cl$	$Et_4N^+Cl^-$ (0.01)	1.14×10^{-4}

Reaction 1 is cleanly first order in the sulfonyl halide but only roughly so in the bromide salt, the deviation from simple second-order kinetics probably deriving to a substantial extent from ionic association.[2] *meta* or *para* substitution has a relatively small influence on the rate of reaction. The nonlinear Hammett plot (see Table I) is akin to those that have been observed in the reaction of nucleophilic reagents with benzyl halides, thereby pointing to a SN2 mechanism.[3,4]

Consistent with this interpretation were the results from ^{13}C kinetic isotope effect studies in which it was found that the presence of ^{13}C at the benzylic carbon slowed the reaction by more than 3% at 25° (k_{12}/k_{13} = 1.035 ± 0.0016).[5] A kinetic isotope effect of such a magnitude in α-phenyl-substituted systems has previously been found in bimolecular processes,[6] whereas unimolecular solvolysis of such species shows a much smaller isotope effect.[7]

Stereochemical evidence for the SN2 mechanism was obtained using (*R*)-phenylmethanesulfonyl-1-*d* bromide[8] (PhC^*HDSO_2Br), which gave mainly the *inverted* product, (*S*)-benzyl-1-*d* bromide.[9] It is estimated that at least 60% of the product is formed by inversion, but it is not yet possible to assign a more precise value owing to uncertainty in the optical purity of the sulfonyl bromide.

There remains the question of whether the leaving anion is simply SO_2X^- (which subsequently decomposes into SO_2 and X^-), or whether the reaction is a SN2–fragmentation process in which the S–X bond is partially broken in the transition state. The distinction between the two possible mechanisms may be summarized by structures I and II, which represent the respective transition states for the two pathways. Evidence suggesting the second mechanism is as follows. The reaction of $PhCH_2SO_2Cl$ with $Et_4N^+Cl^-$ in methylene chloride is more than 200 times slower than that of $PhCH_2SO_2Br$ with $Et_4N^+Br^-$. Since tetraethylammonium bromide and chloride were found to be almost identical in their rate of reaction with benzyl tosylate in methylene chloride under conditions comparable to those used in the desulfonation reaction, this difference probably does not derive from a difference in nucleophilicity toward benzylic carbon between the chloride and bro-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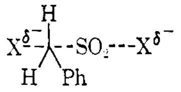
II

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(1) Previous work: J. F. King and T. Durst, *J. Am. Chem. Soc.*, **87**, 5684 (1965); *Can. J. Chem.*, **44**, 819 (1966).

(2) *Cf.* S. Winstein, L. G. Savedoff, S. Smith, I. D. R. Stevens, and J. S. Gall, *Tetrahedron Letters*, 24 (1960), and references cited.

(3) C. G. Swain and W. P. Langsdorf, Jr., *J. Am. Chem. Soc.*, **73**, 2813 (1951); R. F. Hudson and G. Klopman, *J. Chem. Soc.*, 1062 (1962).

(4) The possibility that the benzyl halide, under favorable circumstances, might be formed *via* a sulfene was excluded by the finding that the reaction of *p*-nitrophenylmethanesulfonyl-1,1-d_2 bromide in the presence of triethylamine and excess $Et_3NH^+Br^-$ gave *p*-nitrobenzyl-1,1-d_2 bromide with no significant loss of deuterium detected.

(5) These experiments were carried out in collaboration with Dr. J. B. Stothers and Mr. A. J. McNamara, and will be described in detail at a later date.

(6) J. B. Stothers and A. N. Bourns, *Can. J. Chem.*, **40**, 2007 (1962); *cf.* also A. Fry, *Pure Appl. Chem.*, **8**, 409 (1964). Recent reinvestigation (J. B. Stothers and J. Bron, private communication) has shown that in the reaction of α-phenylethyl bromide with ethoxide ion (at 25°) k_{12}/k_{13} = 1.030, a higher value than that previously reported.

(7) J. B. Stothers and A. N. Bourns, *Can. J. Chem.*, **38**, 923 (1960).

(8) The sulfonyl bromide was prepared from optically active benzyl-1-*d* bromide by a procedure adapted from the preparation of the sulfonyl chloride described by J. L. Kice, R. H. Engebrecht, and N. E. Pawlowski, *J. Am. Chem. Soc.*, **87**, 4131 (1965).

(9) This finding, especially when taken in conjunction with our observation that the reaction is unaffected by the presence of oxygen or styrene, clearly distinguishes the halide-catalyzed reaction from the pyrolytic decomposition of alkanesulfonyl halides, which has been found to show the properties of a free-radical chain process (H. F. Herbrandson, W. S. Kelly, and J. Versnel, *ibid.*, **80**, 3301 (1958); G. Geiseler, *et al.*, *Z. Physik. Chem.* (Frankfurt), **28**, 24, 33 (1961); **33**, 264 (1962); **36**, 23 (1963)).

mide ions in this system. More striking is the observation that benzyl trifluoromethyl sulfone ($PhCH_2SO_2CF_3$) does *not* react at all[10] with tetraethylammonium bromide under these conditions. A similar lack of reaction[10] was also observed with dibenzyl sulfone ($PhCH_2SO_2CH_2Ph$), benzyl phenacyl sulfone ($PhCH_2SO_2CH_2COPh$), and phenyl phenylmethanesulfonate ($PhCH_2SO_2OPh$), the last being also unaffected by sodium phenoxide. To account for these observations in terms of a reaction proceeding *via* I would require that one explain why a $BrSO_2^-$ group is a better leaving group than either $CF_3SO_2^-$, $PhCOCH_2SO_2^-$, $PhOSO_2^-$, or $PhCH_2SO_2^-$ by more than five orders of magnitude in each case. We find it much simpler to interpret these observations on the basis of the concerted fragmentation process (*i.e.*, *via* II), the observed rate order then reflecting the normal order of Br, Cl, CF_3, etc., as leaving anions ("nucleofugal" groups[11]).

In the light of this conclusion it is pertinent to inquire into the possibility of other concerted fragmentation processes that involve S_N2 reaction on carbon. A case for such a mechanism, based on $\Delta S^{\ddagger}$ values, has been made by Buncel and Millington[12] for the solvolysis of alkyl chlorosulfates. Two other reactions, the chloride ion catalyzed decomposition of alkyl chloroformates[13] and the analogous cleavage of alkyl chlorosulfites,[14] are sufficiently similar as to strongly suggest that they too may be fragmentation reactions, though direct evidence on the point is lacking at present. The twofold problem of elucidating the mechanism of the known processes and of devising and testing possible new members of this class of reactions is now under active study.

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(10) Control experiments show that a reaction with $k_2 > 10^{-7}$ l. mole^{-1} sec^{-1} would have been readily detected. Lack of reaction in these cases therefore corresponds to a rate at least 2×10^5 times slower than reaction 1.

(11) J. Mathieu, A. Allais, and J. Valls, *Angew. Chem.*, **72**, 71 (1960); see also C. A. Grob and P. W. Schiess, *ibid.*, **79**, 1 (1967).

(12) E. Buncel and J. P. Millington, *Can. J. Chem.*, **43**, 556 (1965).

(13) J. Kenyon, A. G. Lipscomb, and H. Phillips, *J. Chem. Soc.* 2275 (1931); D. N. Kevill, G. H. Johnson, and W. A. Neubert, *Tetrahedron Letters*, 3727 (1966).

(14) E. S. Lewis and G. M. Coppinger, *J. Am. Chem. Soc.*, **74**, 308 (1952).

(15) Alfred P. Sloan Research Fellow.

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Bicyclo[6.2.0]deca-2,4,6,9-tetraene

Sir:

Numerous recent publications describe thermally and photolytically induced rearrangements of unsaturated hydrocarbons.[1] The behavior of the title compound (**1**) is of particular interest because several modes of isomerization are conceivable for this compound,[2] *e.g.* (i) ring opening to give *trans(cis)*[4]-1,3,5,7,9-cyclodecapentaene (**2**); (ii) subsequent rearrangement of **2** to *trans*-9,10-dihydronaphthalene (**3**); (iii) sigmatropic rearrangement to bicyclo[4.2.2]deca-2,4,7,9-tetraene (**4**);[1b,c] (iv) degenerate bond isomerization to give the same compound; (v) ring opening to afford (*cis*)[5] cyclodecapentaene (**5**)[1d] followed by secondary reactions; and (vi) ring closure leading to the tricyclo compound **6** (stereochemistry unspecified). We describe herein the synthesis of this intriguing molecule and further present a preliminary account of its chemistry.[3]

A solution of bicyclo[6.1.0]nona-2,4,6-triene-*trans*-9-carboxaldehyde tosylhydrazone (**7**)[1c,4] in dry tetrahydrofuran containing an equivalent amount of sodium methoxide was irradiated at 0 or −30° with a Hanovia mercury lamp using a Pyrex filter. Evolution of the theoretical amount of nitrogen usually required 5–6 hr. Gas chromatography (10% silicone rubber, 90°) of the distillable product mixture provided **3**, naphthalene (the combined yield of **3** and naphthalene was 45%), cyclooctatetraene (27%), **4** (7%), and a new compound (**6′**) (21%) (*vide infra*). This product distribution is similar to that of the thermolysis of **7** (dry salt)[1c] except that no trace of *cis*-9,10-dihydronaphthalene (**8**) was found in the photolysis products. When the products were kept below 0° throughout the entire work-up process[5] we obtained another new compound (**1**) at the expense of **3** and naphthalene.

Compound **1** (calcd mol wt for $C_{10}H_{10}$, 130.0783 and for $C_9{}^{13}CH_9$, 130.0738; found, *m/e* 130.0758 (intensity, 20% of M − 1 base peak); calcd for $C_{10}H_9$, 129.0704; found, *m/e* 129.0704)[6] showed a maximum at λ_{max}^{EtOH} 258 mμ ($\epsilon \sim 1300$).[7] The nmr spectrum showed a sharp singlet at τ 3.98 (2 H) characteristic of the olefinic signal of symmetrically (σ) substituted cyclobutenes,[8] a broad singlet at τ 6.32 ascribed to two allylic protons, and other olefinic signals (6 H) at τ 4.1 to ∼4.3, similar to those of the bicyclo[6.1.0]nona-2,4,6-triene system. These spectral data are consistent with the formulation of structure **1**.

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(1) For the bond isomerization of several $C_{10}H_{10}$ hydrocarbons, for instance, see (a) W. von E. Doering and J. W. Rosenthal, *J. Am. Chem. Soc.*, **88**, 2078 (1966); (b) *Tetrahedron Letters*, 349 (1967); (c) M. Jones, Jr., and L. T. Scott, *J. Am. Chem. Soc.*, **89**, 150 (1967); (d) E. E. van Tamelen and T. L. Burkoth, *ibid.*, **89**, 151 (1967); (f) J. A. Elix, M. V. Sargent, and F. Sondheimer, *ibid.*, **89**, 180 (1967).

(2) R. B. Woodward and R. Hoffmann, *ibid.*, **87**, 395 (1965); H. C. Longuet-Higgins and E.W. Abrahamson, *ibid.*, **87**, 2045 (1965); R. B. Woodward and R. Hoffmann, *ibid.*, 87, 2511 (1965).

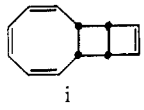
(3) Our original aim was to prepare the carbocyclic analog of 4-azabicyclo[5.2.0]nonatriene and compare the properties of the two series of compounds; see S. Masamune and N. T. Castellucci, *Angew. Chem. Intern. Ed. Engl.*, **3**, 582 (1964).

(4) The reaction product of ethyl diazoacetate and cyclooctatetraene consisted of an approximately 19:1 mixture of *trans* and all-*cis* (with respect to the substituents of the cyclopropane ring) esters. Because of the necessity of confirming the earlier stereochemical assignments [K. F. Bangert and V. Boekelheide, *J. Am. Chem. Soc.*, **86**, 905, 1159 (1964)], the known acid derived from the major component was converted to cyclopropane-*trans*-1,2,3-tricarboxylic acid with permanganate–periodate. The minor acid, mp 146–147°, was isolated in pure form and the three cyclopropane ring protons showed the same chemical shift (τ 7.95): S. Masamune, unpublished.

(5) The final purification involved alumina chromatography (Woelm, neutral grade 1, pentane) followed by distillation at 0°, 0.1 mm.

(6) Taken with a direct insertion probe (MS-9) by first freezing a sample with liquid nitrogen.

(7) Compound i exhibited a maximum, λ_{max}^{hexane} 258 mμ (ε 1300): G. Schröder and W. Martin, *Angew. Chem. Intern. Ed. Engl.*, **5**, 130 (1966).



i

(8) For instance, see ref 3. For a revised set of coupling constants of cyclobutene itself, see E. A. Hill and J. D. Roberts, *J. Am. Chem. Soc.*, **89**, 2047 (1967).