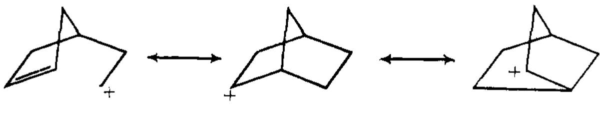
ment (process 4) in HOAc than in HCOOH would be consistent with the more nucleophilic nature of HOAc. On these grounds, processes 1, 2, 3, and 4 may be preferable to 1, 2, 3′, and 4′.

The present results indicate that differences in the extents of isotopic rearrangements do exist in the σ and π routes to the norbornyl cation. Factors that could contribute to these differences may include the fact that the leaving groups were not the same and that unlike the earlier work,[2,7] no acetate or formate ions were added to the reaction mixtures during solvolyses of II-^{14}C. The major difference, however, is the possible involvement of the process of concerted rearrangement depicted by VIIIa or VIIIb. Such a process, if proven valid on further experimentation, could be the result of a greater contribution of Xa to the hybrid ion Xa–c produced by the π route.[11] It may also be suggested that the concerted rearrangement occurs following the formation of the Wagner–Meerwein intermediate. Since only minor secondary kinetic isotope effects were observed in the solvolyses of II-1,1-d_2[6], the hydride shift in the concerted rearrangement likely does not take place in a slow step competitive with the formation of VIIa.



Xa Xb Xc

Experimental Section

2-(Δ^3-Cyclopentenyl)-2-^{14}C-ethyl *p*-Nitrobenzenesulfonate (II-2-^{14}C). This compound was prepared from diethyl 2-^{14}C-malonate and 4-bromocyclopentene by the procedures analogous to those used in the preparation of II-1,1-d_2.[6]

Solvolytic Reactions. A solution of 3.0 g (0.01 mole) of II-2-^{14}C in 30 ml of HOAc or in 50 ml of HCOOH was heated in a water bath at 60° for 30 hr. The resulting material was extracted and worked up to give *exo*-I-OH-^{14}C in the manner described in the preceding paper.[2] The over-all yields of the alcohol were about 50 and 45%, respectively, for acetolysis and formolysis.

Degradation of *exo*-I-OH-^{14}C. Each sample of *exo*-I-OH-^{14}C was degraded to *cis*-cyclopentane-1,3-dicarboxylic acid (III), to *cis*-cyclopentane-1,3-diamine (IV), to succinic acid (V), to ethylenediamine (VI) by methods already described,[2,7] with the exception that the conversion of V to VI was effected by the Schmidt reaction instead of using the Curtius reaction.[7] The amines IV and VI were converted to their respective dibenzamides. The derivative from IV melted at 212–214° (lit.[7] mp 213–215°). *Anal.* Calcd for $C_{19}H_{20}O_2N_2$: C, 74.00; H, 6.54; N, 9.09. Found: C, 74.22; H, 6.48; N, 9.02. The dibenzamide of VI melted at 248–249° (lit.[12] mp 249°). *Anal.* Calcd for $C_{16}H_{16}O_2N_2$: N, 10.44. Found: N, 10.46.

Samples of the acids III and V and the dibenzamides of IV and VI were repeatedly recrystallized until their specific activities were constant. All calculations of isotopic rearrangements were based on the activities of these purified samples.

Acknowledgment. We wish to express our sincere appreciation to Professors P. D. Bartlett and P. von R. Schleyer for valuable comments and constructive criticisms on the work reported in this and the preceding papers.

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[11] P. von R. Schleyer, M. M. Donaldson, and W. E. Watts, *J. Am. Chem. Soc.*, **87**, 375 (1965), have obtained kinetic evidence suggesting that contribution of Xa to the hybrid ion from the σ route may be very small. In a private communication, Professor Schleyer also pointed out that in going from II to VIII, the positive charge develops far from the position of the anion. This charge separation can be reduced by the concerted hydride shift and this may be supplying the driving force for process 4.

[12] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd ed, John Wiley and Sons, Inc., New York, N. Y., 1948, p 234.

Pyrolysis and Mass Spectrum of Dibenzothiophene 5,5-Dioxide

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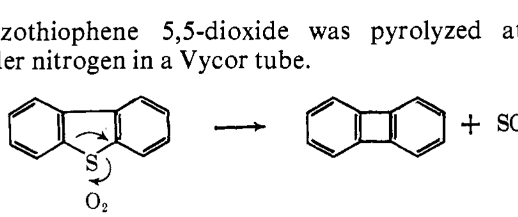
Contribution from the Research Department, Amoco Chemicals Corporation, and the Research and Development Department, American Oil Company, Whiting, Indiana. *Received March 25, 1966*

Abstract: Pyrolysis of dibenzothiophene 5,5-dioxide gave dibenzofuran, instead of the expected biphenylene. Evidently the dioxide rearranged to the sulfinate ester and eliminated SO to close the dibenzofuran ring. This decomposition closely parallels its behavior under electron impact.

Carbon–carbon bonds have been formed by elimination of sulfur dioxide from sulfones.[1] Formation of benzyne from *o*-sulfobenzoic anhydride[2] and of free aryl radicals from sulfonyl halides[3] gives additional evidence that sulfur dioxide is a good leaving group. Thermal elimination of sulfur dioxide from dibenzothiophene 5,5-dioxide could provide a direct and easy synthesis of biphenylene. To test this surmise, dibenzothiophene 5,5-dioxide was pyrolyzed at 690° under nitrogen in a Vycor tube.



All the dibenzothiophene dioxide had reacted. No biphenylene was observed. Instead, the major products, accounting for about 95% of the total, were dibenzofuran and dibenzothiophene in the ratio 6:1. The predominant reaction, therefore, involved over-all loss of SO rather than of SO_2.

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[1] M. P. Cava and A. A. Dean, *J. Am. Chem. Soc.*, **81**, 4266 (1959); H. Drews, E. K. Fields, and S. Meyerson, *Chem. Ind.* (London), 1403 (1961); W. Z. Heldt, *J. Org. Chem.*, **30**, 3897 (1965).

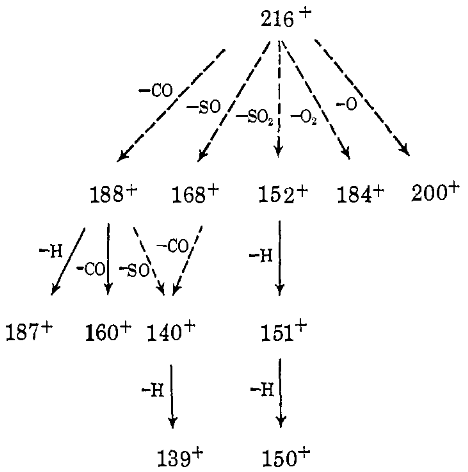
[2] S. Meyerson and E. K. Fields, *Chem. Commun.*, in press.

[3] P. J. Bain, E. J. Blackman, W. Cummings, S. A. Hughes, E. R. Lynch, E. B. McCall, and R. J. Roberts, *Proc. Chem. Soc.*, 186 (1962); E. K. Fields, *J. Chem. Soc.*, 5766 (1965).

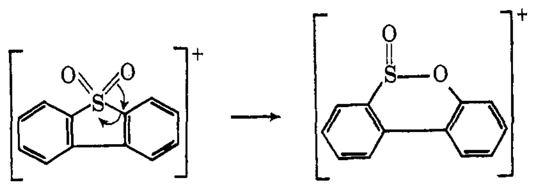
Table I

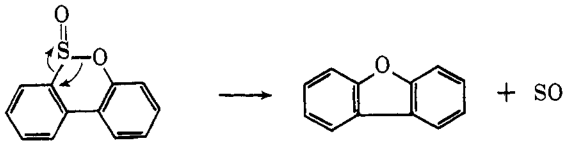
Mass	Relative intensity
216	100.0
200	0.24
188	11.46
187	36.1
184	3.95
168	40.8
160	32.5
152	5.10
151	11.69
150	14.33
140	4.38
139	27.3

To help clarify these results, we examined the mass spectrum of the original dibenzothiophene dioxide. The 70-v spectrum shows the relative intensities listed in Table I. The decomposition scheme shown can account for the major ionic products (solid arrows denote a supporting metastable peak).



Clearly, the major primary decomposition processes are loss of SO and loss of CO, both of which require prior formation of a C–O bond. This virtually demands isomerization to an internal sulfinate ester, paralleling the isomerization of alkyl aryl and dialkyl sulfones to sulfinate esters under electron impact.[4] Apparently, dibenzothiophene dioxide upon pyrolysis behaves similarly, rearranging to the sulfinate ester and then eliminating sulfur monoxide. The driving force may be the formation of the strainless dibenzofuran ring rather than the strained, four-membered cyclobutadiene ring in biphenylene.





This is another rather striking example of parallel behavior of an organic molecule in low and relatively high energy processes, pyrolysis and electron impact.[5] Other such examples are being investigated.

Experimental Section

Dibenzothiophene 5,5-dioxide was commercial material, recrystallized twice from ethanol, mp 230° (lit.[6] mp 229–230°). A 2.16-g (0.01 mole) sample was vaporized by a stream of high-purity dry nitrogen flowing at a steady rate of 60 ml/hr and carried into a Vycor pyrolysis tube filled with Vycor beads. The contact time was 15 sec. The product (1.1 g) was analyzed by mass spectrometry on a Consolidated Model 21-103c instrument with the inlet system at 250°. The usual 70-v spectrum was supplemented by a low-voltage (7.5 ionizing v, uncor) spectrum to help identify parent peaks.

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(4) S. Meyerson, H. Drews, and E. K. Fields, *Anal. Chem.*, **36**, 1294 (1964); S. Meyerson and J. D. McCollumn, 136th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1959, Abstracts, p 29S; A. Quayle, *Chimia* (Aarau), (Colloquium Spectroscopium Internationale VIII), 259 (1959).

(5) See, for example, the formation of benzyne from phthalic anhydride: E. K. Fields and S. Meyerson, *Chem. Commun.*, 474 (1965); and the pyrolysis of deuterated benzene: E. K. Fields and S. Meyerson, *J. Am. Chem. Soc.*, **88**, 21 (1966).

(6) O. Kruber, *Ber.*, **53**, 1566 (1920).