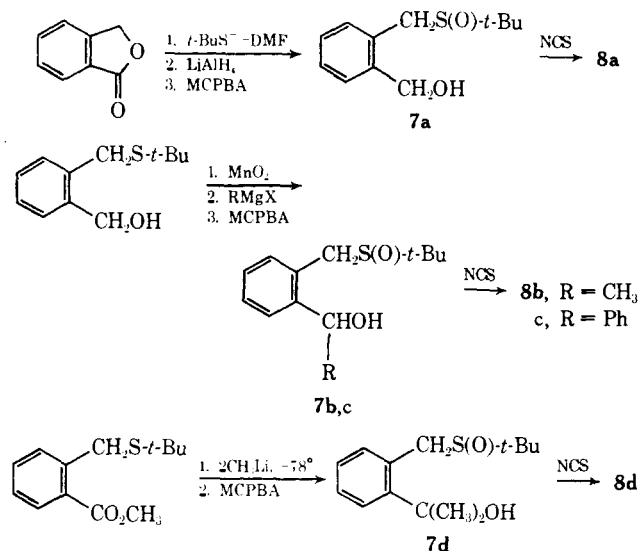


ing the direction of rotation of the substituents at C₂ and C₆ during the cycloreversion.

In order to prepare a stable 3,6-dihydro-1,2-oxathiin 2-oxide, we turned our attention to the benz-fused compounds **8**. The required hydroxy sulfoxides, **7**, were readily prepared from phthalide as shown in Scheme II.

Scheme II



Reaction of **7a-d** with NCS gave **8a-d** in 75–95% yield. When the parent compound **8a**¹⁴ was heated in refluxing benzene it cleanly isomerized to 1,3-dihydrobenzo[*c*]thiophene 2,2-dioxide (**10a**)¹⁵ ($t_{1/2} = 6$ hr). That this isomerization represented a cycloreversion to *o*-quinodimethane (**9a**) and SO₂ followed by a typical SO₂ + 1,3-diene cycloaddition¹⁶ was shown by carrying out the thermolysis in the presence of a very reactive dienophile such as maleic anhydride. Under these conditions the tetrahydronaphthalene derivative, **11**,¹⁷ was obtained in over 95% yield. The sulfinate esters **8** have thus considerable potential as precursors for the generation of variously substituted *o*-quinodimethanes under very mild conditions.¹⁸ In contrast to the above, the generation of *o*-quinodimethane from the sulfone **10a** requires heating in refluxing diethylphthalate (300°) for approximately 1 hr.¹⁶ These results again illustrate the ease with which SO₂ is lost in a retro-Diels–Alder reaction from 3,6-dihydro-1,2-oxathiin 2-oxides compared to the cheletropic extrusion from the isomeric 2,5-dihydrothiophene 1,1-dioxide.

The designation of the SO₂ extrusion from **3**, **5**, and **8** as a $\pi_4s + \pi_2s$ cycloreversion implies concertedness and stereospecificity for these reactions. The results obtained with **5** indicate, but do not conclusively prove, these properties.¹⁹ The variations in the relative rates

(14) Colorless oil; nmr CH₂ α to S at δ 3.51 and 4.37 ($J = 15$ Hz), CH₂ α to O at δ 4.91 and 5.27 ($J = 14$ Hz); ir 1105 cm⁻¹ (S=O).

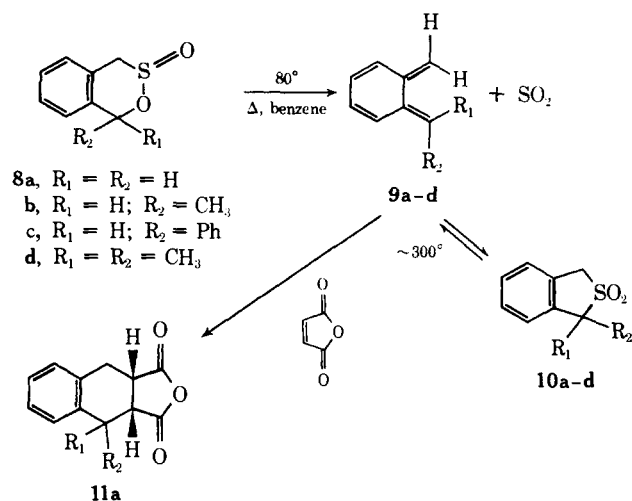
(15) M. P. Cava and A. A. Deana, *J. Amer. Chem. Soc.*, **81**, 4266 (1959).

(16) See F. R. Jensen, W. E. Coleman, and A. J. Berlin, *Tetrahedron Lett.*, 15 (1962); and F. R. Jensen and W. E. Coleman, *J. Amer. Chem. Soc.*, **80**, 6149 (1958) for an example of the addition of SO₂ to a substituted *o*-quinodimethane.

(17) R. D. Haworth and F. H. Slinger, *J. Chem. Soc.*, 1321 (1940).

(18) A number of groups have recently utilized the electrocyclic ring opening of benzocyclobutenes as a route to *o*-quinodimethanes. These reactions are reported to occur at temperatures ranging from 110 to 200°: B. J. Arnold and P. G. Sammes, *J. Chem. Soc., Chem. Commun.*, **30**, 1074 (1972); W. Oppolzer, *J. Amer. Chem. Soc.*, **93**, 3833 (1971).

(19) It would have been preferable to have substituents of known stereochemistry at both C₃ and C₆ in the oxathiin. We have not been able to prepare such a system up to this point.



of rearrangement of the oxathiins **8** to the sulfones **10** (**8a**:**8b**:**8c**:**8d** = 1.0:1.9:200:0.023) and the insensitivity of the rates to solvent change (**8a**; benzene *vs.* CH₃CN = 1.0:1.3) are not in agreement with a dipolar or diradical intermediate resulting from initial C–O bond cleavage. They are more reasonable on the basis of a concerted loss of SO₂ from **8** → **9**, followed by rapid reaction of **9** + SO₂ → **10**. The oxathiine **8b** and **8c** would be expected to react faster than the parent compound because of the stabilization by the substituent of the intermediates **9b** and especially **9c**; **8d** should be strongly retarded because of an adverse steric effect which prevents **9d** from becoming planar.^{20, 21}

(20) Similar effects have been observed in the ring opening of *cis*- and *trans*-1,2-diphenylbenzocyclobutene to the expected *o*-quinodimethanes: R. Huisgen and H. Seidel, *Tetrahedron Lett.*, 3381 (1964); G. Quinkert, K. Opitz, W. W. Weisdorf, and M. Finke, *ibid.*, 3009 (1965).

(21) Financial support by the National Research Council of Canada is gratefully acknowledged.

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Duality of Mechanism in the Electrophilic Bromination of Aromatic Compounds^{1,2}

Sir:

In an aromatic substitution reaction, a bond is formed and a bond is broken. If the substitution reagent furnishes no electrons to the new bond, the substitution is termed "electrophilic."

Conceptually, the timing of bond making and bond breaking for straightforward substitution at a single site may conform to one of three patterns: (1) the new bond from aromatic carbon to electrophile may form first, after which the old bond to the electrofugic substituent ruptures; (2) formation of the new bond may be concerted with rupture of the old bond; or (3) the old bond may break first, after which the new bond forms.

The first pattern is familiar in the many aromatic electrophilic substitutions which proceed *via* σ -complex intermediates; the electron pair needed to form

(1) Based on the Ph.D. Thesis of M. H. Mach, University of California, Santa Cruz, 1973.

(2) Research supported in part by the National Science Foundation.

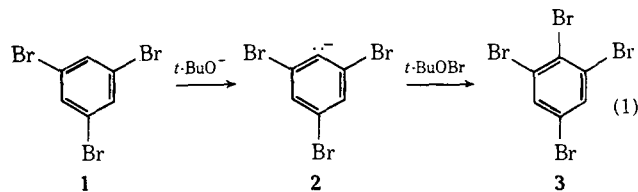
the new bond is borrowed from the π -electron system. The second pattern has been recognized as a possibility,^{3,4} but there are few if any authentic examples of it. The third pattern, which implies a carbanion intermediate, is represented by numerous well-studied reactions, but prominent discussions of aromatic electrophilic substitution have failed to acknowledge it.³⁻⁹

The reason for this curious neglect of a well-authenticated mechanism is no doubt that the numerous cases of it, some of which are mentioned in a recent review,¹⁰ are otherwise classified in the minds of chemists. For example, they may be thought of as decarboxylation, carbonyl cleavage, hydrogen isotope exchange, or organometallic reactions.

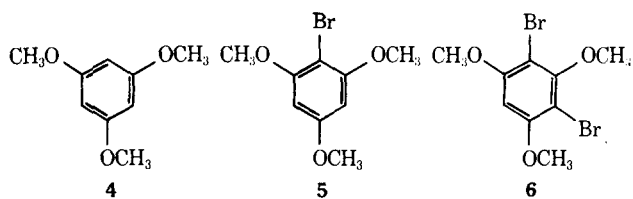
Originally, aromatic substitution meant the introduction of substituents in place of hydrogen on an aromatic ring, and that point of view still prevails to some extent. If a common reaction such as bromination could be demonstrated to occur by the third pattern above, the carbanion mechanism, the whole family of such substitutions might gain acceptance into the community in which they belong.

We now present evidence of aromatic bromination by the carbanion mechanism.

1,3,5-Tribromobenzene (**1**) is quite unreactive with *tert*-butyl hypobromite¹¹ (*t*-BuOBr) in dimethylformamide (DMF) or hexamethylphosphoramide (HMPA) solution.¹² During a 5-min exposure in HMPA no detectable bromination occurs. However, **1** is rapidly brominated by *t*-BuOBr in the presence of potassium *tert*-butoxide (*t*-BuOK); during 10 sec in DMF, tetrabromobenzenes¹³ were formed in 47% yield as well as 16% of pentabromobenzene. Thus, bromination of **1** is base-catalyzed, and the carbanion mechanism (eq 1) comes to mind.



1,3,5-Trimethoxybenzene (**4**) is readily brominated by *t*-BuOBr; during a 5-min reaction with a twofold excess of *t*-BuOBr in HMPA, 59% of its 2-bromo (**5**) and 41% of its 2,4-dibromo derivative (**6**) are formed. The fact that ring rather than methyl carbons are



brominated gives assurance that electrophilic rather than radical substitution is involved.¹⁴⁻¹⁶

However, reaction of *t*-BuOBr with **4** and *t*-BuOK, admixed in HMPA, gave after 1 min only 4% of **5** and 7% of **6**, 87% of **4** remaining unreacted; results after 60 min were nearly the same. In DMF, reaction of **4**, *t*-BuOK, and *t*-BuOBr for 1 min yielded only 6% of **5**, 0.2% of **6**, and 90% recovery of unreacted **4**. Electrophilic bromination of **4** is thus not accelerated by *t*-BuOK to the same extent as for **1**, if at all. The fact that less bromination of **4** occurs in the presence than in the absence of *t*-BuOK is attributed to degradation of *t*-BuOBr through the action of *t*-BuOK.¹⁷ **4**, **5**, and **6** are unaffected by *t*-BuOK in HMPA.

These effects are also evident in reactions of mixtures of equimolar amounts of **1** and **4** with *t*-BuOBr, in the absence and in the presence of *t*-BuOK. In the absence of base, only bromination of **4** occurs; in 1 min, 59% of **5** and 7% of **6** are formed in HMPA or 75% of **5** and 16% of **6** in DMF. In the presence of *t*-BuOK, mainly **1** is brominated; during 1 min in DMF, 34% of tetrabromobenzenes, 2% of pentabromobenzene, 13% of 1,2,4-tribromobenzene (isomerization product¹⁰), and 0.3% of dibromobenzenes (disproportionation products¹⁰) but no **5** or **6** are formed; during 1 min in HMPA, 13% of tetrabromobenzenes, 31% of 1,2,4-tribromobenzene, 3% of dibromobenzenes, 2% of **5**, and 1% of **6** are produced. These experiments confirm that bromination of **1** is greatly accelerated relative to that of **4** in the presence of *t*-BuOK, despite degradation of *t*-BuOBr by the base.

We can dismiss the possibility that both bromination reactions occur by the usual σ -complex mechanism. Even in the unlikely event that, in the absence of base, proton removal were rate limiting in the σ complex from **1** but not in that from **4**, catalysis by a base could not cause bromination of **1** to become faster than of **4**, because the three methoxy groups of **4** accelerate electrophilic attack relative to the three bromine atoms of **1**.

However, the results are intelligible in terms of competition between two mechanisms. The usual σ -complex mechanism obtains in neutral DMF or HMPA and is faster for **4** for the reason mentioned. In the presence of *t*-BuOK, formation of the 2,4,6-tribromophenyl anion occurs rapidly,¹⁰ and this anion captures a positive bromine fragment from *t*-BuOBr (eq 1). However, formation of the 2,4,6-trimethoxyphenyl anion is less favored,¹⁸⁻²¹ and therefore **4** is a poor competitor under these conditions.

(14) The photoinduced chlorination of anisole by *t*-BuOCl produces phenyl chloromethyl ether.¹⁵ *t*-BuOBr resembles *t*-BuOCl in chemical behavior.¹⁶

(15) C. Walling and M. J. Mintz, *J. Amer. Chem. Soc.*, **89**, 1515 (1967).

(16) C. Walling, *Pure Appl. Chem.*, **15**, 69 (1967).

(17) J. Kjellgren, Thesis, Columbia University, 1966; *Diss. Abstr. B*, **28**, 581 (1967).

(18) H-isotope exchange through the action of KNH₂ in ammonia occurs 2000 times faster ortho to F in fluorobenzene than ortho to OCH₃ in anisole.¹⁹ The effects of F, Cl, and Br on aryl anion stability are quite similar.²⁰

(3) E. Berliner, *Progr. Phys. Org. Chem.*, **2**, 253 (1964).

(4) J. G. Hoggett, R. B. Moodie, J. R. Penton, and K. Schofield, "Nitration and Aromatic Reactivity," Cambridge University Press, London, 1971, p 107.

(5) P. B. D. de la Mare and J. H. Ridd, "Aromatic Substitution," Butterworths, London, 1959.

(6) R. O. C. Norman and R. Taylor, "Electrophilic Substitution in Benzenoid Compounds," Elsevier, Amsterdam, 1965.

(7) J. March, "Advanced Organic Chemistry: Reactions, Mechanisms, and Structure," McGraw-Hill, New York, N. Y., 1968.

(8) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," 2nd ed, Cornell University Press, Ithaca, N. Y., 1969.

(9) Cf. comment by J. F. Bunnett, *J. Chem. Educ.*, **43**, A358 (1966).

(10) J. F. Bunnett, *Accounts Chem. Res.*, **5**, 139 (1972).

(11) C. Walling and A. Padwa, *J. Org. Chem.*, **27**, 2976 (1962).

(12) Some of our reactions were conducted in DMF, some in HMPA, and some in both. The phenomena we describe are much the same in either solvent.

(13) A mixture of 1,2,3,5- and 1,2,4,5-tetrabromobenzene was formed; these isomers rapidly interconvert on exposure to *t*-BuOK in DMF or HMPA.¹⁰

Supplemental Material Available. Experimental details will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-936.

- (19) A. I. Shatenshtein, *Advan. Phys. Org. Chem.*, **1**, 187 (1963).
 (20) J. F. Bunnett, J. H. Miles, and K. V. Nahabedian, *J. Amer. Chem. Soc.*, **83**, 2512 (1961).
 (21) Cf. S. A. Krueger and W. W. Paudler, *J. Org. Chem.*, **37**, 4188 (1972).
 (22) Grateful recipient of University of California fellowships, 1969–1970 and 1972–1973, and of a National Science Foundation Traineeship, 1970–1972.

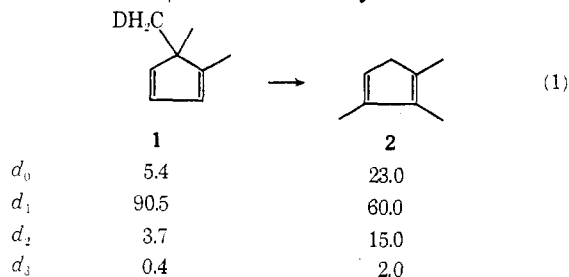
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 Received August 13, 1973

Intermolecular Methyl Transfer during Pyrolysis of 1,5,5-Trimethylcyclopentadiene

Sir:

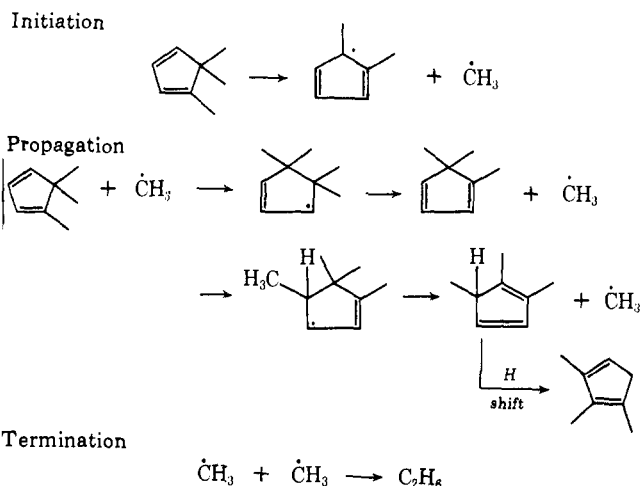
Sigmatropic (1,5) hydrogen shifts in substituted dienes are thoroughly documented,¹ and the intramolecularity of the reaction is firmly established.^{2–4} A corresponding (1,5) methyl shift has characteristics which, by every previous experimental test, were also consistent with intramolecular processes.^{5–6} We report here a new investigation, pyrolysis of a mono-deuterated trimethylcyclopentadiene, which reveals a previously undetected intermolecular component in the (1,5) sigmatropic methyl shift.

Deuterium labeled 1,5,5-trimethylcyclopentadiene (**1**)⁷ was pyrolyzed at 350° for 20 min in a stirred flow reactor. The partial pressure of **1** was ca. 10 Torr in a 1 atm N₂ stream. Isotopic analysis of **1** and of vpc purified **2** by low-voltage mass spectroscopy revealed the label distribution shown in eq 1.⁸ The average deuterium content was 1.0 atom/molecule in every case.



- (1) A summarizing viewpoint and leading reference is R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970, pp 123–124.
 (2) W. R. Roth and J. König, *Justus Liebigs Ann. Chem.*, **699**, 24 (1966).
 (3) S. McLean and R. Haynes, *Tetrahedron Lett.*, 2385 (1964).
 (4) A. P. terBorg, H. Kloosterziel, and N. van Meurs, *Recl. Trav. Chim. Pay-Bas*, **82**, 1189 (1963).
 (5) J. W. deHaan and H. Kloosterziel, *Recl. Trav. Chim. Pay-Bas*, **87**, 298 (1969).
 (6) V. A. Mironov, E. V. Sobolev, and A. N. Elizarova, *Tetrahedron*, **19**, 1939 (1963).
 (7) M. R. Willcott III, and C. J. Boriack, *J. Amer. Chem. Soc.*, **93**, 2354 (1971).
 (8) Nearly identical distributions of D were found when **1** and **2** were isolated from the pyrolysis of bornylene-9-*d*. This study will be reported separately: M. R. Willcott and J. M. Rathburn, unpublished results.

These results, incompatible with intramolecular methyl migration, suggest the following radical chain reactions



The observed exclusive appearance of trimethyl products^{5,6} is assured by the propagation steps we have written here, and propagation by transfer of methyl groups limits the deuterium distribution to discrete units of CH₂D (*i.e.*, the labels must be *d*₀, *d*₁, *d*₂, or *d*₃). A degenerate 1,5,5- to 1,5,5-trimethylcyclopentadiene rearrangement reconciles the appearance of *d*₀ and *d*₂ deuterium labels in this compound. Finally, the preponderance of the 1,2,3 isomer in the reaction mixture is readily justified by the stability of the allylic radical involved in its formation. This scheme, internally consistent for our results, is not in conflict with previous experimental work. Indeed, the rates of disappearance of starting materials and product distribution accord well with those reported by Kloosterziel for the cyclopentadienes.⁵

A subtlety of this class of rearrangement is pointed out by a more quantitative consideration of the isotope distribution. The 60% *d*₁ label of the 1,2,3 isomer can only result from incomplete intramolecular mixing.⁹ Even though an isotope effect could be postulated as the cause, it would be unprecedentedly large. We prefer to think the discrepancy in the distribution is due to the superposition of a radical chain (intermolecular) and concerted (intramolecular) reaction path. This then forces the conclusion that the two paths are finely balanced in this case.¹⁰ The stabilization energy of 20 kcal/mol for the cyclopentadienyl radical¹¹ can be coupled with known bond dissociation energies in neopentane (80 kcal/mol)^{11b} to provide a predicted activation energy of 60 kcal/mol for the bond homolysis reaction. The kinetics of the dimethyl substituted cyclopentadienes are no longer easy to interpret since two processes must be separated. A consistent explanation is that the *E*_a for the concerted path is near 42 kcal/mol while that for the radical path

- (9) The rigorous analysis of the expected deuterium distribution is nontrivial, but a simple analysis, made by counting the number of ways the reactions in the radical chain can occur, predicts 50% *d*₁ and 25% each *d*₀ and *d*₂ labels.
 (10) Our attempts to suppress or to divert the radical chain have failed thus far. This feature is under continuing investigation. For a discussion of the experimental problem involved in rate inhibition for this particular case see ref 12.
 (11) (a) S. Furuyana, D. M. Golden, and S. W. Benson, *Int. J. Chem. Kinet.*, **3**, 237 (1971); (b) S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968, p 215.