***tert*-Butylthioacetaldehyde Dimethyl Acetal *S*-Oxide (11).** Sulfoxide **11** was prepared in 92% yield (8.9 g) by method B using sulfide **10** (8.91 g, 50.0 mmol): bp 82–84 °C (0.06 torr); ^{1}H NMR ($CDCl_3$, 8.8% v/v) δ 4.79 (dd, 1 H, J = 4.75, 7.07 Hz, $(CH_3O)_2CH$), 3.46 (s, 3 H, OCH_3), 3.39 (s, 3 H, OCH_3), 2.72 (d, 1 H, J = 7.07 Hz, $S(O)CH_2$), 2.69 (d, 1 H, J = 4.75 Hz, $S(O)CH_2$), 1.25 (s, 9 H, CH_3). Anal. Calcd for $C_8H_{18}SO_3$: C, 49.43; H, 9.34. Found: C, 49.61; H, 9.28.

Sulfones. The sulfonyl derivatives were prepared using potassium permanganate in water[9] as described in the preparation of methyl sulfone **3**. This procedure will be referred to as method C.

Methylthioacetaldehyde Dimethyl Acetal *S,S*-Dioxide (3). A solution of sulfoxide **2** (3.04 g, 20.0 mmol) in 45 mL of water was added (1 h) to a solution of potassium permanganate (3.16 g, 50.0 mmol) in 100 mL of water at 25 °C. After 4 h, the solution was titrated with an aqueous solution of sodium metabisulfite. The resulting solution was extracted with chloroform (4 × 100 mL) and the combined organic layers were dried (anhydrous magnesium sulfate) and concentrated to dryness (rotary evaporator) to afford a colorless oil. Vacuum distillation under reduced pressure (0.08 torr) gave a homogeneous, colorless material (2.85 g, 85% yield): 82–84 °C; ^{1}H NMR ($CDCl_3$, 15% v/v) δ 4.78 (t, 1 H, J = 5.21 Hz, $(CH_3O)_2CH$), 3.36 (s, 6 H, CH_3O), 3.22 (d, 2 H, J = 5.21 Hz, CH_2), 2.91 (s, 3 H, SO_2CH_3). Anal. Calcd for $C_5H_{12}SO_4$: C, 35.70; H, 7.19. Found: C, 37.40; H, 7.50.

Ethylthioacetaldehyde Dimethyl Acetal *S,S*-Dioxide (6). Sulfone **6** was prepared in 87% yield (3.16 g) according to method C using sulfoxide **5** (3.31 g, 20.0 mmol): bp 84 °C (0.075 torr); ^{1}H NMR ($CDCl_3$, 12% v/v) δ 4.76 (t, 1 H, J = 5.80 Hz, $(CH_3O)_2CH$), 3.34 (s, 6 H, CH_3O), 3.16 (d, 2 H, J = 5.80 Hz, CH_2SO_2), 3.00 (q, 2 H, J = 7.6 Hz, SO_2CH_2), 1.30 (t, 3 H, J = 7.6 Hz, CH_3). Anal. Calcd for $C_6H_{14}SO_4$: C, 39.55; H, 7.74. Found C, 39.40; H, 7.70.

Isopropylthioacetaldehyde Dimethyl Acetal *S,S*-Dioxide (9). Sulfone **9** was synthesized in 93% yield (3.64 g) by method C using sulfoxide **8** (2.50 g, 13.0 mmol): bp 90 °C (0.12 torr); ^{1}H NMR ($CDCl_3$, 10% v/v) δ 4.77 (t, 1 H, J = 5.07 Hz, $(CH_3O)_2CH$), 3.33 (s, 6 H, CH_3O), 3.30 (m, 1 H, J = 6.92 Hz, $(CH_3)_2CH$), 3.17 (d, 2 H, J = 5.07 Hz, CH_2), 1.31 (d, 6 H, J = 6.92 Hz, CH_3). Anal. Calcd for $C_7H_{16}SO_4$: C, 42.82; H, 8.23. Found: C, 43.02; H, 8.30.

***tert*-Butylthioacetaldehyde Dimethyl Acetal *S,S*-Dioxide (12).** Sulfone **12** was prepared in 88% yield (3.69 g) by method C using sulfoxide **11** (3.89 g, 20.0 mmol): bp 104 °C (0.48 torr); ^{1}H NMR ($CDCl_3$, 15% v/v) δ 4.89 (t, 1 H, J = 4.83 Hz, $(CH_3O)_2CH$), 3.34 (s, 6 H, CH_3O), 3.12 (d, 2 H, J = 4.83 Hz, CH_2), 1.37 (s, 9 H, CH_3). Anal. Calcd for $C_8H_{18}SO_4$: C, 45.69; H, 8.63. Found: C, 45.66; H, 8.60.

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Effect of Increasing Electron Demand upon the Product-Determining Transition State in the Reaction of 4-Substituted 2-Nitrobenzenesulfenyl Chlorides and Benzenesulfenyl Chlorides with Bicyclo[2.2.1]hepta-2,5-diene

Dennis G. Garratt* and Pierre L. Beaulieu

Department of Chemistry, University of Ottawa, Ottawa, Ontario, Canada K1N 9B4

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The effect of increasing electron demand upon the product-determining transition state in the reaction of arenesulfenyl chlorides with bicyclo[2.2.1]hepta-2,5-diene has been investigated. As the electron-donating ability of the remote substituents on the phenyl ring of the sulfenyl chloride is varied from nitro to methoxy, the relative proportion of nortricyclene adduct is found to decrease relative to that of simple exo-anti addition. An ortho nitro group was found to lead to a stabilizing interaction only in the case of 2,4-dinitrobenzenesulfenyl chloride. A mechanism involving the competition of three neighboring-group effects is suggested, wherein the neighboring groups are respectively the 5,6 double bond of the substrate, the sulfur atom from the electrophile, and the ortho nitro substituent. In the first two cases the competition is with respect to the stabilization of positive charge at C-2. In the latter case the ortho nitro group is able to stabilize charge development on sulfur while the sulfur atom is itself acting as a neighboring group.

It is generally acknowledged that most changes in molecular structure which result in a change in neighboring-group participation also involve a change in the steric environment of the centers being studied. Evidence has, however, been provided that in certain cases, utilizing a series of molecules of essentially identical steric environment within the vicinity of the reactive sites, neighboring-group participation is a linear function of the electron demand of the incipient ionic species.[1] While such investigations have been traditionally involved with solvolytic behavior,[2] it seems apparent that the concept should apply equally well to electrophilic additions to carbon–carbon double bonds.

An example of such an application is readily found in the bromination of ring-substituted 1-phenylpropenes.[3] These additions are normally nonstereospecific, although

(1) (a) C. D. Johnson, *J. Org. Chem.*, **43**, 1814 (1978); (b) P. G. Gassman and A. F. Fentiman, *J. Am. Chem. Soc.*, **92**, 2549 (1970).

(2) (a) H. C. Brown, M. Ravindranathan, and M. M. Rho, *J. Am. Chem. Soc.*, **98**, 4216 (1976); (b) H. C. Brown, S. Ikegami, K.-T. Liu, and G. L. Tritle, *ibid.*, **98**, 2531 (1976); (c) H. C. Brown, E. N. Peters, and M. Ravindranathan, *ibid.*, **99**, 505 (1977); (d) H. C. Brown, C. Gundu Rao, and M. Ravidranathan, *ibid.*, **99**, 7663 (1977); **100** 1218 (1978); (e) H. C. Brown and M. Ravindranathan, *J. Org. Chem.*, **43**, 1709 (1978); (f) G. A. Olah, G. K. Prakash, and G. Liang, *J. Am. Chem. Soc.*, **99**, 5683 (1977).

(3) See for example G. H. Schmid and D. G. Garratt in "The Chemistry of the Functional Groups: Supplement A: The Chemistry of Double-Bonded Functional Groups", S. Patai, Ed., Wiley, London, 1977, pp 764–85.

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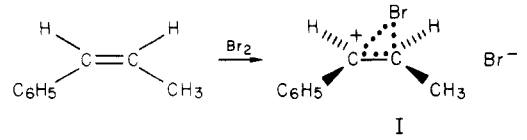
anti addition is favored. Stereospecific anti addition is found only when the cumulative effect of the ring substituents is equal to or more electron withdrawing than that observed in the reaction with (*E*)- or (*Z*)-1-(3′-nitrophenyl)propene. These results are taken as evidence that the intermediates in the bromination of 1-phenylpropenes resemble a weakly bridged benzylic-like ion, I, a hypothesis which leads to the conclusion that the product-determining transition state also has a weakly bridged structure.

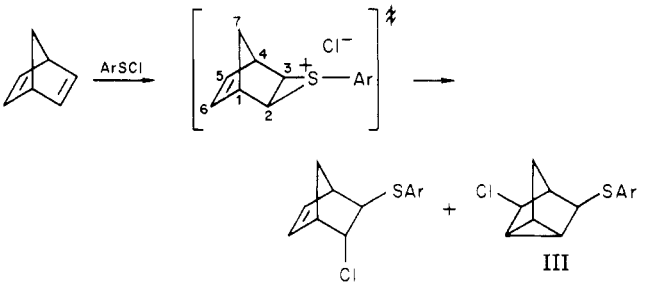


I

The break in product stereospecificity may be taken as indicative of a change in the mechanistic aspects of the electrophilic additions. For substituents less capable of stabilizing a benzylic carbonium ion than the meta nitro group, neighboring group participation by the bromine atom was important. For substituents such as para chloro or para methoxy, which are better at stabilizing the incipient benzylic carbonium ions than the meta nitro group, participation by the bromine atom was not needed in the product-determining step and hence did not occur.

An extension of the concepts given above has been used in an analysis of both rate- and product-determining transition states in the reaction of 2,4-dinitrobenzenesulfenyl chloride to ring-substituted 1-phenylpropenes.[4] In this case the rate data expressed in terms of a $\rho-\sigma$ plot is indicative of participation by sulfur throughout the series, whereas the product studies gave confirmation of a clear-cut division between the involvement and noninvolvement of an arylthio neighboring group. Thus, while the electronic demands in the rate-determining transition state are similar throughout the series, the product-determining transition state changes from a bridged one for para methyl and more electron-withdrawing substituted 1-phenylpropenes to an open ion-like one for 1-phenylpropenes with ring substituents which are more electron-donating than methyl.

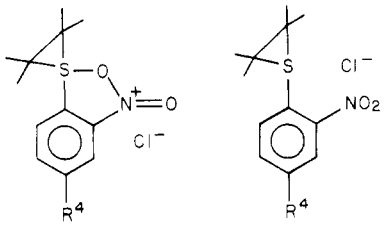
We wish to report at this time our investigations concerning the effect of increasing electron demand upon the product-determining transition state in the reactions of 4-substituted 2-nitrobenzenesulfenyl chlorides and benzenesulfenyl chlorides with bicyclo[2.2.1]hepta-2,5-diene. This substrate was chosen on the basis of previous product studies which demonstrated the importance of homoallylic π participation of the remaining double bond in the product-determining step.[5] It can be seen that our approach differs from those previously discussed in that the effect of varying substituents on the electrophile itself is investigated, thus changing the bridging ability or degree of neighboring-group participation of the arylthio moiety while holding the second potential neighboring group, in this case the homoallylic double bond, constant. The relative proportions of adducts II and III as a function of R^2 and R^4 should therefore give a measure of the electron demand on the sulfur atom toward stabilizing charge development of C-2 of the norbornenyl system relative to



II

π participation by the C-5,C-6 double bond.

The use of three series of arenesulfenyl chlorides, namely, those possessing the ortho nitro substituent and those with only ortho or para substituents, was the result of concern raised in a number of quarters over the possible bonding interaction of an oxygen atom from the ortho nitro group, in *o*-nitrobenzenesulfenyl halides, with the adjacent sulfur atom leading to a spirosulfurane intermediate IV instead of the commonly accepted thiiranium ion V.[6]



IV V

Studies correlating thiiranium ion structure with product geometry have provided considerable insight into the nature of thiiranium ions and have demonstrated that simple alkane- and arenesulfenyl halides often react in a manner quite different from that of *o*-nitroarenesulfenyl halides.

Of paramount importance, in addition to the effects of electron demand, is the determination of what effect, if any, the ortho nitro substituent is really contributing to the reactions under consideration. For example, in addition to the above-mentioned possible stabilization of a positive charge on sulfur by delocalization into the adjacent nitro group, one can envision a destabilization through inductive electron withdrawal and/or a steric effect.

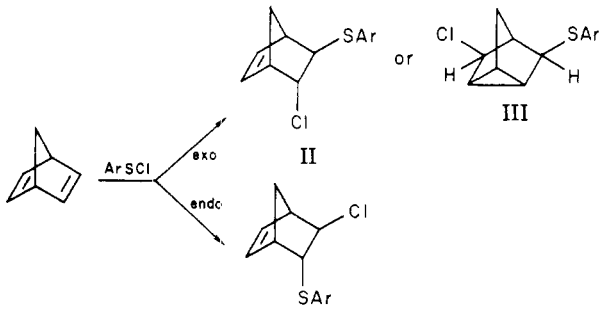
Results and Discussion

Several groups have previously reported that the reactions of arenesulfenyl chlorides with bicyclo[2.2.1]-hepta-2,5-diene in chlorinated hydrocarbons as solvent form one, two, or all three of the adducts II, III, and VI via competitive exo and endo attack.[5] The relative amounts of each product depend upon the nature of the electrophile, solvent, and temperature. In this investigation all reactions were carried out in anhydrous methylene chloride solution at 25 °C. Product analyses were based upon the previously defined criteria utilizing ^1H and ^{13}C NMR spectroscopy.[5b] In all cases mixtures of the previously reported three adducts were obtained. The kinetically controlled product distributions were determined by immediate ^1H and ^{13}C NMR analyses of the reaction mixtures (Table I). Control experiments using

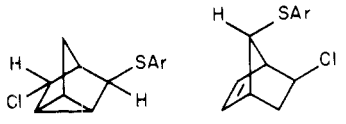
(4) (a) G. H. Schmid and V. J. Nowlan, *J. Org. Chem.*, **37**, 3086 (1972); (b) G. H. Schmid and V. J. Nowlan, *Can. J. Chem.*, **54**, 695 (1976); (c) K. Izawa, T. Okuyama, and T. Fueno, *Bull. Chem. Soc. Jpn.*, **47** 1480 (1974).

(5) (a) S. J. Cristol, R. P. Arganbright, G. D. Brindell, and R. M. Heitz, *J. Am. Chem. Soc.*, **79**, 6035 (1957); (b) G. H. Schmid and T. C. Morrill, private communication; (c) N. S. Zefiov, N. K. Sadovaya, R. Sh. Akhomedova, and V. Bodrikov, *Zh. Org. Khim.*, **14**, 662 (1978); *Chem. Abstr.*, **89**, 42641 (1978).

(6) (a) D. C. Owsley, G. K. Helmkamp, and M. F. Rettig, *J. Am. Chem. Soc.*, **91**, 5239 (1969); (b) D. R. Hogg, *Mech. React. Sulfur Compd.*, **5**, 87 (1970); (c) E. N. Givens and H. Kwart, *J. Am. Chem. Soc.*, **90**, 378, 386 (1968); (d) N. Kharasch in "Organic Sulfur Compounds", Vol. 1, N. Kharasch, Ed., Pergammon Press, Oxford, 1961, p 379; (e) W. H. Mueller and P. E. Butler, *J. Am. Chem. Soc.*, **88**, 2866 (1966); (f) W. H. Mueller and P. E. Butler, *ibid.*, **90**, 2075 (1968); (g) W. A. Thaler, *J. Org. Chem.*, **34**, 871 (1969).



individual samples of the respective adducts, obtained via preparative TLC or column chromatography on silica gel, indicate that subsequent isomerizations are much slower than the initial addition process. Minor quantities of two further "adducts" were isolated via these chromatography experiments in yields of less than 5% of the total mixture employed for separations. It was observed, however, that these samples were not stable under our chromatography conditions and thus may be artifacts of the chromatographic procedure and *not* true products of the initial addition. NMR analyses of these minor components showed them to be *trans*-3-(arylthio)-5-chlortricyclo-[2.2.1.$0^{2,6}$]heptane (VII) and *syn*-7-(arylthio)-*exo*-2-chlorobicyclo[2.2.1]hept-5-ene (VIII), respectively.

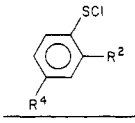


Assignment of the configuration indicated above for species VII follows from the presence of seven aliphatic carbon resonances in its ^{13}C NMR spectrum, three of which resonate at higher field than those normally associated with the norbornane ring structure. The absence of olefinic carbons and the presence of these high-field carbons suggest that VII is isomeric with species III. A diamagnetic shift in the resonance of C-3 in VII relative to that of III suggests that the chlorine on C-5 is oriented in a γ-gauche type interaction with C-3, indicating, therefore, the probable trans configuration of the two substituents. Furthermore, C-7 is shifted downfield by approximately 2 ppm in VII relative to III, indicative of the absence of a second γ effect and thus the trans-periplanar orientation of the chlorine atom relative to C-7. The marginal shift in resonances for C-5 in species VII and III serve to confirm our assignment.

The structure of VIII is most easily ascertained from its mass spectrum which shows a "retro-Diels–Alder"-type fragmentation to give an arylthio-substituted cyclopentadiene fragment plus a chloroethene fragment. This fragmentation contrasts with those found for species II and VI which give rise to very strong fragments at m/e 66 corresponding to $C_5H_6^+$. This latter observation served as strong evidence for species II and VI having only protons in positions C-1, C-4, C-5, C-6, and C-7.

An examination of the primary product distributions (Table I) shows a number of trends. Regarding first of all the results from *o*-nitrobenzenesulfenyl chlorides (entries 1–5), one observes that the ratio of exo attack to endo attack, (II + III):VI, is essentially constant. In contrast, the ratio of exo-anti addition to transannular π participation, II:III, varies from 40:60 to essentially the reverse 59:41 as the electron-donating ability of the para substituent on the arenesulfenyl chloride is varied from nitro, a poor donor, to methyl, a good donor. This type of

Table I. Effect of Increasing Electron Demand on the Kinetically Controlled Product Distributions for the Addition of Arenesulfenyl Chlorides to Bicyclo[2.2.1]hepta-2,5-diene



			product, %			ratio of attack	
R^2	R^4	entry	II	III	VI	II:III	(II + III):VI
NO_2	NO_2	1	30	49	21	40:60	79:21
NO_2	Cl	2	34	45	21	43:57	79:21
NO_2	H	3	41	39	20	51:49	80:20
NO_2	CH_3	4	47	33	20	59:41	80:20
NO_2	CH_3O	5	46	35	19	57:43	81:19
H	NO_2	6	13	71	16	15:85	84:16
H	Cl	7	40	45	15	47:53	85:15
H	H	8	45	42	13	52:48	87:13
H	C_6H_5	9	45	38	17	55:45	83:17
H	CH_3	10	51	28	21	65:35	79:21
H	C_2H_5	11	46	32	22	58:42	78:22
H	CH_3O	12	48	33	19	59:41	81:19
CH_3	H	13	52	33	15	61:39	85:15
CH_3O	H	14	57	24	19	70:30	81:19

variation is much more dramatic in the absence of the ortho nitro substituents as is shown in entries 6–12, the change going from 15:85 to 65:35.

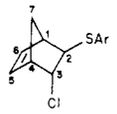
It is interesting to note here that 2,4-dinitrobenzenesulfenyl chloride (entry 1) appears to be much better at stabilizing charge development on sulfur than 4-nitrobenzenesulfenyl chloride (entry 6). This statement is based on the very high percentage of transannular participation in the latter case, which we interpret as neighboring-group assistance for the weakly stabilized thiiranium ion. A further examination of Table I, however, indicates that little if any extra stabilization is obtained from an ortho nitro group when the para substituent is more electron-donating than nitro. For example, comparing entries 2 and 7, 3 and 8, or 5 and 12, we see essentially the same propensity for transannular participation. In fact, a comparison of entries 4 and 10 suggests that, if anything, in this case the ortho nitro substituent on 4 is destabilizing charge development on sulfur in the product-determining transition state. This is, of course, reasonable since nitro groups are generally considered as electron-withdrawing groups.

On the basis of the above it appears that only in the case of 2,4-dinitrobenzenesulfenyl chloride, entry 1, does the ortho nitro substituent lead to a stabilizing interaction, possibly via formation of a spirosulfurane intermediate such as IV. This neighboring group assistance by the ortho nitro substituent would appear to occur as a result of the dual electron withdrawal of both nitro groups, since, as we have noted above, in the presence of more electron-donating substituents in the para position one observes only the electron-withdrawing properties of the ortho nitro group.

Our scenario is further supported by a comparison of entries 1, 8, 13, and 14 where the ortho substituent is varied. While minor variations are noted with respect to the propensity of exo vs. endo attack, we observe a continual increase in the proportion of exo-anti addition relative to transannular participation as the electron-donating ability of the substituent increases. These data once again attest to the lack of a special stabilizing interaction by the ortho nitro group under our conditions, except as indicated above.

It is of interest to note that an ortho methoxy group is better at stabilizing the thiiranium ion than is an ortho

Table II. Carbon-13 NMR Parameters (ppm) for the 2-*exo*-(Arylthio)-3-*endo*-chloronorborn-5-enes Synthesized During This Investigation

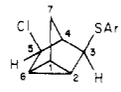


Ar substituents	C-1	C-2	C-3	C-4	C-5	C-6	C-7	other carbons (excluding aromatics)
2-NO_2, 4-NO_2	48.95	54.38	64.35	49.67	136.35	136.39	46.37	
2-NO_2, 4-Cl	48.89	54.27	64.51	49.59	136.04	136.48	46.29	
2-NO_2, 4-H	48.89	54.16	64.45	49.51	135.93	136.58	46.25	
2-NO_2, 4-CH_3	48.88	54.29	64.55	49.53	135.87	136.66	46.24	20.49, $ArCH_3$
2-NO_2, 4-CH_3O	48.87	54.96	64.59	49.55	135.78	136.71	46.16	55.94, $ArOCH_3$
4-NO_2	48.73	56.29	65.06	49.25	136.31	136.72	45.89	
4-Cl	48.92	58.69	64.93	49.42	134.76	136.82	45.99	
4-H	48.94	58.48	64.74	49.42	134.76	136.82	45.99	
4-C_6H_5	49.27	56.07	64.42	50.21	134.14	136.66	45.77	
4-CH_3	49.24	56.52	64.45	50.62	134.94	136.81	45.67	20.76, $ArCH_3$
4-C_2H_5	48.76	56.46	64.49	50.55	134.95	136.81	45.69	28.19 t, 15.16 q, $ArCH_2CH_3$
4-CH_3O	49.50	57.74	64.58	49.50	135.28	137.04	45.84	56.24, $ArOCH_3$
2-CH_3	49.46	55.60	64.55	49.46	135.29	137.05	46.09	20.60, $ArCH_3$
2-CH_3O	48.93	57.10	64.77	49.64	135.55	136.96	46.25	56.40, $ArOCH_3$

Table III. Carbon-13 NMR Parameters (ppm) for the 2-*endo*-(Arylthio)-3-*exo*-chloronorborn-5-enes Synthesized during This Investigation

Ar substituents	C-1	C-2	C-3	C-4	C-5	C-6	C-7	other carbons (excluding aromatics)
2-NO_2, 4-NO_2	50.18	53.52	65.14	49.63	137.02	135.93	46.82	
2-NO_2, 4-Cl	52.70	56.94	65.43	47.46	137.35	135.46	46.98	
2-NO_2	52.67	56.77	65.48	47.40	137.50	135.29	46.93	
2-NO_2, 4-CH_3	52.67	56.91	65.53	47.39	137.51	135.21	46.92	20.49, $ArCH_3$
2-NO_2, 4-CH_3O	52.58	57.70	65.52	47.45	137.44	135.15	46.86	55.94, $ArOCH_3$
4-NO_2	50.45	53.98	65.19	49.18	136.87	135.32	46.43	
4-Cl	50.48	56.35	65.43	47.36	137.40	132.81	46.58	
4-H	50.19	56.14	65.13	47.36	137.40	132.81	46.58	
4-C_6H_5	50.40	56.40	65.27	48.50	137.16	134.94	46.38	
4-CH_3	50.48	56.29	65.01	48.52	137.37	134.61	46.26	20.56, $ArCH_3$
4-C_2H_5	50.32	56.30	65.03	48.56	137.43	134.52	46.29	28.04 t, 15.16 q, $ArCH_2CH_3$
4-CH_3O	52.09	56.36	64.98	47.28	137.43	134.92	46.52	56.36, $ArOCH_3$
2-CH_3	52.39	57.96	65.47	47.37	137.65	135.00	46.63	20.60, $ArCH_3$
2-CH_3O	52.60	57.02	65.52	47.37	137.72	135.23	46.87	56.64, $ArOCH_3$

Table IV. Carbon-13 NMR Parameters (ppm) for the 3-(Arylthio)-5-chloronortricyclenes Synthesized during This Investigation



Ar substituents	C-1	C-2	C-3	C-4	C-5	C-6	C-7	other carbons (excluding aromatics)
2-NO_2, 4-NO_2	15.18	15.81	48.44	41.61	64.49	20.12	29.63	
2-NO_2, 4-Cl	15.05	15.97	48.30	41.61	64.75	20.07	29.46	
2-NO_2	15.04	16.01	48.09	41.60	64.89	20.03	29.46	
2-NO_2, 4-CH_3	15.00	16.07	48.28	41.65	64.93	20.06	29.41	20.49, $ArCH_3$
2-NO_2, 4-CH_3O	14.94	16.20	49.01	41.75	64.88	20.11	29.34	55.94, $ArOCH_3$
4-NO_2	14.54	15.85	48.24	41.52	64.25	19.80	29.11	
4-Cl	14.63	16.51	49.42	41.90	64.55	20.21	29.20	
4-H	14.64	16.69	51.02	41.99	64.74	20.21	29.29	
4-C_6H_5	14.47	16.36	48.69	41.74	64.75	20.04	29.03	
4-CH_3	14.39	16.49	49.12	41.79	64.29	20.05	28.95	20.56, $ArCH_3$
4-C_2H_5	14.40	16.51	49.23	41.84	64.49	20.01	28.98	28.19 t, 15.16 q, $ArCH_2CH_3$
4-CH_3O	14.60	16.69	48.75	41.98	64.73	20.35	29.14	55.98, $ArOCH_3$
2-CH_3	14.79	16.61	48.96	41.94	64.85	20.24	29.44	20.60, $ArCH_3$
2-CH_3O	14.85	16.59	48.33	41.99	64.64	20.38	29.53	56.14, $ArOCH_3$

methyl substituent (entries 13 and 14), since we have also found that a para methyl group is better than a para methoxy with respect to the identical problem (entries 4 and 5, and 10 and 12). This latter point appears indicative of the lack of, or at least greatly attenuated, specialized long-range stabilization by through-resonance interactions. Deviations of this type which are not normally expected from the simple through-resonance picture for +T substituents[12] have been previously reported.[11]

In conclusion, our studies indicate a definitive interplay of three neighboring-group effects (i.e., the 5,6 double bond of the substrate, the sulfur atom, and the ortho nitro group) in the additions of arenesulfenyl chlorides to bicyclo[2.2.1]hepta-2,5-diene, wherein the kinetically controlled product distributions reflect the effect of increasing electron demand in the product-determining transition state. Further studies are currently under way to determine if such interactions are of importance in the analogous rate-determining step.

Experimental Section

General Methods. All melting points were measured on a Fisher-Johns block and are uncorrected. ^{1}H NMR spectra were recorded on Varian Associates T-60 and HA-100 spectrometers. ^{13}C NMR spectra were recorded on a Varian FT80-16K spectrometer. Chloroform-*d* was used as an internal lock and reference. All spectral parameters are referenced to Me_4Si as an internal standard.

Bicyclo[2.2.1]hepta-2,5-diene was available commercially (Aldrich) and purified by distillation; bp 88–89 °C (758 mmHg).

2,4-Dinitrobenzenesulfenyl chloride was prepared by the method of Lawson and Kharasch from bis(2,4-dinitrophenyl) disulfide. The compound was recrystallized from CCl_4; mp 96–96.5 °C (lit.[7] mp 97–98 °C).

(7) D. Lawson and N. Kharasch, *J. Org. Chem.*, **24**, 857 (1956).

2-Nitro-4-chlorobenzenesulfenyl chloride was prepared by the method of Turner and Conner using 1,4-dichlorobenzene as starting material; mp 98 °C (lit.[8] mp 97.5–98 °C).

2-Nitrobenzenesulfenyl chloride was commerically available (Aldrich) and was recrystallized from CCl_4; mp 76 °C (lit.[10] mp 74.5–75 °C).

2-Nitro-4-methylbenzenesulfenyl chloride was prepared from the analogous aniline by the procedure of Zincke and Röse[9] and was recrystallized from CCl_4; mp 89–90 °C.

2-Nitro-4-methoxybenzenesulfenyl chloride was prepared from the analogous aniline as above and crystallized as brillant orange needles from CCl_4; mp 106–107 °C.

The remaining arenesulfenyl chlorides were prepared from the corresponding commercially available thiols or disulfides by chlorination with molecular chlorine in CCl_4 with cooling (0–4 °C). All physical data were as expected.[10]

General Reaction Procedure. Product studies were carried out as previously described.[5] In the cases of 4-substituted-2-nitrobenzenesulfenyl chlorides, ^{1}H NMR analysis was carried out during the course of the reactions and thereafter to ensure the establishment of kinetically controlled product distributions. Because of the essentially instantaneous nature of the reactions of arenesulfenyl chlorides which lack the ortho nitro substituent, only the slow isomerizations postaddition were observable by ^{1}H NMR. Samples of individual adducts were isolable via preparative TLC on silica gel with CH_2Cl_2 or 80:20 cyclohexane–ethyl acetate as elutant depending upon the substituents. ^{13}C NMR parameters for the various adducts are listed in Tables II–IV.

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(11) See for example L. P. Hammett in "Physical Organic Chemistry, Reaction Rates, Equilibria, and Mechanisms", 2nd ed., McGraw-Hill, New York, 1970, pp 357–69.
(12) +T is Ingold's symbol; Wheland's corresponding symbol is -R.

Photochemical Reactions of Isomeric N,N-Dimethyltoluidines in CCl_4, $CHCl_3$, and CH_2Cl_2

Tadeusz Latowski and Bogumil Zelent*

Institute of Chemistry, University of Gdańsk, 80-952 Gdańsk, Poland

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Products of photochemical reactions of *N,N*-dimethyl-*p*-toluidine (DMpT), *N,N*-dimethyl-*m*-toluidine (DMmT), and *N,N*-dimethyl-*o*-toluidine (DMoT) in CCl_4, $CHCl_3$, and CH_2Cl_2 have been isolated and identified. Mechanisms of partial reactions have been advanced to account for similarities and differences of photochemical transformations in the given media. Particular attention has been paid to participation of the methyl group bound with the benzene ring in the reactions.

Electronic excitation of *N,N*-dimethylaniline (DMA) in bromobenzene,[1] tetrachloromethane,[2,3] trichloromethane,[4] and dichloromethane[5] has been found to initiate two simultaneous photochemical processes: cleavage of the *N*-methyl bond and irreversible electron transfer onto the solvent molecule. The former process does not have a decisive effect on further transformations of the amine in these media. The latter affords a radical cation of DMA as well as the radical R and the halogen ion X^-, which are formed by heterolytic dissociation of the C–X bond of an electron-acceptor molecule. The extent of further transformations is determined by a high lability of the DMA radical cation and by the chemical reactivity of the radical R. Secondary reactions occurring in the cage of the solvent afford still other active species involving either the α radical or the carbocation β (eq 1 and 2).

In CH_2Cl_2, $CHCl_3$, and CCl_4 the recombination of the DMA radical cation with the appropriate chloromethane

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