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THE ADDITION OF p-NITROBENZENESULFONYL PEROXIDE TO cis- AND trans- STILBENE

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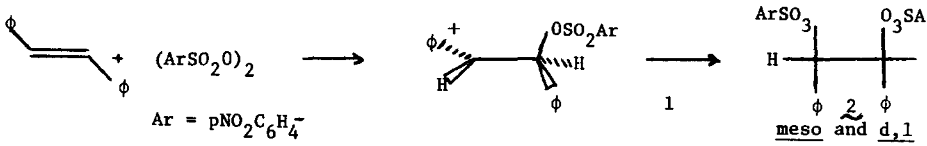
While the reaction of arylsulfonyl peroxides with aromatic substrates has been well elucidated,[1] reactions with simple olefinic substrates have been little investigated. An early report in this journal claimed that stereospecific anti addition to trans-stilbene was obtained with p-toluenesulfonyl peroxide.[2] Further experiments showed that the addition was not in fact stereospecific but that a small amount of (10%) products could be explained by a non-stereospecific addition process.[3]

Since other data indicates that cationic intermediates are formed in the reaction of sulfonyl peroxides and olefins, it was concluded that the addition of arylsulfonyl peroxides to trans-stilbene involves the formation of a non-bridged carbenium ion(Eq 1).[3] The neighboring group effect of the sulfonoxy group has not been determined but bridging could occur via three- or five-membered ring formation (2 or 3). Thus the stereoselectivity in the addition of arylsulfonyl peroxides to stilbenes[3] might relate to the structure of the intermediate cation and to the extent of bridging by the sulfonoxy group. The intervention of a freely rotating carbenium ions along the reaction pathway should yield the same product mixture from cis- and trans-stilbene.



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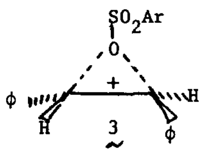

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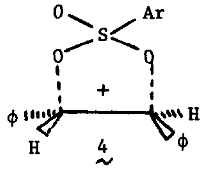

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It was therefore undertaken to measure the amount of *meso* and *d,l* isomers from the addition of p-nitrobenzenesulfonyl peroxide to *cis*- and *trans*-stilbene at various temperatures.

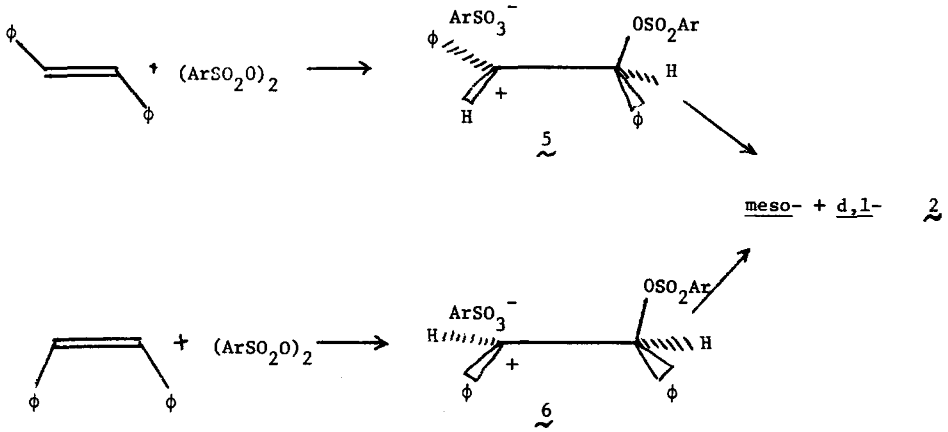
A solution (200 ml) of the olefin (0.28 g, 1.55 mmol) was equilibrated at the desired temperature and p-nitrobenzenesulfonyl peroxide (0.6 g, 1.5 mmol) was added. The products of addition were isolated by filtration after reducing the reaction mixture to dryness *in vacuo*, adding methanol (20 ml) and cooling in ice. Yields ranged from 50-60%. The proportion of *meso* and *d,l* isomers in the product mixture was determined by infrared analysis. Standard mixtures of *meso* and *d,l*-1,2-bis(p-nitrobenzenesulfonoxy)1,2-diphenylethane were prepared[4] and the relative intensity of bands at 812 cm^{-1} and 900 cm^{-1} (KBr) were used to prepare a calibration curve.[5a] Mixtures of these products from the reaction of p-nitrobenzenesulfonyl peroxide and *cis*- or *trans*-stilbene were analyzed by infrared and compared to the calibration curve. In this fashion the composition could be measured to within 3%.[5]

The results of these experiments are given in Table I. The source of disparate results between this work and earlier data[2a 3] is not known. The much greater solubility of the *d,l* than the *meso* isomer ($>10^2$ greater in $CHCl_3$) may be a particular problem when isolation of individual isomers is attempted.[2a,3] The present data are quite reproducible and quite different than earlier results.[3]

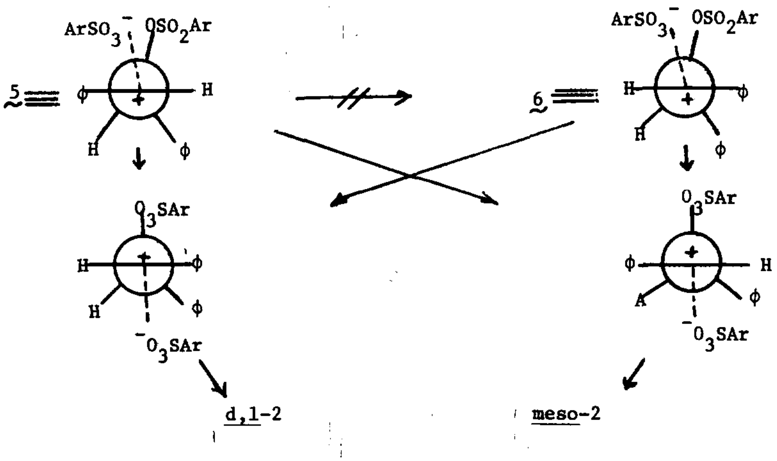
Table I. Isomer Distribution of Products from the Addition of p-Nitrobenzenesulfonyl Peroxide to Stilbene[6]

Temp (°C)	cis-Stilbene % d,l:% meso		trans-Stilbene % d,l:% meso	
	$CHCl_3$	CH_3NO_2	$CHCl_3$	CH_3NO_2
-20	30:70	28:72	48:52	45:55
- 0	30:70	27:73	49:51	48:52
+22	30:70	28:72	46:54	42:58
+59	45:55		47:53	
0			10:90[3]	

As can be seen from the isomer ratios in Table I, syn addition is the major route for *cis*-stilbene (*meso* product) while *trans*-stilbene gives almost random syn and anti addition products. Changing the solvent dielectric constant from 4.7 D (chloroform) to 38.6 D (nitromethane) lead to no change in product distribution or yield from either olefin. It is evident that different species are formed on addition of p-nitrobenzenesulfonyl peroxide to *cis*- or *trans*-stilbene and that these intimate ion pairs are not chemically responsive to changes in solvent polarity. Hence the competition between direct collapse to product and rotational isomerism and then collapse to product occurs in the intimate ion pair. (Scheme I). The stereochemical results also mitigate against any significant interaction between the sulfonoxy group and the benzylic carbenium ion as in **3** or **4**.



Product formation can occur by collapse of first formed ions in a syn sense or may undergo rotational transformation to give anti ions and then products (Scheme II). We cannot distinguish



these alternatives at present. The lack of solvent effect on the product distribution argues against any mechanism involving migration of the anionic addend to the anti face of the ethylenic bond by a solvent separated ion pair. The solvation of such an ion pair by solvent should be facilitated by nitromethane over chloroform. Increased syn addition due to decreased internal return[7b,8b] is predicted whereas no such effect is seen for either starting olefin. Isomerism between pro-d,l and pro-meso ions occurs without solvent influence i.e. in the intimate ion pair stage.

The observed additions of p-nitrobenzenesulfonyl peroxide towards the stilbenes contain features of both chlorination[8] and bromination[9] but are distinctly different than either.[10] The factors responsible for these differences are currently being investigated.

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References

1. R.L. Dannley and W.R. Knipple, J. Org. Chem., 38, 6 (1973) and references therein. P.K. Tornstrom, JOC, 40, 2278 (1975).

2. a) J. Bolte, A. Kergomard, and S. Vincent, Tet. Lett., 1965, 1529.
   b) The resulting meso derivative was identified by melting point comparison with the authentic isomer. However, the same derivative was obtained from cis-stilbene which requires syn addition. No attempt to reconcile this point was made.

3. J. Bolte, A. Kergomard, and S. Vincent, Bull. Soc. Chim. Fr., 1972, 301. The isomers were isolated and identified by melting point and elemental analysis

4. The respective 1,2-di p-nitrobenzenesulfonoxy-1,2-diphenylethanes were prepared from meso- and d,l-dihydrobenzoin and p-nitrobenzenesulfonyl chloride in pyridine. They were characterized by infrared and each gave a satisfactory elemental analysis (0.3% C, H, and N).

5. a) R.T. Conley, "Infrared Spectroscopy", Allyn and Bacon, Inc., Boston, Mass., 1966, pg. 225.
   b) The precision was checked by carrying out the determination on known mixtures.

6. Isomer distributions given are the results of multiple runs that consistently agreed 2%. Furthermore, cis-trans isomerization of the olefin was shown not to occur under the reaction conditions.

7. a) P. D. B. de la Mare, M. D. Johnson, J. S. Lomar, and V. Sanchez del Olmo, J. Chem. Soc., B, 1960, 827.
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   b) R.E. Buckles, J.L. Miller, R.J. Thurmaier, J. Org. Chem., 32, 888 (1967); R.E. Buckles, J.M. Bader, and R.J. Thurmaier, ibid, 27, 4523 (1962).
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9. a) M.L. Poutsma, Science, 157, 997 (1967).
   b) R.C. Fahey and C. Schubert, J. Amer. Chem. Soc., 87, 5172 (1965).

10. Other mechanisms such as radical-cation or free radical are not consistent with (1) rearranged products which comprize the remainder of the products, nor (2) with the capture of intermediates by nucleophilic solvents, nor (3) with the same product mix formed in the presence of or absence of free radical inhibitors; R.D. Bishop, unpublished work. However, at the highest temperature it appears that free radical decomposition may be occurring.