spectrum of **1**. In a similar experiment, the potassium methoxide solution was added dropwise with the spectrum recorded after each addition of methoxide. The development of peaks ascribable to **1** and the disappearance of those due to **4** were observed; after the addition of 1 equiv of base, only the peaks due to the complex were observed. In neither experiment were peaks ascribable to any third species observed; the initial observations of the spectra of these solutions were made within 20 sec of the time of addition of methoxide ion. No changes were observed in the spectra of solutions of complexes **1–3** which had been allowed to stand at room temperature for extended periods of time. This solution behavior is one manifestation of the greater stability of these complexes as compared to those of the 2,4-dinitrophenyl ethers which undergo a relatively rapid rearrangement to the isomeric 1,2 complexes.[5,36] No exchange of ring protons with solvent deuterons (from DMSO-d_6) was observed for solutions of **1–3**, but, in the presence of excess base, exchange is rapid and complete. Addition of a large excess of potassium methoxide in methanol to a solution of **4** in DMSO-d_6 led to the immediate development of the spectrum of **1**, but the intensities of the aromatic resonances of **1** underwent a rapid decrease and after 3–5 min all of the aromatic protons appeared to have exchanged with a concomitant increase in the intensity of the DMSO-d_5 peak.

(36) E. J. Fendler, W. E. Byrne, J. H. Fendler, and C. E. Griffin, unpublished results.

Registry No.—**4**, 13772-69-5; **5**, 15352-94-0.

Acknowledgment.—We are indebted to Drs. S. Castellano and J. J. Burke for helpful discussions and to Dr. B. D. Martin for assistance in the determination of pmr spectra. This work was supported, in part, by the U. S. Atomic Energy Commission and instrumentation provided by a grant (FR 00292) from the National Institutes of Health was used.

Nucleophilic Addition–Elimination Reactions of 1,2-Di-*p*-toluenesulfonylethene[1]

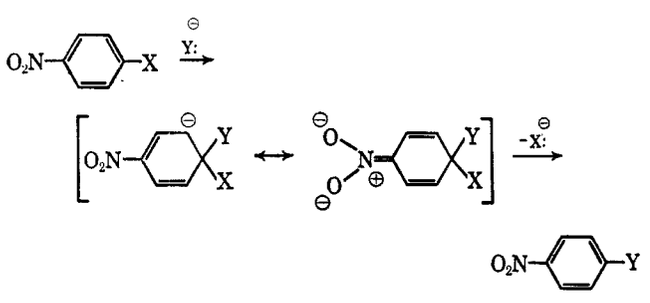
JOHN S. MEEK AND JOANNA S. FOWLER[2]

Department of Chemistry, University of Colorado, Boulder, Colorado 80302

Received September 20, 1967

The addition–elimination reactions of *cis*- and *trans*-1,2-di-*p*-toluenesulfonylethene (**1** and **2** in text) with azide, methoxide, and thiophenoxide ions occur with a high degree of retention of configuration of the substrate. Trimethyl phosphite reacts with both **1** and **2** to yield dimethyl *trans*-2-*p*-toluenesulfonylethenephosphonate and methyl *p*-toluenesulfinate. With cyclohexylamine, the *trans*-addition–elimination product is obtained with both **1** and **2**. Ethylenimine gives an adduct with **1** and **2** plus the expected addition–elimination product. Phenylmagnesium bromide reacts with **1** to give *trans*-β-styryl *p*-tolyl sulfone. *cis*-1,2-Di-*p*-toluenesulfonylethene reacts with diazomethane to give 3(5)-*p*-toluenesulfonylpyrazole. Sodium azide reacts with **1** in dimethyl sulfoxide to give 4(5)-*p*-toluenesulfonyltriazole which has been shown to arise from the cyclization of *trans*-2-azidovinyl *p*-tolyl sulfone under basic conditions.

Although nucleophilic substitution reactions at aryl carbon atoms are generally difficult, they occur readily when electron-withdrawing groups are substituted *ortho* or *para* to the leaving group, owing to the stabilization of the transition state (or in some cases, an intermediate).[3]



Similarly, the replacement of vinylic halides is facilitated by electron-withdrawing groups β to the site of substitution. Addition–elimination reactions of this type have been reviewed by Patai and Rappaport,[4] and nucleophilic substitution reactions of β-halovinyl ketones,[5] β-chloroacrylonitrile,[6] β-halovinyl sulfones,[7] and β-halovinyl fluorides[8] are well documented in the literature. However, disulfonylethenes where the sulfone group is both the activating and leaving group have received scant attention. The only nucleophilic addition–elimination reactions so far reported are those of *cis*- and *trans*-1,2-dibenzenesulfonylethene, 1,2-di-*p*-nitrobenzenesulfonylethene, and 1-benzenesulfonyl-2-*p*-nitrobenzenesulfonylethene with cyclohexylamine and piperidine.[9] In order to extend the scope of these reactions *cis*- and *trans*-1,2-di-*p*-toluenesulfonylethene (**1** and **2**) were chosen for study.

Results and Discussion

Scheme I summarizes the reaction products without specifying stereochemistry. In the stereochemical studies the reactions of both **1** and **2** were carried out

(1) This paper was presented in part at the 153rd National Meeting of the American Chemical Society, April 1967, Miami, Beach, Fla.

(2) National Institutes of Health Predoctoral Fellow, 1966–1967.

(3) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart, and Winston, Inc., New York, N. Y., 1959, p 452 ff.

(4) S. Patai and Z. Rappoport, "The Chemistry of Alkenes," Interscience Publishers, Inc., New York, N. Y., 1964, p 525 ff.

(5) A. E. Pohland and W. R. Benson, *Chem. Rev.*, **66**, 161 (1966).

(6) F. Scotti and E. J. Frazza, *J. Org. Chem.*, **29**, 1800 (1963).

(7) (a) L. Maioli and G. Modena, *Gazz. Chim. Ital.*, **89**, 854 (1959); (b) G. Modena and P. E. Todesco, *ibid.*, **89**, 866 (1959); (c) G. Modena, P. E. Todesco, and S. Tonti, *ibid.*, **89**, 878 (1959); (d) S. Ghersetti, G. Lugli, G. Melloni, G. Modena, P. E. Todesco, and P. Vivarelli, *J. Chem. Soc.*, 2227 (1965).

(8) J. D. Park and W. C. Frank, *J. Org. Chem.*, **32**, 1333 (1967); J. D. Park, J. R. Dick, and J. H. Adams, *ibid.*, **30**, 400 (1965).

(9) F. Montanari, *Gazz. Chim. Ital.*, **87**, 149 (1957).

TABLE I

REACTIONS OF NUCLEOPHILES WITH *cis*- AND *trans*-1,2-DI-*p*-TOLUENESULFONYLETHENE

cis- or *trans*-TsCH=CHTs + N: ⟶ TsCH=CHN + Ts^-

Sulfone	N	Solvent	Temp, °C	Time, hr	Yield, %	% *cis*	% *trans*	Other, %	Mp, °C	Lit. mp, °C
1	N_3^-	CH_3CN-H_2O	25	17.5	58	90	10		*cis*, 43–45	48–50[a]
2	N_3^-	CH_3CN-H_2O	25	17.5	39	0	60	18, 40	72–74	75–76[a]
1	C_6H_5SH-$(C_2H_5)_3N$	CH_3CN	25	20	69	90	10			
2	C_6H_5SH-$(C_2H_5)_3N$	CH_3CN	25	20	69	0	100		107–110	111–112[b]
1	$C_6H_{11}NH_2$	CH_3CN	25	26	88	0	100		130–132	131.5–132.5[b]
2	$C_6H_{11}NH_2$	CH_3CN	25	25	95	0	100			
1	CH_3O^-	CH_3CN	25	20	83	95	5		*cis*, 82–83	87[c]
2	CH_3O^-	CH_3CN	25	20	88	0	100		*trans*, 62–63	67[c]
1	$(CH_3O)_3P$	None	25	0.017	70	0	100		108–110	
2	$(CH_3O)_3P$	None	90	0.17	83	0	100		108–110	

[a] Reference 7b. [b] Reference 7c. [c] Reference 7a.

TABLE II

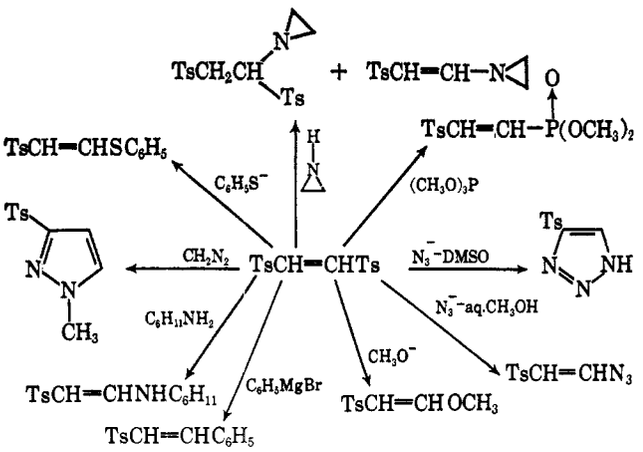
REACTIONS OF NUCLEOPHILES WITH 1 IN VARIOUS SOLVENTS

N	Solvent	Temp, °C	Time, hr	Yield, %	% *cis*	% *trans*	Other %	Mp, °C
N_3^-	CH_3OH-H_2O	25	43–72	29	40	60		*cis* to *trans* isomerism under reaction conditions
N_3^-	CH_3CN-H_2O	25	17.5	58	90	10		
N_3^-	DMSO	25	28	46			18, 45	156–158
C_6H_5SH-$(C_2H_5)_3N$	Ether	25	24	38	90	10		99–101 (lit.[a] 103–104)
C_6H_5SH-$(C_2H_5)_3N$	CH_3CN	25	20	69	80	20		
C_6H_5SH-$(C_2H_5)_3N$	CH_3OH	25	27	68	80	20		
C_6H_5SH-OCH_3^-	CH_3OH	25	18	37	75	25		
$C_6H_{11}NH_2$	CH_3OH	25	24	89	0	100		
$C_6H_{11}NH_2$	Ether	25	24	91	0	100		
$C_6H_{11}NH_2$	CH_3CN	25	26	88	0	100		
OCH_3^-	CH_3OH	25	20	59	100	0		
OCH_3^-	CH_3CN	25	20	83	95	5		*cis* to *trans* isomerism occurs with heating

[a] Reference 7b.

SCHEME I

SUMMARY OF REACTION PRODUCTS



with nucleophiles in acetonitrile at room temperature unless otherwise specified. Product isomer content was obtained from the nmr spectrum of the crude product to preclude postisomerization during the reaction work-up. Since the products contain both α and β vinyl protons, their coupling constants could be used as a basis for configurational assignments.[10] The stereochemistry of the products is summarized in Table I, and a summary of the *cis*/*trans* ratio of products in various solvents is presented in Table II. Nmr data are summarized in Table III.

TABLE III

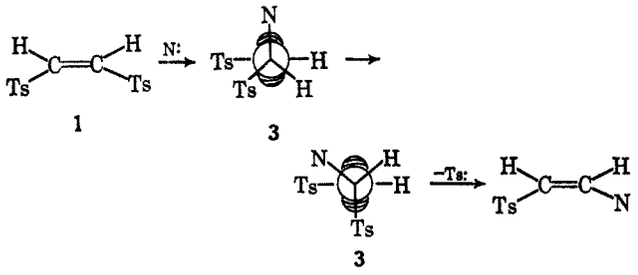
NMR DATA FOR $TsCH^{\alpha}=CH^{\beta}N$[a]

Isomer	N	Hβ, ppm	Hα, ppm	*J*, cps
cis (1)	N_3	6.9	5.75	8
trans (2)	N_3	*b*	6.1	13
cis (3)	OCH_3	6.4	5.5	6.5
trans (4)	OCH_3	*b*	5.75	12
cis (5)	SC_6H_5	*b*	6.25	10
trans (6)	SC_6H_5	*b*	6.00	14
trans (7)	NC_6H_{11} (H)	*b*	5.05	13
trans	$P(OCH_3)_2$ (O)	*b*	6.72	16

[a] All chemical shifts are reported in parts per million (ppm) relative to TMS. Spectra were taken in $CDCl_3$. [b] This proton is obscured by the aromatic signals.

The high degree of stereospecificity in the reactions of **1** and **2** with azide, thiophenoxide, and methoxide ions is best rationalized in terms of an attack by the nucleophile at the π orbital of the olefin to generate an intermediate in which the carbon atom adjacent to the carbon atom under attack is coplanar. Rotation of the tetrahedral carbon atom in this intermediate, **3**, occurs so as to experience the least eclipsing of large groups until the leaving group is in the plane of the developing p orbital of the product. Elimination of the leaving

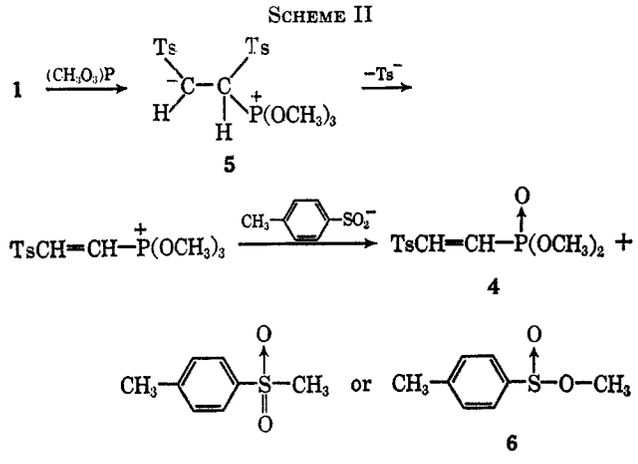
(10) L. M. Jackman, "Applications of N. M. R. Spectroscopy to Organic Chemistry," Pergamon Press Inc., New York, N. Y., 1959, pp 85–87.



group of the intermediate will give a product with retention of configuration whereas rotation in the opposite direction will lead to the *trans* product.[11] Possibly, the methoxide ion is basic enough to convert **1** into *p*-toluenesulfonylacetylene which could then add methanol to give the *cis* product. The other nucleophiles used do not seem basic enough to give elimination then addition.

We have observed that, when **1** reacts with trimethyl phosphite at room temperature without solvent, heat is evolved within 1 min at which time **1** dissolved in the methyl phosphite. Within another minute dimethyl *trans*-2-*p*-toluenesulfonylethenephosphonate (**4**) crystallized. The isolation of the *trans*-phosphonate was surprising in view of the stereospecificity encountered in the previous reactions. In an effort to see if the *cis*-phosphonate was formed and was isomerized thermally, the reaction of **1** with trimethyl phosphite was carried out in an nmr tube in deuteriochloroform at −30°. However, no signals from the *cis* compound were detected and only the formation of the *trans* compound was evident. Possibly isomerization is occurring by reversible addition of methyl phosphite to the phosphonium intermediate. The primary step in this reaction is probably the formation of the betaine intermediate **5** which could form the product by one of two possible paths. Either it could eliminate a *p*-toluenesulfinate anion which could be alkylated as shown in Scheme II or the alkylation and elimination could take

SCHEME II



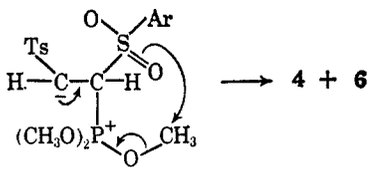
place in one concerted step as outlined in Scheme III. It can be seen that *p*-toluenesulfinate anion is an ambident ion and could undergo alkylation at either sulfur or oxygen to yield methyl *p*-tolyl sulfone or methyl *p*-toluenesulfinate. On the other hand, with a concerted mechanism one can envision a six-membered cyclic transition state leading only to O alkylation.

(11) S. I. Miller and P. K. Yonan [*J. Amer. Chem. Soc.*, **79**, 5931 (1957)] have discussed a similar mechanism.

Bissey and coworkers[12] have suggested a similar mechanism involving five- and seven-membered transition states for the reaction of certain vinylic halides with trialkyl phosphites, but their systems predict identical products by either mechanism. However, in all alkylations involving the *p*-toluenesulfinate anion with various alkylating agents, only S alkylation seems to have been observed and sulfones are isolated.[13]

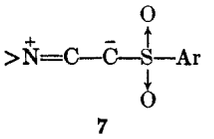
At first only methyl *p*-toluenesulfinate was isolated from the reaction of **1** with trimethyl phosphite which indicated that either the cyclic concerted mechanism of Scheme III was occurring or else the trimethyl phos-

SCHEME III



phonium group gives a high degree of O alkylation similar to the reaction of *p*-toluenesulfinic acid with diazomethane which gives methyl *p*-toluenesulfinate in quantitative yield. When methyl phosphite and **1** were allowed to react in methyl iodide, then a 20–30% yield of methyl *p*-tolyl sulfone could be detected. Careful examination of the original reaction revealed that 5% of the product was methyl *p*-tolyl sulfone. Therefore the mechanism in Scheme II is occurring since methyl iodide did not convert methyl *p*-toluenesulfinate into methyl *p*-tolyl sulfone. Thus there is as yet no evidence for Scheme III and the formation of methyl *p*-toluenesulfinate is best regarded as an alkylation of the *p*-toluenesulfinate anion by a hard alkylating agent which leads mainly to O alkylation. The methyl iodide was able to trap the anion and give the sulfone since it is a soft alkylating agent.

Compounds **1** and **2** react with cyclohexylamine to give only the *trans* product and this is in accord with the observations of others. Recently, Truce and Brady[14] have found that in the addition of amines to acetylenic sulfones, the *cis* product is formed at low temperatures and isomerizes to the *trans* isomer at room temperature. However, the addition of ethylenimine to acetylenic sulfones results in the formation of the *cis*-vinylamine. Vinylic displacements on 2-chlorovinyl aryl sulfones using ethylenimine as a nucleophile results in retention of the configuration about the double bond.[15] Truce has suggested that the spontaneous isomerization from *cis* to *trans* at room temperature is probably due to the immonium structure, **7**, and that



strain in the ethylenimine adducts prevents this structure from facilitating *cis* to *trans* isomerization.[14]

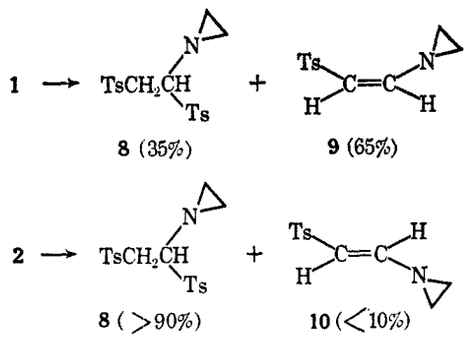
(12) J. E. Bissey, H. Goldwhite, and D. G. Rowsell, *J. Org. Chem.*, **32**, 1542 (1967).

(13) C. R. Noller, "Chemistry of Organic Compounds," W. B. Saunders Co., Philadelphia, Pa., 1965, p 312.

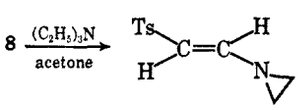
(14) W. E. Truce and D. G. Brady, *J. Org. Chem.*, **31**, 3543 (1966).

(15) W. E. Truce, J. E. Parr, and M. L. Gorbarty, *Chem. Ind.* (London), 660 (1967).

We have carried out the reaction of ethylenimine with **1** and **2** and have observed the results shown below.

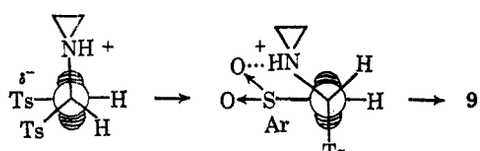


The formation of 1,2-di-*p*-toluenesulfonyl-1-ethyleniminoethane, **8**, represents the only case where an addition product has been isolated in our reactions. However, this is not an intermediate in the formation of *cis*-1-ethylenimino-2-(*p*-toluenesulfonyl)ethene, **9**, for it is stable to elimination under the reaction conditions and even when it is refluxed in triethylamine in acetone for 0.5 hr, less than 10% of it eliminates to give only *trans*-1-ethylenimino-2-(*p*-toluenesulfonyl)ethene, **10**.

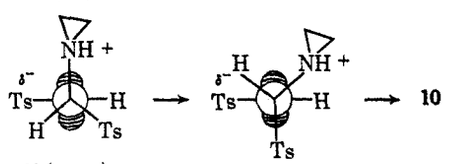


One rationalization for the formation of the adduct **8** is that the low basicity of the ethylenimine[16] renders its conjugate acid sufficiently acidic for protonation to become a favorable reaction. Thus the initial adduct of ethylenimine has two energetically favorable reaction pathways available to it, *i.e.*, intramolecular protonation and elimination.

Another interesting aspect of this reaction is that the protonated adduct is highly favored with the *trans* substrate, whereas elimination predominates with the *cis* substrate. In the initial intermediate **11** from the *trans* sulfone, rotation is necessary through a conformation having an eclipsed hydrogen atom and a sulfone group before elimination can occur. With the *cis* sulfone, the intermediate only has a hydrogen–hydrogen interaction barring rotation before elimination can occur. Therefore, elimination is favored in the reaction of ethylenimine with **1** and less of **8** is formed. In addition, rotation in the *cis* case to the conformation necessary for elimination would be favored by the electrostatic attraction between the sulfone and the ethylenimmonium



11 (*cis*)



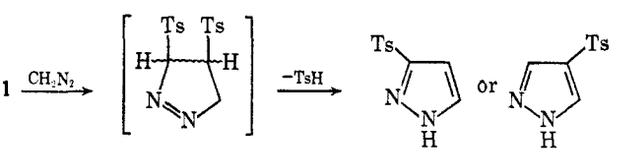
11 (*trans*)

group.[15] Rotation in the *trans* intermediate has to separate these charged centers.

The addition of Grignard reagents to α,β-unsaturated sulfones has been carried out by Kohler and coworkers who have found that the reaction proceeds slowly in moderately low yields.[17] We have added phenylmagnesium bromide to **1** and isolated a small amount of *trans*-β-styryl *p*-tolyl sulfone after chromatography over alumina. It is not known what degree of stereospecificity the reaction has since chromatography might have caused isomerization.

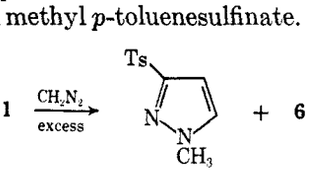
The addition of diazomethane to β-halo vinyl ketones results in the formation of pyrazoles.[6] It has been suggested that the reaction proceeds through the dipolar addition of diazomethane followed by the loss of hydrogen chloride to form the aromatic pyrazole.

In the reaction of diazomethane with **1** there is the possibility of the formation of two different pyrazoles, **12** and **13**, depending on the direction of loss of *p*-toluenesulfinic acid from the initial adduct.



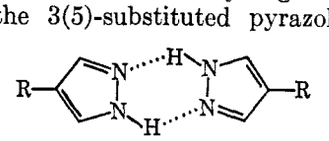
12 13

Pyrazole **12** can be isolated when excess diazomethane is removed immediately after the vigorous nitrogen evolution has ceased. This is consistent with the removal of the most acidic proton from the intermediate adduct. If **1** is allowed to stand overnight with excess diazomethane N-methyl-3(5)-*p*-toluenesulfonylpyrazole (**14**) is formed. The *p*-toluenesulfinic acid produced in the reaction proceeded to react with excess diazomethane to form methyl *p*-toluenesulfinate.



14

The structure of **12** was ascertained from its nmr spectrum. 4-Substituted pyrazoles show a singlet in the nmr spectrum for the annular protons which has been rationalized in terms of a hydrogen bonded dimer (**15**).[18] In the 3(5)-substituted pyrazoles, however,



15

the ring protons appear as an AB quartet with a splitting of about 2 cps. The nmr spectrum of **12** showed an AB quartet for the ring protons.

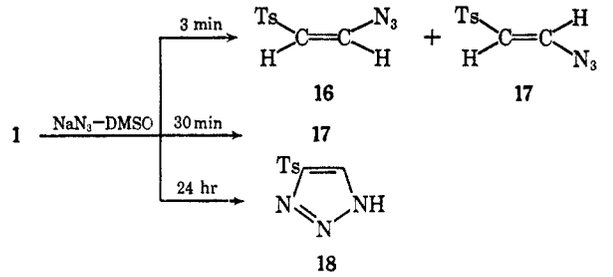
The reaction of sodium azide with **1** in methanol leads to the formation of **16** and **17**. The reaction time used was approximately 3 days, the yields were poor, and the separation of isomers was time consuming. When the reaction was carried out in dimethyl sulfoxide for 24 hr, a 50% yield of 4(5)-*p*-toluenesulfonyltriazole (**18**) was isolated. When the reaction time in dimethyl sulfoxide was shortened to 3 min, the

(16) P. A. Gembitskii, N. M. Loim, and D. S. Zhuk, *Russ. Chem. Rev.*, **35**, 105 (1966).

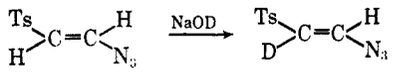
(17) E. P. Kohler and H. Potter, *J. Amer. Chem. Soc.*, **57**, 1316 (1935).

(18) J. K. Williams, *J. Org. Chem.*, **29**, 1377 (1964).

product composition was 85% *cis* and 15% *trans*, and at 30-min reaction time only the *trans* isomer in 43% yield was isolable. The preparation of the *trans*-vinyl azide in dimethyl sulfoxide is more convenient because the reaction time is shorter and no isomer separation is involved.



The isomerization of vinyl azide **17**, to triazole **18** has been discussed in a preliminary communication[19] and it was concluded that it is unique because the hydrogen atom α to the sulfone is acidic and produces under the reaction conditions, a carbanion which can cyclize without the loss of stabilization energy. To further substantiate this conclusion the acidity of the hydrogen atom α to the sulfone in **17** has been demonstrated by deuterium exchange. Thus, when the vinyl azide in deuteriochloroform is shaken with a sodium–deuterium oxide solution, there is a slow exchange of the proton α to the sulfone group. The reaction was 70% complete in 48 hr. The possibility that the exchange occurred through the addition of deuterium oxide followed by the elimination of HOD is not completely excluded. However, the exchange was closely monitored by nmr spectroscopy and no extraneous signals were detected.



4(5)-*p*-Toluenesulfonyltriazole was independently synthesized using *p*-toluenesulfonylacetylene and trimethylsilyl azide patterned after a method of triazole synthesis developed by Birkofer and Wegner.[20]

$$TsC{\equiv}CH + (CH_3)_3SiN_3 \longrightarrow \mathbf{18}$$

Experimental Section

All nmr spectra were run on a Varian A-60 or A-60A spectrometer using tetramethylsilane as an internal standard. Infrared spectra were obtained using a Beckman IR-5. All melting points were obtained on a Fischer-Johns melting point block and are uncorrected. Analyses of all new compounds were performed by Galbraith Laboratories, Knoxville, Tenn.

cis-**1,2-Di-*p*-toluenesulfonylethene** (**1**) was prepared according to the method of Snyder and Hallada[21] using *cis*-dichloroethylene instead of dibromoethylene in 45% over-all yield, mp 143–145° (lit.[21] mp 146–148°).

trans-**1,2-Di-*p*-toluenesulfonylethene** (**2**).—A mixture of 1.1 g of **1** and 1 ml of triethylamine in 100 ml of acetone was refluxed for 13 hr. The reaction mixture was cooled and 0.5 g of **2** was filtered, mp 225–228° (lit.[22] mp 228–229°).

Reaction of 1 and 2 with Sodium Azide in Aqueous Acetonitrile.—A solution of 2.0 g of **1** or **2** in 40 ml of acetonitrile and 16 g of sodium azide in 50 ml of water was stirred for 17.5 hr at room temperature. The reaction mixture was extracted with two 50-ml portions of ethyl acetate. The ethyl acetate extracts were washed twice with 100 ml of water and then dried over magnesium sulfate. The solvent was evaporated without using heat yielding a crude product which was weighed and the product isomer content determined by nmr. Yields are summarized in Table I, and nmr spectra are described in Table III.

Reaction of 1 with Sodium Azide in Aqueous Methanol.—A mixture of 6 g of **1** in 250 ml of methanol and 42 g of sodium azide in 150 ml of water was allowed to react at room temperature for 43 hr. Saturated sodium chloride was added to the reaction mixture and the product was extracted with ethyl acetate. The ethyl acetate extracts were dried and the solvent removed without heat yielding 1.5 g of crude product. Nmr analysis showed that 77% of this was composed of a 4:6 mixture of the *cis* and *trans* vinyl azides. Chromatography over alumina (Merck #71707) eluting with benzene and chloroform yielded 0.6 g of **17**, mp 72–74° (lit.[7b] mp 75–76°), and 0.3 g of **16**, mp 43–45° (lit.[7b] mp 48–50°). Nmr data are given in Table III. The *cis*-vinyl azide **16** isomerizes to the *trans*- (**17**) under the reaction conditions.

Reaction of Thiophenol with 1 and 2 in Various Solvents.—A mixture of 2.0 g of **1** or **2**, 0.65 ml of thiophenol, and 0.82 g of triethylamine in 50 ml of acetonitrile was allowed to react at room temperature for *ca.* 20 hr. The reaction mixture was extracted with 150 ml of ethyl acetate and washed with 1 *N* NaOH. The ethyl acetate extracts were dried and the solvent removed without heat. The crude product was weighed and the product isomer content determined by nmr. The reactions of **1** in ether and methanol were carried out as described above for 24 and 27.5 hr, respectively. Tables I, II, and III give yields and nmr data.

Reaction of 1 and 2 with Sodium Methoxide.—A mixture of 1.0 g of **1** or **2** and 16.5 ml of a sodium methoxide solution (prepared from 0.4 g of sodium metal and 100 ml of methanol) in 50 ml of acetonitrile was allowed to react at room temperature for 20 hr. To the reaction mixture was added 50 ml of a saturated sodium chloride solution. The reaction mixture was then extracted with ethyl acetate, the extracts were dried and the solvent removed without heat (*cis* to *trans* isomerization occurs with heating). The reaction of **1** in methanol was carried out as described above. Tables I, II, and III give yields and nmr data.

Reaction of 1 with Trimethyl Phosphite.—A mixture of 1.0 g of **1** and 0.5 ml of trimethyl phosphite was allowed to react at room temperature for approximately 1 min at which time the reaction mixture became warm, liquefied, and resolidified. The solid was dissolved in ethyl ether and recrystallized yielding 0.6 g (70%) of white needles, mp 105–107°. After three recrystallizations the melting point was 108–110°.

Anal. Calcd for $C_{11}H_{15}O_5PS$: C, 45.51; H, 5.21. Found: C, 45.29; H, 5.32.

The reaction was repeated and an nmr spectrum of the crude reaction mixture revealed the presence of methyl *p*-toluenesulfinate and methyl *p*-tolyl sulfone in a ratio of 95:5. The presence of the small amount of sulfone was confirmed by glpc.

The reaction of 2 with trimethyl phosphite occurred after 0.7 g of **2** was combined with 0.35 ml of trimethyl phosphite. The reaction mixture was heated on a steam cone for 10 min until it liquefied. The reaction mixture was then cooled and purified as described above yielding 0.5 g of a white solid (83%), mp 105–108°. The compound had an identical nmr spectrum with the product derived from the reaction of **1** with trimethyl phosphite. The reaction was repeated using 0.2 g of **2** and 0.09 g of trimethyl phosphite. An nmr spectrum of the crude reaction mixture showed the formation of methyl *p*-toluenesulfinate and methyl *p*-tolyl sulfone in a ratio of 93:7.

Isolation of Methyl *p*-Toluenesulfinate from the Reaction of 1 with Trimethyl Phosphite.—The reaction of **1** with trimethyl phosphite was carried out as described above. The solvent was removed from the mother liquor of the first crystallization leaving 0.72 g of a yellow oil. The nmr spectrum showed that this was a 2:1 mixture of methyl *p*-toluenesulfinate and **4**. Shaking the yellow oil with pentane caused the selective solution of the ester which had identical spectral properties with an authentic sample of methyl *p*-toluenesulfinate.

Methyl *p*-toluenesulfinate was prepared by the action of diazomethane on *p*-toluenesulfinic acid (prepared according to the method of Field and Grunwald[23] in 57% yield) in 62% yield

(19) J. S. Meek and J. S. Fowler, *J. Amer. Chem. Soc.*, **89**, 1967 (1967).
(20) L. Birkofer and P. Wegner, *Chem. Ber.*, **99**, 2512 (1966).
(21) H. R. Snyder and D. P. Hallada, *J. Amer. Chem. Soc.*, **74**, 5595 (1952).
(22) W. E. Truce and R. J. McManimie, *ibid.*, **75**, 1672 (1953).
(23) L. A. Field and F. A. Grunwald, *J. Org. Chem.*, **16**, 946 (1951).

as a colorless oil, bp 100–104° (2.5 mm) (lit.[24] bp 82–85° (0.1 mm)). The nmr spectrum ($CDCl_3$) showed signals at 2.39 (3 H singlet), 3.42 (3 H singlet), and 7.3 and 7.68 ppm (4 H aromatic quartet, J = 8 cps).

Reaction of 1 with Trimethyl Phosphite in Methyl Iodide.—To 0.5 g of 1 in 1 ml of methyl iodide was added 0.25 ml of methyl phosphite. The reaction mixture was allowed to stand at room temperature for 0.5 hr and then the excess methyl phosphite and methyl iodide were removed under reduced pressure. An nmr spectrum of the residual mixture showed that it contained methyl *p*-toluenesulfinate and methyl *p*-tolyl sulfone in a ratio of 2:1.

Reactions of 1 and 2 with Cyclohexylamine in Various Solvents.—To 1.0 g of 1 or 2 in 50 ml of acetonitrile was added 0.75 ml of cyclohexylamine. A precipitate formed immediately. After standing for 26 hr at room temperature the reaction was diluted with water and extracted with ethyl acetate. The ethyl acetate extracts were dried and evaporated. The product after crystallization from benzene–pentane had mp 131–132° (lit.[8c] mp 131.5–132.5°). The reaction of 1 with cyclohexylamine was similarly carried out in ether and methanol. Yields and nmr data are summarized in Tables I, II, and III.

Reaction of 1 with Ethylenimine in Ether.—To 1.0 g of 1 in 50 ml of ether was added with stirring at 0° 0.15 ml of ethylenimine in 3 ml of ether. The reaction mixture was worked up as described for the reactions in acetonitrile. After the ether was removed, the residue was dissolved in a small amount of ether and allowed to cool overnight. White crystals were filtered and had mp 106–108°. Since the melting point was depressed by further crystallizations (though the nmr spectrum did not change), the product was analyzed without further purification with satisfactory results. The nmr spectrum ($CDCl_3$) showed a doublet centered at 1.87 (4 H, ethylenimino protons), a singlet at 2.44 (6 H, tolyl methyl protons), an eight-line multiplet between 3.1 and 4.1 (3 H, α-sulfonyl protons), and an A_2B_2 aromatic quartet centered at 7.35 and 7.76 ppm, J = 8 cps (8 H).

Anal. Calcd for $C_{18}H_{21}NO_4S_2$: C, 57.02; H, 5.58; N, 3.69. Found: C, 56.93; H, 5.67; N, 3.58.

Reaction of *cis*-1,2-Di-*p*-toluenesulfonylethene with Ethylenimine.—To 1.0 g of 1 in 30 ml of acetonitrile at 0° was added with stirring 0.16 g of ethylenimine in 3 ml of acetonitrile. The reaction mixture was stirred for 4 min at 0° and 30 ml of water was added. The product was extracted with 100 ml of ether. The ether was dried and removed leaving 0.612 g of crude product which nmr analysis showed to be 65% *cis*-1-ethylenimino-2-(*p*-toluenesulfonyl)ethene and 35% 1,2-di-*p*-toluenesulfonyl-1-ethyleniminoethane.

Reaction of *trans*-1,2-Di-*p*-toluenesulfonylethene with Ethylenimine.—To 0.5 g of 2 in 15 ml of acetonitrile at 0° was added with stirring 0.08 ml of ethylenimine in 2 ml of acetonitrile. The reaction mixture was stirred for 4 min and 20 ml of water was added. Starting material 0.11 g was filtered, mp 222–227°. The ether was washed with water, dried, and removed without heat leaving 0.351 g of a white solid, mp 98–102°. The nmr spectrum of this solid showed that it was composed of at least 90% 1,2-di-*p*-toluenesulfonyl-1-ethyleniminoethane and less than 10% of 10. The nmr spectra of 9 and 10 were reported by Truce and were used for comparison.[15]

Reaction of 8 with Triethylamine in Acetone.—A solution of 0.065 g of 8 and 0.05 ml of triethylamine in 3 ml of acetone was refluxed for 0.5 hr. The solvent was removed using a stream of air and the residue analyzed by nmr. The nmr spectrum showed that less than 10% of the adduct had undergone elimination to 10 and that the remainder was unchanged starting material.

Reaction of Phenylmagnesium Bromide with 1.—A solution of phenylmagnesium bromide was prepared from 2.0 g of magnesium metal and 9 ml of bromobenzene in 40 ml of anhydrous ether. To 2.0 g of 1 in 100 ml of ether was added 6 ml of the above solution in 14 ml of ether. The solution was stirred at room temperature for 9 hr and then extracted with 100 ml of 10% sulfuric acid. The ether solution was treated with Norit, dried, and filtered. The ether was removed under reduced pressure without heat. The brown oil remaining was chromatographed and yielded 0.435 g of *trans*-β-styryl *p*-tolyl sulfone, mp 118–121° (lit.[17] mp 121°). The nmr spectrum ($CDCl_3$) showed signals at 2.38 (3 H singlet), 6.9 and 7.65 (2 H AB quartet, J = 15 cps), 7.84 and 7.3 (4 H quartet, J = 8 cps), and 7.38 ppm (5 H singlet).

(24) A. J. H. Houssa, J. Kenyon, and H. Phillips, *J. Chem. Soc.*, 1700 (1929).

3(5)-*p*-Toluenesulfonylpyrazole.—A solution of diazomethane, prepared from 3 g of N-nitrosomethylurea, in 400 ml of ether was dried for 1 hr over KOH pellets. This solution was then added to 1.1 g of 1. The solid dissolved slowly with nitrogen evolution, and after it had all gone into solution half of the volume of the ether and the excess diazomethane was removed using a stream of dry air. The remaining solution was cooled overnight. The remaining ether was removed and the oily residue was dissolved in ether–ethyl acetate and washed with 5% sodium carbonate solution. The organic layer was dried and the solvent removed. The remaining oil was chromatographed over a dry column of deactivated alumina (Merck #71707 which had been deactivated by adding 40 ml of water to 1 lb of alumina and heating under reduced pressure for 8 hr), and was eluted with pentane, benzene, and chloroform. The product (0.12 g) which was eluted with chloroform had mp 162.5–164.5° after recrystallization from ether–pentane. The infrared spectrum showed –NH absorption at 3370 cm^{-1}. The nmr spectrum ($CDCl_3$) showed signals at 2.36 (3 H singlet), 6.8 (1 H doublet, J = 2.5 cps), 8.05 (1 H doublet, J = 2.5 cps), and 7.85 and 7.25 ppm (4 H A_2B_2 aromatic quartet, J = 8 cps).

Anal. Calcd for $C_{10}H_{10}N_2O_2S$: C, 54.03; H, 4.54; N, 12.61. Found: C, 53.93; H, 4.60; N, 12.51.

N-Methyl-3(5)-*p*-toluenesulfonylpyrazole.—A solution of diazomethane prepared as described above was added to 1.0 g of 1 which dissolved slowly with nitrogen evolution. The pale yellow color of the diazomethane remained after solution was complete and the reaction mixture was allowed to stand overnight at room temperature. The solvent was then removed with a stream of air and the residue dissolved in a small amount of ether and washed with a 5% sodium carbonate solution. The organic phase was dried and the solvent removed leaving an oily residue which was chromatographed as described above and yielded 0.11 g of methyl *p*-toluenesulfinate, and 0.4 g of the N-methylpyrazole. The analytical sample from ether–pentane had mp 73–74°. The infrared spectrum showed no –NH absorption. The nmr spectrum ($CDCl_3$) showed signals at 2.42 (3 H singlet), 4.02 (3 H singlet), 6.85 (1 H doublet, J = 2 cps), 7.5 (1 H doublet, J = 2 cps), and 7.3 and 7.85 ppm (4 H, A_2B_2 quartet, J = 8 cps).

Anal. Calcd for $C_{11}H_{12}N_2O_2S$: C, 55.91; H, 5.12; N, 11.86. Found: C, 55.77; H, 5.17; N, 11.86.

Reaction of 1 with Sodium Azide in DMSO.—To a solution of 2.0 g of compound 1 in 50 ml of DMSO was added 2.0 g of sodium azide; a brilliant yellow color appeared immediately. The reaction mixture was allowed to stand at room temperature for 28 hr and then poured onto ice and extracted with ethyl acetate. The ethyl acetate extracts were washed several times with water, dried and evaporated without heat to yield 0.6 g of a semicrystalline solid which after crystallization from water had mp 156–158°. There was no azide absorption in the infrared spectrum, and an –NH peak showed at 3.18 μ. The compound was soluble in 1 N NaOH and reprecipitated with acid. The nmr spectrum ($CDCl_3$) showed the presence of a *p*-toluenesulfonyl group and a signal at 8.5 ppm integrating for one proton relative to the *p*-toluenesulfonyl group.

Anal. Calcd for $C_9H_9N_3O_2S$: C, 48.42; H, 4.06; N, 18.82. Found: C, 48.44; H, 3.95; N, 18.87.

Reaction of 1 with Sodium Azide in DMSO for 3 Min.—A solution of 4.44 g of sodium azide and 2.06 g of 1 in 30 ml of DMSO was allowed to stand at room temperature for 3 min, poured onto ice, and extracted with ether. The ether extracts were washed well with water, dried, and evaporated leaving 0.83 g of an oil which nmr analysis showed was composed of 85% of the *cis*-vinyl azide 16 and 15% of the *trans*-vinyl azide 17.

Reaction of Sodium Azide with 1 in DMSO for 30 Min.—To a solution of 14 g of 1 in 70 ml of DMSO was added 18 g of sodium azide. The reaction was stirred at room temperature for 30 min and then poured onto ice. The reaction was extracted twice with 50-ml portions of ether. The ether extracts were washed well with 1 N NaOH to remove any triazole 18 which might have formed and then with 1 l. of water in several portions. The ether was dried over anhydrous magnesium sulfate and then removed at reduced pressure without heat. The addition of ether to the residual oil and cooling caused the precipitation of *trans*-2-azidovinyl *p*-tolyl sulfone (4 g, 43%), mp 60–65° (lit.[7b] mp 75–76°). The nmr spectrum of this material showed that it was not contaminated with the *cis*-vinyl azide and did not show any other impurities.

Conversion of *trans*-2-Azidovinyl *p*-Tolyl Sulfone into 4(5)-*p*-Toluenesulfonyltriazole.—All isomerizations were carried out in

DMSO solution. The reaction mixtures were worked up by pouring them onto ice and extracting with ethyl acetate. The ethyl acetate extracts were washed several times with water and the solvent removed without heat. The composition of the crude products was determined by nmr and is described below.

Reaction of 17 with Sodium Azide and Sodium *p*-Toluenesulfinate.—A mixture of 0.66 g of **17**, 0.88 g of sodium azide, and 0.53 g of sodium *p*-toluenesulfinate dihydrate in 30 ml of DMSO was allowed to react at room temperature for 20.5 hr. The reaction was worked up as described above and yielded 0.39 g of a semicrystalline mass. The nmr spectrum showed that this was 57% triazole **18** and 43% starting vinyl azide.

Reaction of 17 with Sodium *p*-Toluenesulfinate.—A mixture of 0.5 g of **17** and 0.4 g of sodium *p*-toluenesulfinate dihydrate in 30 ml of DMSO was allowed to react at room temperature for 22.5 hr. The reaction was worked up and yielded 0.28 g of crude product which nmr analysis shows to be 62% triazole **18**, and 38% vinyl azide **17**. The addition of ether to the crude product caused the precipitation of a white solid, mp 147–151°, having an identical infrared spectrum with that of authentic **18**.

Reaction of 17 with Potassium *t*-Butylate in DMSO.—A mixture of 0.32 g of **17** and 0.3 g of potassium *t*-butylate in 30 ml of DMSO was allowed to react for 18 hr at room temperature. The reaction turned deep red-brown at its initiation and bubbled. Acidification, of the reaction mixture and work-up yielded 0.3 g of the product which the nmr spectrum shows to be 50% of triazole **18** contaminated with DMSO. Crystallization of the material from water yielded 0.13 g of a white solid, mp 151–155° (**18**, mp 156–158°).

Deuterium Exchange of *trans*-2-Azidovinyl *p*-Tolyl Sulfone.—To a solution of 0.155 g of **17** in 0.5 ml of deuteriochloroform was added 1 drop of 6.27% sodium deuteroxide solution. The reaction was monitored by nmr. After 35 min there was no apparent change in the spectrum. After 6.5 hr there was 29% exchange, after 22 hr 50% exchange, and after 48 hr 70% exchange of the proton α to the sulfonyl group.

Preparation of 4(5)-*p*-Toluenesulfonyltriazole.—A mixture of 0.2 g of *p*-toluenesulfonylacetylene[14] and 0.54 g of trimethylsilyl azide[25] was heated on a steam bath (80°) in a glass-stoppered test tube for 20 hr. After heating, 15 ml of water was added and the solution was boiled for 5 min and filtered. The triazole crystallized on cooling yielding 0.119 g (48%) of colorless needles, mp 156–158°, mmp 156–158° with **18**. Infrared and nmr spectra were identical with those of the compound prepared by the reaction of **1** with sodium azide in dimethyl sulfoxide for 28 hr.

Registry No.—**1**, 15645-75-7; **2**, 15717-50-7; **4**, 15717-49-4; **8**, 15717-51-8; **12**, 15717-52-9; **14**, 15645-76-8; **18**, 14631-74-4; 1, 15645-78-0; 2, 15645-79-1; 3, 15717-53-0; 4, 15645-80-4; 5, 15717-54-1; 6, 15717-55-2; 7, 15717-56-3.

(25) L. Birkofer and A. Ritter, *Angew. Chem. Intern. Ed. Engl.*, **4**, 417 (1965).

Small-Ring Epoxides. I. The Synthesis and Reactions of a 4-Methylene-1-oxaspiro[2.2]pentane Derivative

J. K. CRANDALL AND DONALD R. PAULSON

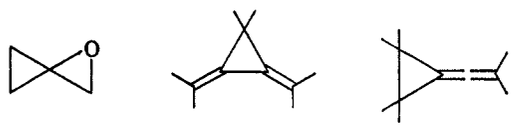
Contribution No. 1524 from the Department of Chemistry, Indiana University, Bloomington, Indiana 47401

Received October 9, 1967

2,2,5,5-Tetramethyl-4-isopropylidene-1-oxaspiro[2.2]pentane (**4**) has been prepared by epoxidation of its dimethylenecyclopropane precursor **2**. Thermolysis of **4** gives the two ketones 2-isopropylidene-3,3,4,4-tetramethylcyclobutanone (**6**) and 2,5-dimethyl-4-isopropylidenehex-5-en-3-one (**7**). Solvolysis of **4** also generates **6** and **7** and, under mild conditions, a new alcohol, 2,5-dimethyl-4-isopropenyl-2,3-hexadien-5-ol (**13**), which is converted into **7** in acid. The mechanistic details of these thermal and solvolytic transformations are discussed in terms of related systems. The mass spectra of several of the compounds encountered in this work are interpreted.

The general subject of small-ring chemistry has received an increasingly large amount of attention in recent years. The advances achieved both in the synthetic and mechanistic aspects of this research area have been enormous and of considerable significance for other areas of organic chemistry. In connection with our interest in the effects of bond-angle strain on the properties and chemical reactivity of molecules, we have initiated a program designed to examine the oxygen analogs of various small-ring hydrocarbons. A comparison of the chemistry of these heterocycles with that of their parent carbocycles should provide further important information with regard to the chemical consequences of ring strain. The present paper is concerned with our initial studies on an interesting derivative of the oxaspiropentane skeleton (**1**).

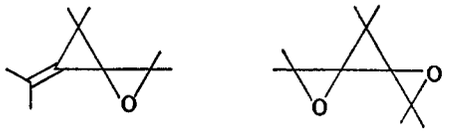
A convenient synthetic entry into this ring system is provided by our recent demonstration that alkenylidenecyclopropanes undergo smooth conversion into dimethylenecyclopropanes upon pyrolysis at reduced pressure in a flow system.[1] This reaction is illustrated by the synthesis of **2** from **3**. Precursor **3** is readily obtained from the base-catalyzed decomposition of 3-chloro-3-methyl-1-butyne[2] or, preferably,



1 **2** **3**

1-bromo-3-methyl-1,2-butadiene[3] in the presence of tetramethylethylene.

The buffered peracetic acid oxidation[4] of **2** proceeded nicely to give monoepoxide **4** in excellent yield along with a small quantity of diepoxide **5** when equivalent amounts of reactants were used.[5] The structure of **4** rests on its mode of synthesis and its spectroscopic properties, particularly the presence of six equivalent sharp singlets with the expected chemical



4 **5**

(1) J. K. Crandall and D. R. Paulson, *J. Amer. Chem. Soc.*, **88**, 4302 (1966).

(2) H. D. Hartzler, *ibid.*, **83**, 4990 (1961).

(3) S. R. Landor, A. N. Patel, P. F. Whiter, and P. M. Greaves, *J. Chem. Soc., Sect. C*, 1223 (1966).

(4) M. Korach, D. Nielson, and W. Rideout, *J. Amer. Chem. Soc.*, **82**, 4328 (1960).

(5) The reactions of diepoxide **5** will be reported in a future publication.