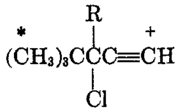
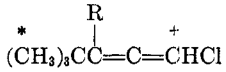
TABLE III
SPECTRAL DATA[a]

		Infrared,[b]	Nmr		
Compd	R	cm^{-1}	*	+	R
 $(CH_3)_3C\overset{*}{}C(R)(Cl)C\equiv CH^{+}$	CH_3	3350 (w) 2130 (w)	8.82 (s)	7.48 (s)	8.21 (s)
	C_2H_5	3330 (s) 2130 (w)	8.83 (s)	7.48 (s)	8.80 (t, CH_3)[c] 8.15 (q, CH_2)
 $(CH_3)_3C\overset{*}{}C(R)=C=CHCl^{+}$	CH_3	1960 (m)	8.90 (s)	4.10 (q), J = 2.5 cps	8.17 (s)
	C_2H_5	1960 (m)	8.90 (s)	3.97 (t), J = 2.5 cps	8.80 (t, CH_3)[c] 8.15 (q, CH_2)
	$HC(CH_3)_2$	1955 (s)[d]	8.90 (s)	3.97 (s)	8.85 [d, $(CH_3)_2$] 7.70 (q, HC)
	$C(CH_3)_3$	1940 (m)[d]	8.78 (s)	4.10 (s)	8.78 (s)

[a] These spectra were determined on mixtures of III and IV; J values were often difficult to determine with any accuracy and are not then reported. Integrations were in agreement with the assignments made. [b] All of these compounds showed a strong band at 740–750 cm^{-1} attributed to the C–Cl band. [c] Bands for the ethyl groups of III and IV overlap so badly that the same average values are given for both. [d] A very weak band at 3310 cm^{-1} is attributed to 2% of III present.

distilled under reduced pressure through a 45-cm column packed with glass beads. With R = methyl or ethyl only propargyl ethers, VI, were detected either with experiments carried only part way (where essentially only III had reacted) or to completion. The starting chlorides and the methyl ethers boil so close together that efficient separation was not attained on the scale employed. Only with R = methyl was separation of quite pure propargyl ether VI possible. In all other cases the spectra and analyses were of the mixtures indicated.

R = Methyl.—The higher boiling fraction came over at 51–59° (31 mm) and contained 20% of starting chlorides (glpc and nmr spectra); spectra indicated that this recovered chloride was essentially all allenic. Careful redistillation of this fraction through the spinning-band column gave material of bp 56° (31 mm) with ir absorptions at 3340 (s), 2110 (w), 2840 (m), 1130 (s) cm^{-1}. Glpc indicated the presence of 1% of the allenyl chloride IV (R = CH_3) and this gave weak ir bands at 735 and 1945 cm^{-1}. The nmr spectrum of the ether showed peaks at τ 8.98 (s, 9), 8.70 (s, 3), 7.62 (s, 1) and 6.71 (s, 3); this is in excellent agreement with the assigned structure.

Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. For $C_9H_{16}O$ containing 1% $C_8H_{13}Cl$: C, 76.94; H, 11.39. Found: C, 76.94; H, 11.32.

R = Ethyl.—The higher boiling fraction, bp 67–70° (27 mm), contained 36% starting chloride, mainly allenic, on the basis of glpc and nmr spectra. Infrared absorptions were at 3335 (s), 2110 (w), 1110 (s), and 2840 cm^{-1} (m) for the ether; bands for chloride impurity as recorded for IV (R = C_2H_5). The nmr peaks for the t-butyl hydrogens and for the methyl hydrogens of the ethyl group overlapped in the τ 9.0 region. The acetylenic hydrogen, 7.51 (s), the methylenic hydrogens, 7.37 (q) and the methoxyl hydrogens, 6.70 (s) were in proper proportions.

Anal. Calcd for $C_{10}H_{18}O$: C, 77.85; H, 11.76. For $C_{10}H_{18}O$ containing 35% $C_9H_{15}Cl$: C, 74.46; H, 10.98. Found: C, 74.54; H, 10.93.

R = Isopropyl.—The higher boiling fraction from the run at reflux temperature, bp 68–69° (13 mm), was free from starting chloride within the error of spectral and analytical determinations. Nmr spectroscopy indicated that it was a mixture containing 80% of the allenyl ether and 20% of the propargyl ether. Infrared absorptions of the mixtures were at 1935 (s), 3340 (m), 2850 (m), 1140 (s) cm^{-1}. In the nmr spectrum the region around τ 9.00 has a complicated band pattern because t-butyl and isopropyl methyls for the two compounds give bands which do not coincide; other bands for VII (R = isopropyl) are at τ 7.90 (q), 6.96 (s), and 3.52 (s) with area ratios close to 1:3:1 and for VI (R = isopropyl) are at 7.69 (s) and 6.72 (s) with a ratio of 1:3. The tertiary hydrogen on the isopropyl group was obscured.

Anal. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.40; H, 11.81.

R = t-Butyl.—The higher fraction from the run at reflux temperature, bp 66–68.5° (7 mm), had the following ir bands: 1940 (s), 3340 (w), 1080 (s), 735 (w) cm^{-1}. The 7.35-cm^{-1} band indicated the presence of a little unreacted chloride. Nmr peaks for VII (R = t-butyl) were at 9.00 (s), 6.90 (s), 3.65 (s); for VI (R = t-butyl) they were at 9.00 (s), 6.72 (s), 7.69 (s). The nmr spectrum suggests that the fraction was a 90:10 mixture of VII and VI. An analysis was not obtained.

The instability of the allenyl ethers to glpc separation should be mentioned.

Registry No.—Sodium methoxide, 124-41-4; methanol, 67-56-1; III (R = CH_3), 16487-11-9; III (R = C_2H_5), 16487-12-0; IV (R = CH_3), 16487-13-1; IV (R = C_2H_5), 16487-14-2; IV [R = $CH(CH_3)_2$], 16487-15-3; IV [R = $C(CH_3)_3$], 16487-16-4; VI (R = CH_3), 16487-17-5; VI (R = C_2H_5), 16487-18-6; VI [R = $CH(CH_3)_2$], 16487-19-7; VI [R = $C(CH_3)_3$], 16487-20-0; VII [R = $CH(CH_3)_2$], 16487-21-1; VII [R = $C(CH_3)_3$], 16487-22-2.

The Addition of 2,4-Dinitrobenzenesulfenyl Chloride to Allenes[1,2]

THOMAS L. JACOBS AND ROGER MACOMBER

Contribution No. 2211 from the Department of Chemistry,
University of California at Los Angeles,
Los Angeles, California 90024

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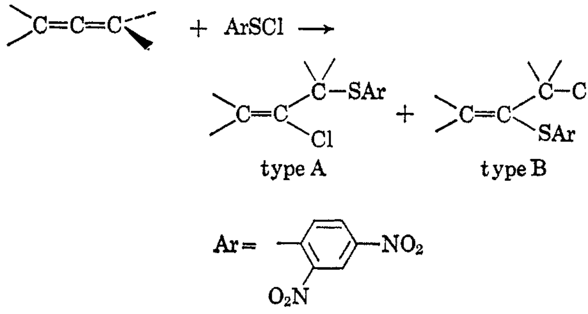
In the reaction of unsymmetrical allenes with 2,4-dinitrobenzenesulfenyl chloride (DBSC), two orientations of adducts are possible at each double bond. These are of two types, as shown in eq 1. We recently



(1)

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[1] This work was presented in part before the Intrascience Conference on the Chemistry of Sulfenyl Compounds, Santa Monica, Calif., Nov 1967.

[2] This research was supported in part by National Science Foundation Grant GP-5530 and in part by the Department of Chemistry under an National Science Foundation Graduate Traineeship to R. Macomber (1966–1968).

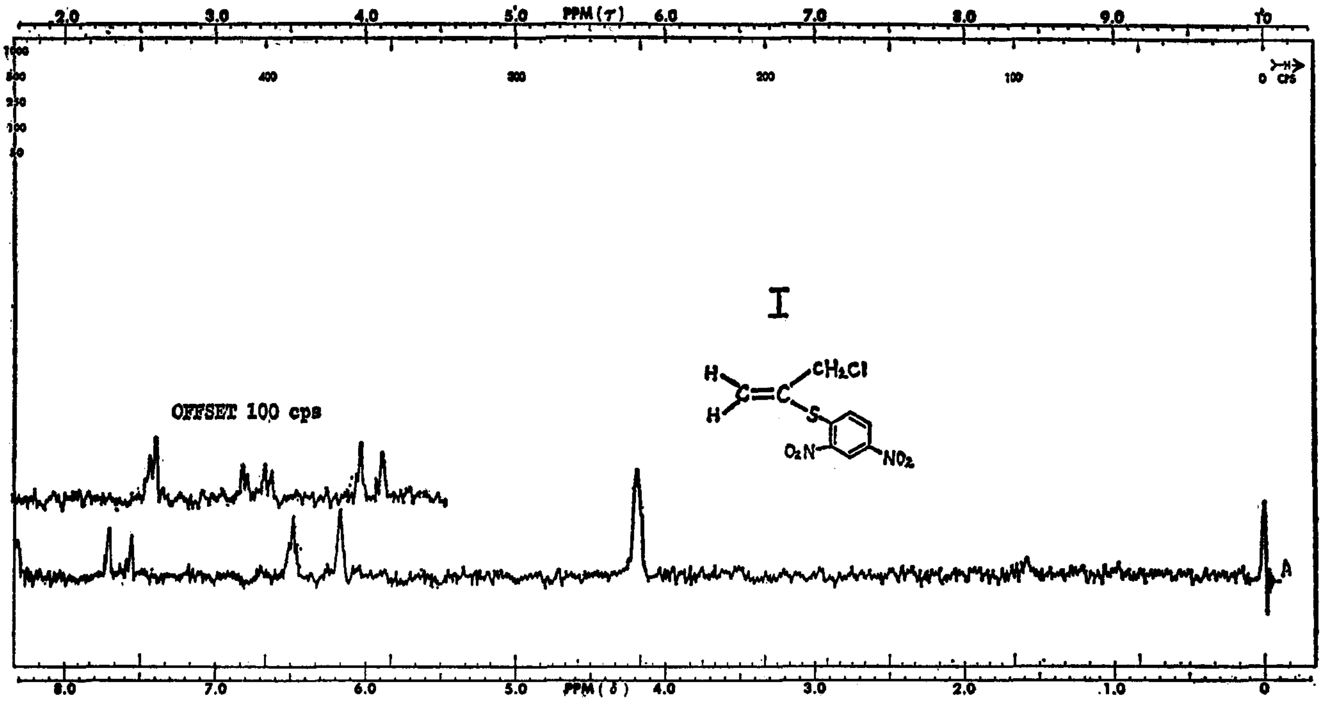

Figure 1.—The pmr spectrum of 3-chloro-2-(2,4-dinitrophenylthio)propene ($CDCl_3$ solution).

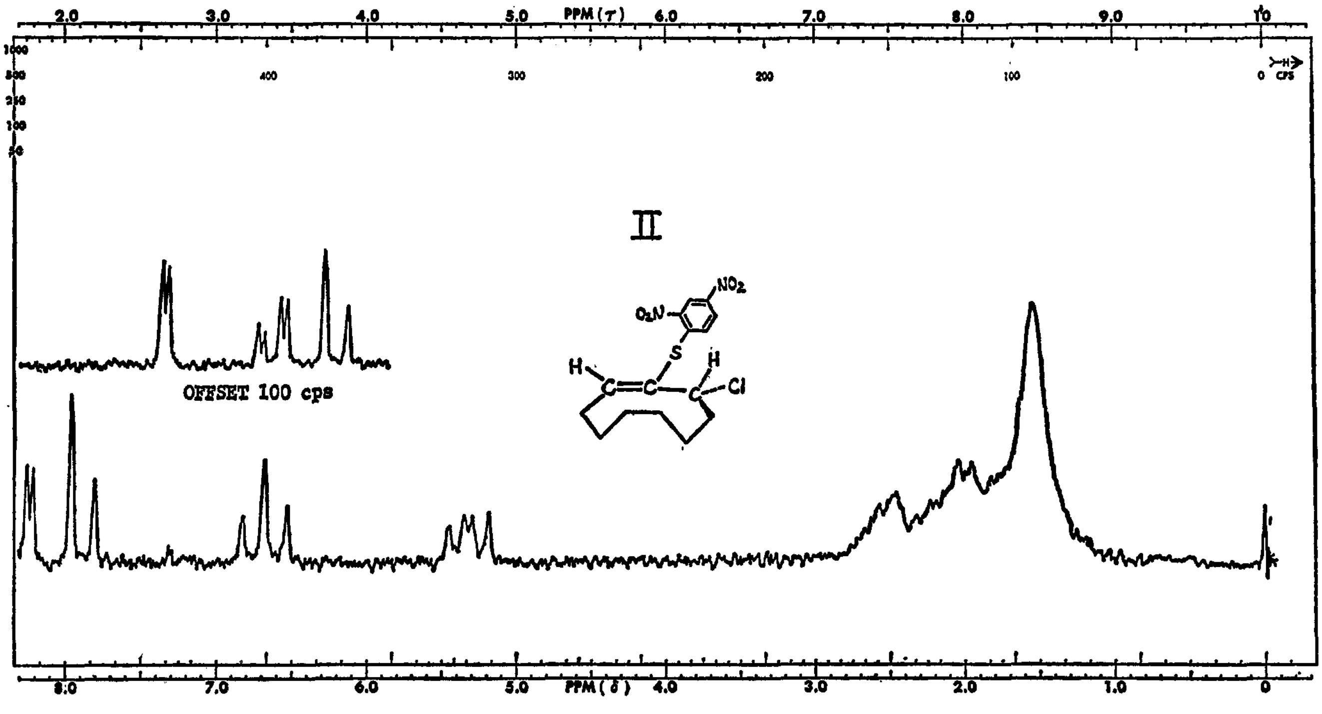

Figure 2.—The pmr spectrum of 3-chloro-2-(2,4-dinitrophenylthio)cyclononene ($CDCl_3$ solution).

reported[3] that addition of DBSC to optically active 2,2-dimethyl-3,4-hexadienol (1) yielded active 3-(2,4-dinitrophenylthio)-1,5,5-trimethyl-Δ^3-dihydropyran, a product of type B orientation. This was explained on the basis of formation of an episulfonium ion at the less hindered double bond, which opened only by direct attack of the nucleophile (in this case, oxygen). Earlier it was reported[4] that allene (1,2-propadiene) and DBSC gave the type B adduct, based on its transformation to chloroacetone. However, the product from DBSC and 1,2-cyclononadiene was assigned A type orientation[5] owing to its lack of reactivity toward alcoholic silver nitrate. We have now reexamined these last two compounds, and also the adduct from 3-methyl-1,2-butadiene, by the use of proton nmr spectroscopy, and in each case only the type B product was observed.

The adducts of DBSC with allene and 1,2-cyclononadiene were prepared as before.[4,5] The reaction of DBSC with excess 3-methyl-1,2-butadiene in carbon tetrachloride gave a 60% yield of a compound, mp 116.8–117.2°, which had the correct elemental composition for a 1:1 adduct. The pmr spectrum (in

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(3) T. L. Jacobs, R. Macomber, and D. Zunker, *J. Amer. Chem. Soc.*, **89**, 7001 (1967).

(4) (a) T. L. Jacobs and R. N. Johnson, *ibid.*, **82**, 6397 (1960); (b) R. N. Johnson, Ph.D. Thesis, University of California at Los Angeles, 1960.

(5) W. R. Moore and R. C. Bertelson, *J. Org. Chem.*, **27**, 4182 (1962).

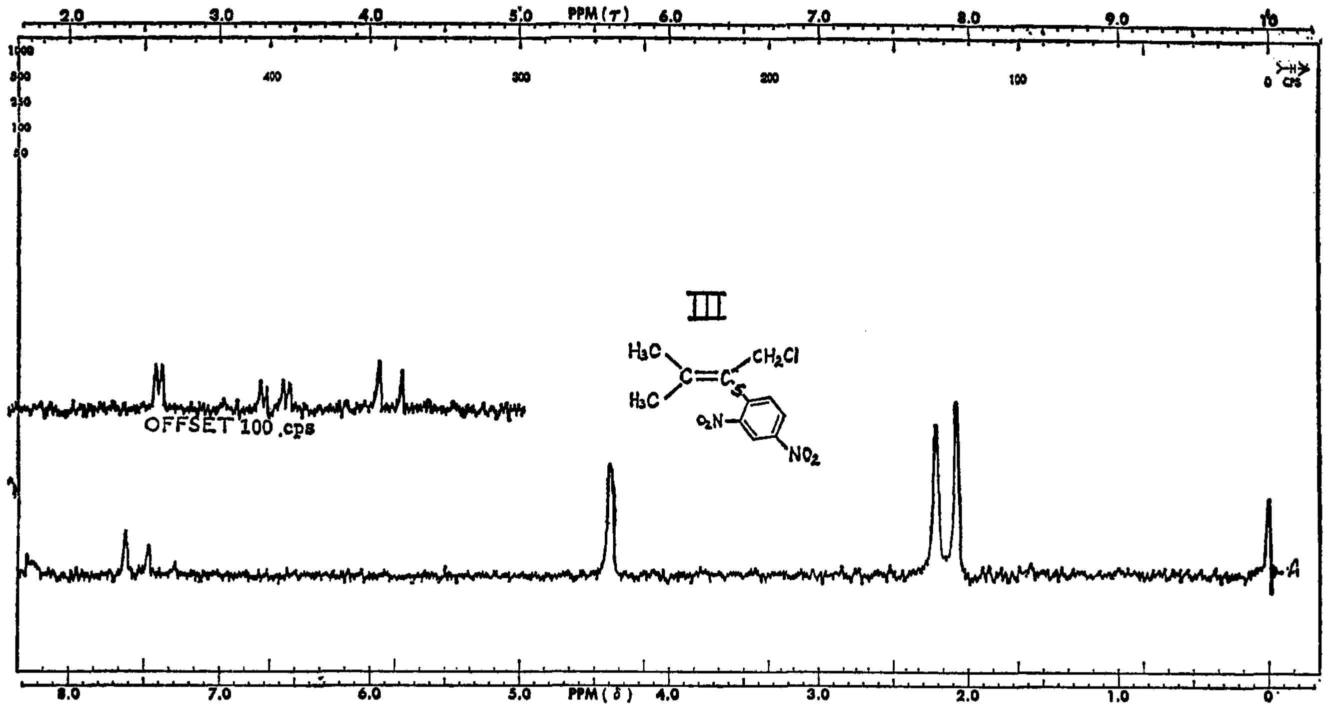


Figure 3.—The pmr spectrum of 4-chloro-3-(2,4-dinitrophenylthio)-2-methyl-2-butene ($CDCl_3$ solution).

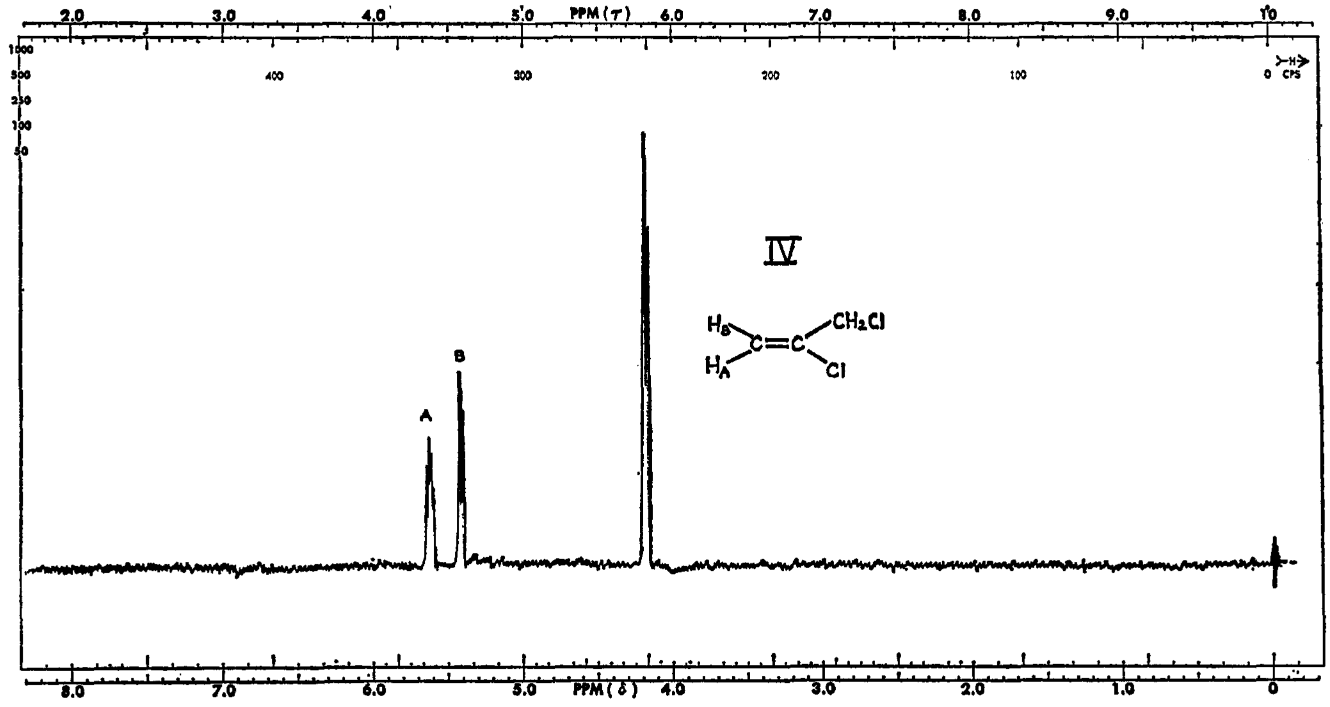


Figure 4.—The pmr spectrum of 2,3-dichloropropene ($CDCl_3$ solution).

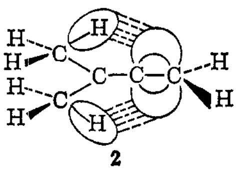
deuteriochloroform) of each is shown (Figures 1–3), together with that of 2,3-dichloropropene (Figure 4), which serves as a model compound.

Comparison of the spectrum in Figure 1 with that of the model compound indicates that the allene adduct is indeed 3-chloro-2-(2,4-dinitrophenylthio)propene, with B type orientation, as evidenced by the chlorine-substituted methylene protons at τ 5.8, and the olefinic protons at 3.5 and 3.8, deshielded 1 ppm from those expected of the type A adduct. The spectrum of the adduct from 1,2-cyclononadiene (Figure 2), shows an olefinic triplet (J = 9 cps) at τ 3.3. Recalling that the pmr spectrum of 1-chlorocyclooctene[6] exhibits an olefinic triplet (J = 8.4 cps) at τ 4.3, there remains little doubt that this adduct also has B type orientation, contrary to the previous report.[5]

Another dimension is added to this study with 3-methyl-1,2-butadiene. *A priori*, attack at the 2,3 double bond would be anticipated because the two methyl groups make it the more electron rich. Such is the observed orientation in bromination, epoxidation and addition of hydrogen chloride to this compound.

(6) M. R. St. Jacques, Ph.D. Thesis, University of California at Los Angeles, 1967.

Figure 3 indicates that in fact attack takes place at the sterically less-hindered 1,2 double bond, yielding 4-chloro-3-(2,4-dinitrophenylthio)-2-methyl-2-butene, a type B product. Although steric approach control is almost certainly important in the preference of this orientation, subtle electronic effects may also be operative. Whereas symmetry forbids overlap of the two mutually perpendicular π bonds of the allene system, there is evidence from the solvolyses of sulfonate esters of **1** that a methyl group increases the electron density in the more distant double bond.[7] This may arise from some type of "homohyperconjugation" effects involving the C–H single bonds of the methyl groups (see structure **2**). The pmr signal of the allenic protons of 3-methyl-1,2-butadiene are centered at τ 5.50 (heptet, J = 3 cps), approximately 0.2 ppm upfield from those of allene itself (τ 5.3), reflecting the increased electron density in the 1,2 bouble bond.



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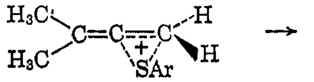
It is possible that 3-methyl-1,2-butadiene gives a mixture of adducts and that the product from attack at the 2,3 double bond was not isolated. This allene gave a crude reaction mixture which was somewhat more difficult to purify than products from any other of the allenes studied. However, the adduct isolated is certainly the major component. With all the other allenes yields were high enough to make it unlikely that type A products were formed in more than trace amounts.

It should perhaps be mentioned that if attack by DBSC on 3-methyl-1,2-butadiene occurs exclusively on one of the double bonds rather than both, a single adduct of type B orientation would be expected on the basis of the mechanism recently established,[3] which involves nucleophilic attack by chloride ion on episulfonium ion **3**. If **3** had opened to allylic cation **4**, one would expect two type B products: the one observed and **5**, because solvolyses of allylic compounds such as 3-chloro-3-methyl-1-butene seem always to give major amounts of the tertiary isomer.[8]



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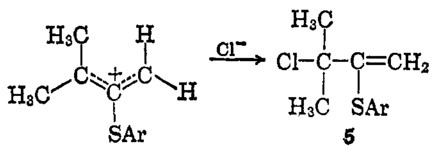

4 **5**

One point deserves further comment. Like the cycloallene adducts,[5] those from allene and 3-methyl-1,2-butadiene exhibit the same lack of reactivity toward silver nitrate. This contrasts with the high reactivity of typical allylic chlorides. Judging from the chemical shifts of the olefinic protons β to the 2,4-dinitrophenylthio moiety, it is likely that the electron density of the carbon–carbon double bond is significantly depleted. This, coupled with the cation destabilizing effect of the sulfur group also β to the incipient cationic center, may account for this anomolous unreactivity.

Registry No.—2,4-Dinitrobenzenesulfenyl chloride, 528-76-7; 3-chloro-2-(2,4-dinitrophenylthio)propene, 16626-76-9; 3-chloro-2-(2,4-dinitrophenylthio)cyclononene, 16626-78-1; 4-chloro-3-(2,4-dinitrophenylthio)-2-methyl-2-butene, 16626-77-0; 2,3-dichloropropene, 78-88-6.

[7] T. L. Jacobs and R. Macomber, *Tetrahedron Lett.*, 4877 (1967).

[8] R. H. DeWolfe and W. G. Young, *Chem. Rev.*, **56**, 794 (1956); "The Chemistry of Alkenes," S. Patai, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, p 702.

Products of Acetolysis of 3-(3-Cyclohexenyl)propyl and 4-(3-Cyclohexenyl)butyl *p*-Toluenesulfonates

ELLIOT N. MARVELL, DAVID STURMER,
AND R. STEVEN KNUTSON

*Department of Chemistry, Oregon State University,
Corvallis, Oregon 97331*

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About five years ago we examined a number of reactions which might serve as synthetic routes to bicyclo[*x*.3.1]alkanes.[1] As part of this effort the solvolysis of 3-(3-cyclohexen-1-yl)propyl and 4-(3-cyclohexen-1-yl)butyl *p*-toluenesulfonates was examined, and, when the results proved unpromising, further work along this line was abandoned. Later Bartlett and his students[2] surveyed in considerable detail the structural features which influence the degree of double-bond participation in solvolysis. Taken in conjunction with the earlier work of Wilcox[3] in the 3-cyclohexen-1-ylcarbinyl system and of Winstein[4] on the 2-(3-cyclohexen-1-yl)ethyl derivatives, our data permit a view of an homologous series with a broader range of carbon chain lengths intervening between the double bond and the incipient cationic center than has previously been possible.

Synthesis of the desired alcohols was achieved in unexceptional manner by elaboration of the side chain in 3-cyclohexene-1-carboxaldehyde as is illustrated in Scheme I. The *p*-toluenesulfonates **1b** and **2b** were obtained in crude form and were used without purification when infrared spectra showed that all alcohol had been converted into the ester. Solvolyses were carried out in anhydrous acetic acid containing a quantity of sodium acetate sufficient to neutralize all strong acid produced in the solvolysis. Both **1b** and **2b** reacted slowly under these conditions and prolonged heating at 113–114° was required to complete the reaction. The product from **1b** was analyzed by glpc, and was found to contain at least 95% **1c**. Identification was made by comparison with an authentic sample. Two trace compo-

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[1] The authors are pleased to make acknowledgment to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

[2] (a) P. D. Bartlett, S. Bank, R. J. Crawford, and G. H. Schmid, *J. Amer. Chem. Soc.*, **87**, 1288 (1965); (b) P. D. Bartlett and G. D. Sargent, *ibid.*, **87**, 1297 (1965); (c) P. D. Bartlett, W. D. Closson, and T. J. Cogdell, *ibid.*, **87**, 1308 (1965); (d) P. D. Bartlett, W. S. Trahanovsky, D. A. Bolon, and G. H. Schmid, *ibid.*, **87**, 1314 (1965).

[3] C. F. Wilcox, Jr., and S. S. Chibber, *J. Org. Chem.*, **27**, 2332 (1962).

[4] S. Winstein and P. Carter, *J. Amer. Chem. Soc.*, **83**, 4485 (1961).