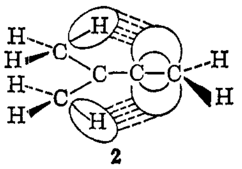
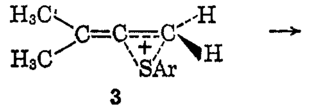
Figure 3 indicates that in fact attack takes place at the sterically less-hindered 1,2 double bond, yielding 4-chloro-3-(2,4-dinitrophenylthio)-2-methyl-2-butene, a type B product. Although steric approach control is almost certainly important in the preference of this orientation, subtle electronic 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.



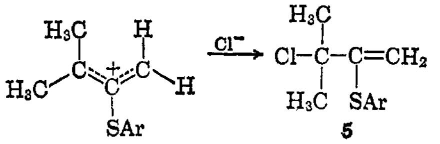
2

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]



3



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.

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[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

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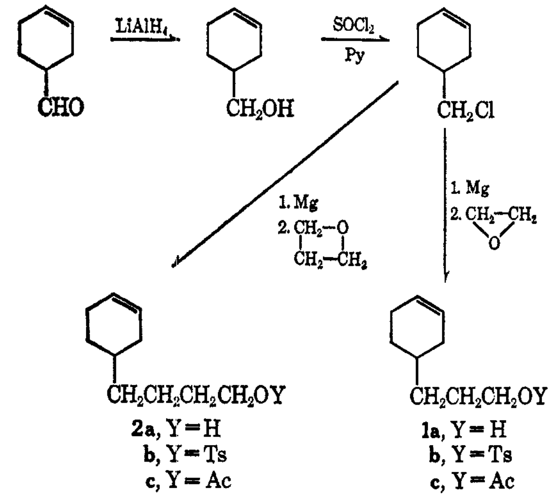
[1] The authors are pleased to make acknowledgment to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

[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).

SCHEME I



nents were not identified. The product from **2b** was similarly analyzed and found to contain not less than 96% **2c**.

Discussion

In Table I are gathered the results of studies of double bond participation of primary arenesulfonates with a double bond in a five- or six-membered ring. In the systems under consideration here, *i.e.*, those having a chain of from five to eight carbon atoms with a 1,2-disubstituted double bond at one end and a solvolyzable function on the other, it is quite clear that participation is most effective for the six-carbon chain. On the basis of the data listed the observation is valid only for double bonds in five- or six-membered rings and for acetolyses leading to a primary carbonium ion. There are, however, some published data which indicate that this suggestion may be applicable over a broader range of compounds and conditions. Thus, for example, both Δ^4-cycloocten-1-yl *p*-bromobenzenesulfonate,[5] and Δ^4-cyclohepten-1-ylmethyl *p*-toluenesulfonate[6] give cyclic products on acetolysis. Also 5-hexenyl *p*-nitrobenzenesulfonate cyclizes in part during acetolysis whereas its 4-pentenyl analog gives only open-chain products.[2c]

TABLE I

PRODUCTS OF ACETOLYSIS OF PRIMARY ARENESULFONATES WITH DOUBLE BONDS IN FIVE- OR SIX-MEMBERED RINGS

	% product		
Alkyl group	With participation	Without participation	Ref
2-(3-Cyclopentenyl)ethyl	100	0	*a*
3-(3-Cyclopentenyl)propyl	0	92–100	2d
2-(2-Cyclopentenyl)ethyl	0	100	*b*
3-(2-Cyclopentenyl)propyl	58	42	*b*
3-Cyclohexenylmethyl	0	100	3
2-(3-Cyclohexenyl)ethyl	80	20	4
3-(3-Cyclohexenyl)propyl	0	95	
4-(3-Cyclohexenyl)butyl	0	96	

[a] R. G. Lawton, *J. Amer. Chem. Soc.*, **83**, 2399 (1961). [b] W. D. Closson and G. T. Kwiatkowski, *ibid.*, **86**, 1887 (1964).

A structural basis for this empirical observation may exist in the possible conformations existing in the carbon chain in the transition state leading to double-bond participation. Bartlett and coworkers[2d] noted that 2-(3,4-dimethyl-3-cyclopentenyl)ethyl *p*-nitrobenzenesulfonate undergoes assisted acetolysis 600 times faster than 3-(3,4-dimethyl-3-cyclopentenyl)propyl *p*-nitrobenzenesulfonate. Of this rate difference a factor of 60 was attributable to an enthalpy difference, and only tenfold to the entropy difference. They suggested that in the transition state leading to double-bond participation every C–C bond with free rotation can attain a staggered conformation with the ethyl side chain, but the propyl side chain necessitates the presence of an eclipsed form. An inspection of models shows that a similar, though not always so pronounced, conformational effect is found in all of the examples of Table I. Thus when participation does occur the chain of methylene groups can be fitted into a series of nicely staggered forms at each C–C bond having free rotation. Conversely when participation does not take place some near eclipsed forms will be present in the chain.

Experimental Section

3-Cyclohexenylcarbinol.—A solution of 330 g (3 mol) of 3-cyclohexene-1-carboxaldehyde in 700 ml of anhydrous ether was added to 57 g (1.5 mol) of lithium aluminum hydride in 150 ml of ether. During the addition 200 ml of ether was added to maintain fluidity in the mixture. The reaction mixture was hydrolyzed with 3 *N* hydrochloric acid and the ether layer was dried (potassium carbonate). The product was distilled through a column packed with glass helices: bp 88–95° (25 mm); $n^{21}\text{D}$ 1.4835; ν 3300, 3020, 1650 w, 1030, 655 cm^{-1}. A boiling point of 102° (19 mm) and $n^{25}\text{D}$ 1.4828 has been reported[3] for this alcohol. The yield was 316 g (94%).

3-Cyclohexenylcarbinyl Chloride.—A mixture of 50 g (0.45 mol) of 3-cyclohexenylcarbinol and 42 g of anhydrous pyridine was added to 57 g (0.48 mol) of thionyl chloride over a 0.5-hr period. The reaction mixture was kept at *ca.* 60° throughout the addition and was then heated to 70–80° for 20 hr. The reaction mixture was taken up in ether, the pyridine-hydrochloride was removed by filtration, and the ether solution was washed with water and dried (potassium carbonate). Distillation gave 35 g (60%) of a clear liquid: bp 67–68 (39 mm); $n^{20}\text{D}$ 1.4831; $\bar{\nu}$ 3070, 1650 (w), 740, 652 cm^{-1}.

Anal. Calcd for $C_7H_{11}Cl$: C, 64.36; H, 8.49. Found: C, 64.42; H, 8.69.

3-(3-Cyclohexenyl)propyl Alcohol (1a).—A solution containing 100 g (0.77 mol) of 3-cyclohexenylcarbinyl chloride in 200 ml of anhydrous ethyl ether was added to 20 g (0.83 g-atom) of magnesium. The solution of the Grignard reagent was cooled to −10° in an ice–salt bath and 75 g (1.7 mol) of ethylene oxide was added over a 30-min period. The reaction mixture was allowed to warm to room temperature and to stand overnight. The mixture was hydrolyzed with dilute sulfuric acid and the ether layer dried over potassium carbonate. Distillation gave 59.5 g (55%) of **1a**: bp 110–112° (12 mm); $n^{25}\text{D}$ 1.4792; $\bar{\nu}$ 3380, 3020, 1055, 652 cm^{-1}; nmr (CCl_4), δ 1.0–2.2 (m), 3.60 (t, J = 6.5 cps), 5.64 (s).

Anal. Calcd for $C_9H_{16}O$: C, 77.20; H, 11.40. Found: C, 77.10; H, 11.38.

3-(3-Cyclohexenyl)propyl Acetate (1c).—A mixture of 1.95 g (14 mmol) of **1a**, 2.5 g of acetic anhydride, 2 ml of anhydrous pyridine, and 70 ml of benzene were heated under reflux for 5 hr. Distillation gave 2.2 g (86%) of **1b**: bp 85° (2 mm); $n^{20}\text{D}$ 1.4613; $\bar{\nu}$ 3020, 1740, 1240, 1045, 653 cm^{-1}; nmr, (CCl_4) δ 1.0–2.2 (m), 1.94 (s, 3, MeCO), 3.98 (t, J = 6.4 cps), 5.60 (s).

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.92. Found: C, 72.51; H, 9.91.

4-(3-Cyclohexenyl)butyl Alcohol (2a).—Grignard reagent from 3.0 g (0.125 g-atom) of magnesium and 16.3 g (0.125 mol) of 3-cyclohexenylcarbinyl chloride was prepared in 100 ml of THF under nitrogen. To this solution was added 4.35 g (0.075 mol) of trimethylene oxide[7] in 20 ml of THF. The reaction solution

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(5) A. C. Cope, J. M. Grisar, and P. E. Peterson, *J. Amer. Chem. Soc.*, **82**, 4299 (1960).

(6) G. LeNy, *Compt. Rend.*, **251**, 1526 (1960).

(7) S. Searles, *J. Amer. Chem. Soc.*, **73**, 124 (1951).

was heated at 45–65° for 24 hr. The Grignard complex was hydrolyzed with saturated ammonium chloride and the organic products were extracted with ethyl ether. Distillation gave 4.3 g (37%) of **2a**: bp 73–75° (0.5 mm); n^{20}_{D} 1.4803; $\tilde{\nu}$ 3300, 3070, 1650 (w), 1032, 730, 652.

Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.60; H, 11.47.

4-(3-Cyclohexenyl)butyl Acetate (2c).—A mixture of **2a** (1.5 g, 9.8 mmol), 4.0 g of acetic anhydride, and 8 ml of pyridine was heated under reflux for 5 min. The mixture was poured on ice and the organic products were taken up in ether. Distillation gave 1.2 g (61%) of **2c**: n^{20}_{D} 1.4638; $\tilde{\nu}$ 3025, 1740, 1650 (w), and 1240; nmr (CCl_4), δ 1.2–2.2 (m), 1.92 (s, 3, CH_3CO), 4.01 (t, J = 6.3 cps), 5.63 (s).

Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.29; H, 10.25.

Acetolyses.—A sample of **1b** was prepared in 87% yield by the method of Tipson:[8] $\tilde{\nu}$ 3020, 1360, 1190, 1175, 955, 930, 653. The crude **1b** (7.16 g, 24.4 mmol) was dissolved in 500 ml of anhydrous acetic acid containing 2.1 g (25.6 mmol) of dry sodium acetate. The solution was stirred at 113–114° for 94 hr. About 500 ml of water was added to the cooled solution, and the organic products were extracted with several portions of hexane. The combined hexane extracts were washed with sodium bicarbonate and then dried and concentrated. The residue weighed 4.16 g (108% calculated as **1c**). Aside from a small amount of hexane, this contained **1c** and two trace components (*ca.* 5% total). Analysis was made by glpc on a 6-ft Carbowax 1500 column at 156° using helium as a carrier gas. Distillation of the crude acetolysis mixture gave 3.52 g (78.5%) of **1c** identical in infrared and nmr spectra with those of the sample prepared directly from **1a**.

Similarly a sample (1.23 g) of **2b** was heated at 113–114° for 72 hr. The organic products were isolated as described above and, after removal of the hexane, 1.0 g (128% calculated as **2c**) of residual material was recovered. This was analyzed by glpc at 171° on a 10-ft UCON nonpolar column, and was found to consist of hexane, **2c**, and two trace components. Exclusive of the hexane, the composition of this mixture was 96% **2c** and 4% trace components. The main component was identified as **2c** by use of an internal standard.

Registry No.—**1a,** 16626-54-3; **1b,** 16626-55-4; **1c,** 16626-56-5; **2a,** 16626-57-6; **2b,** 16626-58-7; **2c,** 16626-59-8; 3-cyclohexenylcarbinyl chloride, 2555-08-0.

[8] S. Tipson, *J. Org. Chem.*, **9**, 235 (1944).

The Electronic Spectra of Some Air-Sensitive Phosphorus Ylides[1,2]

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Air-sensitive alkylidenephosphoranes (phosphinemethylenes, phosphorus ylides) are important in organic synthesis, but very few physical properties have been obtained[3] for these compounds. Recently, proton[4] and phosphorus[5] nuclear magnetic resonance data have been reported.

We report here the ultraviolet-visible spectra in hexane solution of seven of these air-sensitive compounds (Table I). Each of the spectra consists of two main absorptions in the region (200–600 mμ) examined, *viz.*, a structured band centered about 265 mμ and a broad peak at longer wavelength in the 340–400-mμ range. The 265-mμ peak is constant within experimental error for all the compounds in this study. It is due to the benzene absorption and has been discussed previously[6] for the somewhat analogous compound, triphenylphosphine oxide.

TABLE I

ULTRAVIOLET MAXIMA AND ^{31}P CHEMICAL SHIFTS FOR SOME AIR-SENSITIVE PHOSPHORUS YLIDES

Compound[a]	λ_{max}, mμ		δ (ppm) *vs.* 85% H_3PO_4[b]
$(C_6H_5)_3P{=}O$	266		−25.5[c]
$(C_6H_5)_3P{=}CH_2$	265	341	−20.3
$(C_6H_5)_3P{=}CHCH_3$	265	374	−14.6
$(C_6H_5)_3P{=}CHCH_2CH_3$	265	378	−12.2
$(C_6H_5)_3P{=}CH(CH_2)_2CH_3$	264	375	−12.6
$(C_6H_5)_3P{=}CH(CH_2)_4CH_3$	264	377	−12.2
$(C_6H_5)_3P{=}C(CH_3)_2$	265	386	−11.3
$(C_6H_5)_3P{=}C(CH_2)_5$	265	391	−6.4

[a] Registry no. are given in descending order: 791-28-6, 3487-44-3, 1754-88-7, 16666-78-7, 3728-50-5, 16666-79-8, 16666-80-1, 16666-81-2. [b] See ref 5. [c] In dimethyl sulfoxide. Literature values, −23.0 to −27.0: V. Mark, *et al.*, "Topics in Phosphorus Chemistry," Vol. 5, M. Grayson and E. J. Griffith, Ed., Interscience Publishers, Inc., New York, N. Y., 1967, p 285.

The long-wavelength peak varies as the alkylidene group changes, and it is the absorption of interest. It is seen that the substitution of a methyl group for a methylene hydrogen in the parent compound, methylenetriphenylphosphorane, gives rise to a bathochromic shift of 33 mμ. Substitution of longer chain alkyl groups causes only slight further shifts of several millimicrons to longer wavelengths. Substitution by another methyl for the second methylene hydrogen causes an additional bathochromic shift of 12 mμ.

In the case of the resonance-stabilized, charge-delocalized ylides, the more extensive the conjugated system becomes, the greater is the bathochromic shift.[7]

At first glance, these data seem contradictory, *i.e.*, both increasing electron-withdrawing (by delocalization of the methylenic negative charge) character and electron-releasing (by induction of alkyl substituents) character of the groups cause shifts to longer wavelengths. However in the case of the resonance-stabilized ylides, the substituent on the methylene carbon contains a chromophore and extensive conjugation serve to lower the π^* energy levels. The phosphorus in this case probably contributes only slightly as an auxochrome by participating in the conjugation,[7] and the transition is undoubtedly $\pi \rightarrow \pi^*$ (or $n \rightarrow \pi^*$ depending on the nature of the substituent). Further evidence for this slight participation by phosphorus in the resonance-stabilized ylides is provided by their

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[1] Supported by the National Science Foundation uuder Grant No. GP 4483.

[2] Taken from the M.S. Thesis of J. H. Ambrus, University of Maryland, 1966.

[3] A. W. Johnson, "Ylid Chemistry," Academic Press Inc., New York, N. Y., 1966, pp 76–79.

[4] H. J. Bestmann and J. P. Snyder, *J. Amer. Chem. Soc.*, **89**, 3937 (1967), and references cited therein.

[5] S. O. Grim, W. McFarlane, and T. J. Marks, *Chem. Commun.*, 1191 (1967).

[6] H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, p 500.

[7] H. Fischer and H. Fischer, *Chem. Ber.*, **99**, 658 (1966).