A Study of Nucleophilic Additions to Substituted Cyclopropenes[1]

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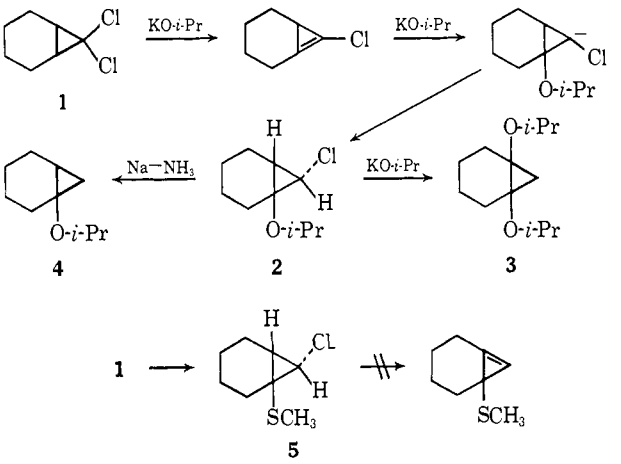
Abstract: The dehydrochlorination of a number of dichlorocyclopropanes in the presence of nucleophiles such as methoxide ion has shown that a reaction sequence involving elimination–addition is quite general. The evidence suggests that when the cyclopropene intermediate possesses an alkyl group on the newly formed double bond, isomerization occurs to the alkylidenecyclopropane if it is not excessively strained. A second dehydrochlorination is believed to occur giving an alkylidenecyclopropene which then experiences attack by a nucleophile. If the nucleophile is also a strong base (alkoxide ion) it plays the role of both base and nucleophile. The use of a nucleophile which is a weak base (mercaptide ion) necessitates the incorporation of a stronger base but one which is a poor nucleophile (*t*-butoxide ion).

The observation that *t*-butoxide ion adds to ethyl 1-cyclopropenecarboxylate[2] poses the problem of whether or not the reaction is formalistically a Michael addition and dependent upon the charge-stabilizing effect of a substituent such as the carbonyl group. We now present data obtained with several systems which demonstrate that the reaction is quite general and not greatly dependent upon the nature of ring substitution.

The reaction of 7,7-dichlorobicyclo[4.1.0]heptane (**1**) with potassium isopropoxide in dimethyl sulfoxide (DMSO) afforded a mixture of two adducts, the ratio of which was found to depend upon mole ratios of reagents. Spectral and analytical data[3] established their structures as *cis*-1-isopropoxy-7-chlorobicyclo[4.1.0]heptane (**2**, 1%) and *cis*-1,6-diisopropoxybicyclo[4.1.0]heptane (**3**, 72%). The most reasonable rationale for the formation of these products is the elimination–addition sequence shown[4] with isopropoxide ion playing the role of both base and nucleophile. The apparent stereospecificity shown in the formation of **2** is probably due to a very rapid protonation of the carbanion intermediate by a DMSO molecule brought into the transition state as nucleophile solvate. A part of the structure proof of **2** is based on its reduction (sodium–ammonia) to 1-isopropoxybicyclo[4.1.0]heptane (**4**) which proved to be different from the other two isomers[5] that might have been formed.

The reaction of **1** with potassium *t*-butoxide–potassium thiomethide in DMSO, a good base–nucleophile combination, gave only *cis*-7-chloro-1-methylthiobicyclo[4.1.0]heptane (**5**, 69%). A further experiment with **5** in the base system demonstrated it to be inert to dehydrochlorination under these conditions.

In the examples described thus far, the directionality of addition is that expected on the basis of stability of the carbanion intermediate. This is further illustrated in the different but predictable behavior of 1,1-dichloro-2-phenylcyclopropane (**6**) under conditions used in the **1** → **5** transformation. The sole product observed was



1,1-bismethylthio-2-phenylcyclopropane (**7**, 79%). The reactivity of **6** proved sufficient to allow the use of potassium hydroxide in methanol to effect elimination and addition. The only isolable product was 1,1-dimethoxy-2-phenylcyclopropane (**8**, 52%).

One of the goals of this study was a simple, modest condition route to members of the methylenecyclopropene family. Although this has not yet been achieved, elimination–addition chemistry has provided encouraging results. The reaction (30°) of potassium isopropoxide and *cis*-1,1-dichloro-2,3-dimethylcyclopropane (**9**) in DMSO afforded 2-isopropoxy-2-methylmethylenecyclopropane (**10**, 31%) and *trans*-2-isopropoxy-3-methylmethylenecyclopropane (**11**, 35%). A similar reaction of **9** with sodium methoxide–potassium *t*-butoxide in DMSO gave the corresponding methoxy homologs, **12** (35%) and **13** (17%). The rationale which best fits these data is a sequential departure from results thus far described.

From results obtained with **1**, it is clear that the addition of a nucleophile to the initial dehydrochlorination product derived from **9** does not occur; only **10** and **12** would be observed. The sequential difference between the route followed here and that taken by **1** must be in the isomerization of the double bond out of the ring to give 2-chloro-3-methylmethylenecyclopropane prior to attack by the nucleophile. The analogous step in the norcarane system would be expected to be difficult due to the apparent strain energy of bicyclo[4.1.0]hept-1-ene.[6]

(1) Reported in part in preliminary form: T. C. Shields, B. A. Shoulders, J. F. Krause, C. L. Osborn, and P. D. Gardner, *J. Am. Chem. Soc.*, 87, 3026 (1965). A survey of background literature is presented there.

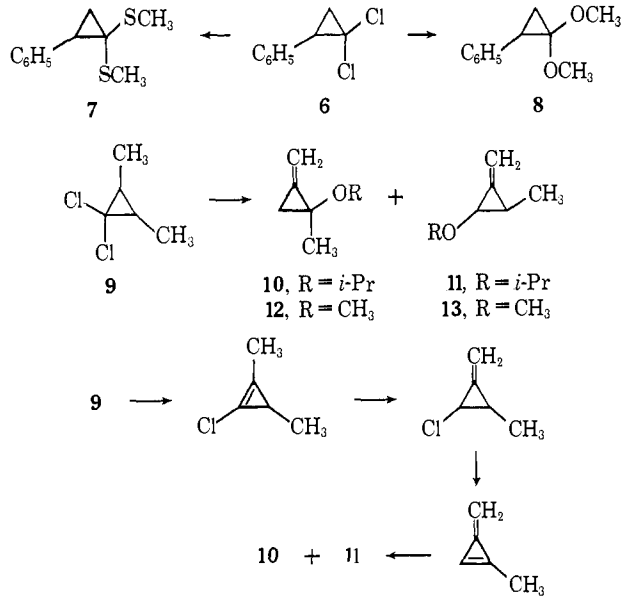
(2) K. B. Wiberg, R. K. Barnes, and J. Albin, *ibid.*, 79, 4994 (1957).

(3) All spectral data and their interpretation are reported in the Experimental Section.

(4) The similar reaction between **1** and potassium *t*-butoxide in DMSO gave a mixture of toluene, *o*-xylene, ethylbenzene, and *o*-ethyltoluene. This astonishing transformation is under investigation.

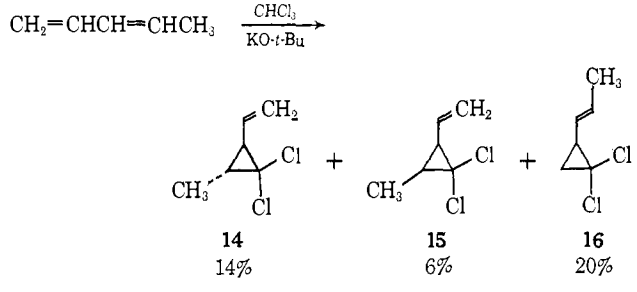
(5) U. Schöllkopf and J. Paust, *Angew. Chem. Intern. Ed. Engl.*, 2, 397 (1963); U. Schöllkopf and W. Pitterhoff, *Ber.*, 97, 636 (1964).

(6) C. L. Osborn, T. C. Shields, B. A. Shoulders, J. F. Krause, H. V. Cortez, and P. D. Gardner, *J. Am. Chem. Soc.*, 87, 3158 (1965).



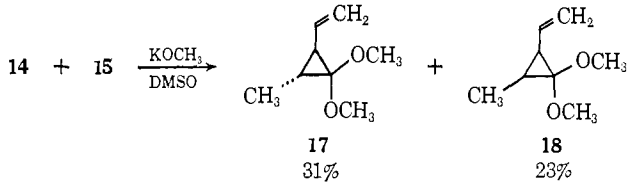
The ratios **10**:**11** and **12**:**13** are about those one would expect from addition of isopropoxide ion and methoxide ion to 1-methyl-3-methylenecyclopropene; they reflect relative stabilities of the carbanion intermediate and relative steric requirements of the two nucleophiles.

To determine the effect of a vinyl group on the course of elimination–addition reactions in dichlorocyclopropanes, the dichlorocarbene adducts of mixed (*cis* and *trans*) 1,3-pentadienes were prepared[7] and examined under conditions employed with others. The summary of the preparation is shown. The stereochemical assignments in **14** and **15** are based largely on the fact



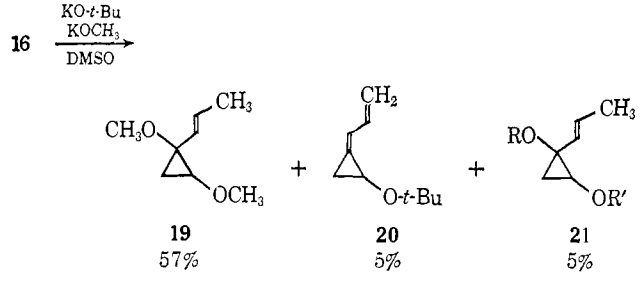
that the predominant pentadiene was the *trans* isomer and it is known that the addition is stereospecific.[8]

The reaction of a mixture of **14** and **15** (2:1) with potassium methoxide in DMSO afforded a mixture of *trans*- and *cis*-2,2-dimethoxy-3-methylvinylcyclopropane (**17**, 31% and **18**, 23%) along with traces of other products. The mechanistic sequence giving rise to these products appears to parallel that observed with **6** (**14** + **15** → 2-chloro-3-methylvinylcyclopropene → 2-chloro-2-methoxy-3-methylvinylcyclopropane → 2-methoxy-3-methylvinylcyclopropene → **17** + **18**). The

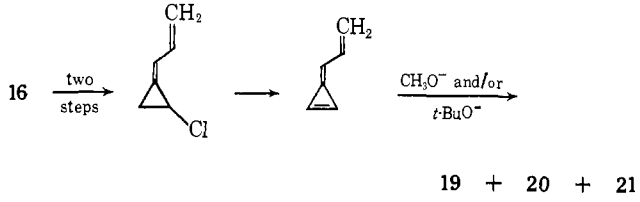


sequence is in accord with predicted relative proton acidities and carbanion stabilities.

The similar reaction of **16** proved to be somewhat more complex. The three products isolated (**19**–**21**) are shown. It is not yet possible to assign stereochemistry in **19** and **21**. Compound **21** possesses one methoxy and one *t*-butoxy group at positions indicated but present data do not permit a precise assignment of group to position. Two quite reasonable sequences can be written to account for the observed results. A part of

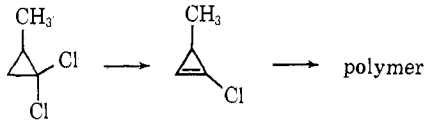


one of these involves the ultimate formation of **21** and **19** from **20** and its methoxy homolog by simple addition of alkoxide ion. A single attempt to add methoxide ion to **20** failed and even though the point is somewhat equivocal it leads us to favor the alternate mechanism shown.



Considerable evidence has accumulated during this study and from earlier work[6,9] which indicates that the base-catalyzed isomerization of a double bond to a position external to a three-membered ring is very facile. In general it occurs faster than nucleophilic addition to the cyclopropene double bond except in systems such as **1** where the rearranged product is very strained. In view of this and the observed behavior of **9**, the propenylidenecyclopropene intermediate proposed seems quite reasonable. It is noteworthy that the reaction of **16** with potassium *t*-butoxide in the absence of an added nucleophile afforded **20** as the only isolable product (40%).

Repeated attempts to dehydrochlorinate 1,1-dichloro-2-methylcyclopropane (**22**) in the absence or presence of nucleophiles have failed to give products of any kind. This is probably a consequence of elimination in the direction shown which provides no avenue of escape for the double bond from the three-membered ring. All that can be concluded is that this particular cyclopropene must be very reactive to polymerization. Base-catalyzed isomerization of the double bond around the



(7) L. Skattebol, *J. Org. Chem.*, **29**, 2951 (1964), prepared the mixture but did not effect a separation.

(8) P. S. Skell and A. Y. Garner, *J. Am. Chem. Soc.*, **78**, 3409 (1956).

(9) J. A. Carbon, W. B. Martin, and L. R. Swett, *ibid.*, **80**, 1002 (1958).

ring and into the methyl group would not be expected as the intermediate cyclopropene anion ("anti-Hückel") is probably too energetic to be formed under these conditions.

Experimental Section[10]

Reaction of 7,7-Dichlorobicyclo[4.1.0]heptane (1) with Potassium Isopropoxide. In a three-necked flask equipped with a stirrer and nitrogen purge system was prepared a solution of 226 g of potassium isopropoxide in 1.4 l. of DMSO.[10] 7,7-Dichlorobicyclo[4.1.0]heptane[11] (**1**, 72 g) was added over a period of 5 min, and the mixture was stirred mechanically for an additional 15 min. Cold water (3.5 l.) was added, and the mixture was extracted with pentane. The usual processing of the extract and removal of solvent followed by fractional distillation of the residue afforded 0.56 g (0.7%) of *cis*-7-chloro-1-isopropoxybicyclo[4.1.0]heptane (**2**), bp 38–39° (0.2 mm), n^{25}D 1.4624, and 67 g (72%) of *cis*-1,6-diisopropoxybicyclo[4.1.0]heptane (**3**), bp 47° (0.2 mm), n^{25}D 1.4488. Compound **2** gave a parent mass peak − Cl, 153. Its nmr signals are at τ 6.11 (J = 6.0 cps, septet, C*H*O, 1 H),[12] τ 6.76 (J = 9.2 cps, doublet, C*H*Cl, 1 H),[13] τ 8.90 and 8.93 (J = 6.5 cps, two sets of doublets, C*H*$_3$, 6 H).[13] This substance is unstable and turns yellow and then brown even at temperatures below 0°. Compound **3** gave a parent mass peak at 212. Its nmr signals are at τ 6.25 (J = 6.0 cps, septet, C*H*O, 2 H),[13] τ 9.60 (J = 6.4 cps, doublet, *endo*-cyclopropyl *H*, 1 H).

Anal. Calcd for $C_{13}H_{24}O_2$: C, 73.53; H, 11.39. Found: C, 73.49; H, 11.26; parent mass peak, 212.

Sodium–Ammonia Reduction of *cis*-7-Chloro[4.1.0]heptane (2). Sodium (8.5 g) was added to 250 ml of dry liquid ammonia contained in a three-necked flask outfitted with a Dry Ice condenser. The mixture was stirred for 20 min and a solution of 10.5 g of **2** in 20 ml of ether was added dropwise during 35 min. The solution was stirred for 5 hr and then treated with sufficient ammonium chloride to discharge its blue color. Ammonia was allowed to evaporate, and the residue was dissolved in a water–ether mixture. The ether extract was processed in the usual manner and fractionally distilled. Flash distillation of the residue *in vacuo* gave 2.8 g (33%) of **4** which was pure by glpc, n^{25}D 1.4490. Its useful nmr signals are at τ 6.24 (J = 6.0 cps, septet, C*H*O, 1 H)[12] and τ 9.56 (J = 6.1 cps, doublet, *endo*-cyclopropyl *H*, 1 H).

Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.26. Found: C, 77.94; H, 11.42; parent mass peak, 154.

Reaction of 7,7-Dichlorobicyclo[4.1.0]heptane (1) with Potassium Thiomethide and Potassium *t*-Butoxide. A solution of potassium *t*-butoxide (49 g) in 500 ml of DMSO[10] was prepared in a three-necked flask outfitted with a mechanical stirrer, dropping funnel, nitrogen purge system, and a dip tube. The mixture was stirred (nitrogen) for a few minutes and 10 g of methyl mercaptan was added through the dip tube into the liquid phase. After 10-min additional stirring, 27 g of **1** in 15 ml of DMSO was added dropwise during 30 min. The flask was cooled in a chilled water bath during the addition and the subsequent 1 hr of stirring. A large volume of water was added, and the product was isolated by extraction with pentane. Removal of pentane and distillation of the residue gave 19.9 g (69%) of *cis*-7-chloro-1-methylthiobicyclo[4.1.0]heptane (**5**), bp 80° (0.3 mm), n^{25}D 1.5260. Pertinent nmr signals are found in its spectrum at τ 6.69 (J = 8.0 cps, doublet, C*H*Cl, 1 H)[13] and τ 7.90 (singlet, SC*H*$_3$, 3 H).

Anal. Calcd for $C_8H_{13}SCl$: C, 54.37; H, 7.42; S, 18.15; Cl, 20.06. Found: C, 54.52; H, 7.53; S, 17.39; Cl, 20.70; parent mass peak, 176.

Reaction of 1,1-Dichloro-2-phenylcyclopropane (6) with Potassium Thiomethide and Potassium *t*-Butoxide. Following the procedure described for preparing **5**, 50.4 g of potassium *t*-butoxide, 10 g of methyl mercaptan, and 23.8 g of **6**[14] in 400 ml of DMSO were allowed to react. There was obtained 21.2 g (79%) of 1,1-bismethylthio-2-phenylcyclopropane (**7**), bp 101° (0.25 mm), n^{25}D 1.5881. Principal nmr signals appear at τ 2.81 (sharp multiplet, aryl, 5 H), τ 7.35 (J = 7.8 cps, apparent triplet, C_6H_5CH, 1 H), τ 7.75 and 8.20 (singlets, SC*H*$_3$, 6 H), and τ 8.49 (J = 7.8 cps, apparent doublet, cyclopropyl *H*, 2 H). In pyridine the apparent triplet is resolved into a quartet centered at τ 7.19 (J = 7.0, 8.8 cps) and the apparent doublet becomes two sets of doublets centered at τ 8.38 (J = 7.0 cps) and τ 8.42 (J = 8.8 cps).[15]

Anal. Calcd for $C_{11}H_{14}S_2$: C, 62.80; H, 6.71; S, 30.49. Found: C, 63.19; H, 6.70; S, 30.28; parent mass peak −1, 209.

Reaction of 1,1-Dichloro-2-phenylcyclopropane (6) with Potassium Hydroxide in Methanol. To a solution of 25 g of potassium hydroxide in 100 ml of methanol (80°, stirring) was added 9.1 g of **6**. The temperature of the mixture was raised to 104° and after a few minutes an exothermic reaction occurred which lasted about 3 min. After quenching with water and extraction with pentane, followed by the usual isolation procedure, there was obtained 4.6 g (52%) of 1,1-dimethoxy-2-phenylcyclopropane (**8**), bp 68° (0.42 mm), n^{25}D 1.5121. Principal nmr signals are observed at τ 2.89 (sharp multiplet, aryl, 5 H), τ 6.67 and 6.92 (singlets, OC*H*$_3$, 6 H), τ 7.72 (J = 9.2, 8.0 cps, quartet, C_6H_5CH, 1 H),[15] τ 8.68 (J = 9.2, 5.4 cps, quartet, cyclopropyl *H*, 1 H), and τ 8.82 (J = 8.0, 5.4 cps, quartet, cyclopropyl *H*, 1 H).

Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.25; H, 7.84; parent mass peak, 178.

Reaction of *cis*-1,1-Dichloro-2,3-dimethylcyclopropane (9) with Potassium Isopropoxide. Using the procedure described for **3**, 20 g of potassium metal, excess isopropyl alcohol,[10] 680 ml of DMSO, and 16.0 g of **9** were employed to prepare 9.6 g (flash distilled) of a mixture of two products. They were separated by glpc below 70°.[16] They were shown to be 2-isopropoxy-2-methylmethylenecyclopropane (**10**, 31%, n^{25}D 1.4220) and *trans*-2-isopropoxy-3-methylmethylenecyclopropane (**11**, 35%, n^{25}D 1.4228). The nmr spectrum of **10** exhibits signals at τ 4.45 and 4.62 (multiplet, vinyl, 2 H),[17] τ 6.20 (J = 6.0 cps, septet, C*H*O, 1 H),[12] τ 8.60 (singlet, methyl, 3 H), and τ 8.70–9.10 (multiplet 8 H).

Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.24; H, 11.41; parent mass peak, 126.

The nmr spectrum of **11** shows signals at τ 4.43 and 4.57 (multiplet, vinyl, 2 H),[17] τ 6.32 (J = 6.0 cps, septet, C*H*O, 1 H),[12] τ 6.85 (W_H = 4.5 cps, C*H*O, 1 H), and τ 8.50–9.05 (multiplet, 10 H).

Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.00; H, 10.92.

Reaction of *cis*-1,1-Dichloro-2,3-dimethylcyclopropane (9) with Sodium Methoxide and Potassium *t*-Butoxide. Using the procedure described for **3**, potassium *t*-butoxide (from 14.5 g of potassium), 90 g of sodium methoxide (commercial), 600 ml of DMSO, and 15.5 g of **9** there was obtained 5.6 g of flash-distilled product. Separation by preparative glpc gave only 2-methoxy-2-methylmethylenecyclopropane (**12**, 35%, n^{25}D 1.4190) and *trans*-2-methoxy-3-methylmethylenecyclopropane (**13**, 17%, n^{25}D 1.4228). Principal signals in the nmr spectrum of **12** are at τ 4.42 and 4.66 (multiplet, vinyl, 2 H),[17] τ 6.79 (singlet, OC*H*$_3$, 3 H), τ 8.62 (singlet, C*H*$_3$, 3 H), and τ 8.50–9.15 (multiplet, cyclopropyl, 2 H).

Anal. Calcd for $C_6H_{10}O$: C, 73.43; H, 10.27. Found: C, 73.45; H, 10.36; parent mass peak, 98.

(10) Boiling points, where given, were obtained during short-path distillations of relatively small quantities and under nonequilibrium conditions. A variety of column packings were used in gas–liquid partition chromatographic analyses (glpc) and separations. In most cases, any number of all-purpose columns were found to be satisfactory. The stationary phase will therefore be described only in cases where one was vastly superior to others. All reactions were monitored (glpc) by periodic withdrawal of 1.0-ml aliquots. Each was terminated upon disappearance of substrate. Aliquots were shaken with 10 ml of water and 1 ml of pentane and frozen in Dry Ice to permit decantation of the pentane solution for analysis. Potassium *t*-butoxide solutions (or suspensions) in DMSO were prepared by the reaction of the metal with *t*-butyl alcohol which had been freshly distilled from calcium hydride. Excess solvent was removed by distillation, first at an aspirator and then on a vacuum pump (100°) for 12 hr. DMSO was then distilled from calcium hydride (0.1 mm) directly into the flask containing the base, and the mixture was used without delay. At no time during this operation was air admitted to the reaction vessel. Potassium isopropoxide solutions were prepared in the same way except that the reaction of potassium with the alcohol was cooled in its initial stages to −31° (Dry Ice, mineral oil bath).

(11) W. von E. Doering and A. K. Hoffmann, *J. Am. Chem. Soc.*, **76**, 6162 (1954).

(12) The increased multiplicity observed here and in other isopropoxy compounds is undoubtedly due to magnetic asymmetry; *cf.* G. M. Whitesides, D. Holtz, and J. D. Roberts, *ibid.*, **86**, 2628 (1964), and references cited therein.

(13) This coupling constant is typical of *cis* protons in cyclopropanes; *cf.* D. J. Patel, M. E. Howden, and J. D. Roberts, *ibid.*, **85**, 3218 (1963); K. B. Wiberg and B. J. Nist, *ibid.*, **85**, 2788 (1963).

(14) K. L. Williamson, C. A. Landford, C. R. Nicholson, *ibid.*, **86**, 763 (1964).

(15) *Cf.* W. I. Awad, A. K. Fateen, and M. A. Zayed, *Tetrahedron*, **20**, 893 (1964).

(16) Partial isomerization of **10** occurred above 70°.[1]

(17) *Cf.* G. Schröder, *Ber.*, **96**, 3178 (1963).

The nmr spectrum of **13** has principal bands at τ 4.40 and 4.57 (multiplet, vinyl, 2 H),[17] τ 6.73 (singlet, OCH_3, 3 H), τ 6.86 (multiplet, W_H = 4.5 cps, CHO, 1 H), and τ 8.40–9.05 (multiplet, 4 H).

Anal. Calcd for $C_6H_{10}O$: C, 73.43; H, 10.27. Found: C, 74.00; H, 10.40.

Dichlorocarbene Adducts of Mixed 1,3-Pentadienes.[7] The mixture of adducts was prepared (43%) in the usual way[7,11] and separated by preparative glpc. There was obtained **14** (14%), **15** (6%), and **16** (20%) as well as 3% of what is presumed to be a bis adduct.[7] The nmr spectrum of **14** exhibits signals at τ 4.07–5.06 (multiplet, vinyl, 3 H) and τ 8.03–8.90 (multiplet containing a sharp peak at τ 8.64, 5 H).

Anal. Calcd for $C_6H_8Cl_2$: C, 47.71; H, 5.34; Cl, 46.95. Found: C, 48.29; H, 5.57; Cl, 46.80; parent mass peaks 151, 152.

The nmr spectrum of **15** shows signals at τ 4.44–4.83 (multiplet, vinyl, 3 H) and τ 7.59–8.93 (multiplet, 5 H containing a doublet at τ 8.78, J = 5.9 cps).

Anal. Calcd for $C_6H_8Cl_2$: C, 47.71; H, 5.34; Cl, 46.95. Found: C, 48.11; H, 5.33; Cl, 47.10.

The nmr spectrum of **16** ($n^{25}D$ 1.4783) shows signals at τ 3.93 and 5.09 (multiplet, vinyl, 2 H) and τ 7.50–8.90 (series of multiplets, 6 H).

Anal. Calcd for $C_6H_8Cl_2$: C, 47.71; H, 5.34; Cl, 46.95. Found: C, 48.03; H, 5.42; Cl, 47.00; parent mass peaks, 150, 152.

Reaction of *cis*- and *trans*-2,2-Dichloro-3-methylvinylcyclopropanes (14 and 15) with Potassium Methoxide. In a three-necked flask equipped with a rubber septum, pressure-equilibrated dropping funnel, and nitrogen purge system, 20 g of potassium *t*-butoxide[10] was mixed with 12 ml of methanol and stirred magnetically for 20 min. After removal of alcohols by heating under aspirator vacuum, 78 ml of DMSO[10] was introduced and stirring was continued for another 20 min. A 95% pure mixture of **14** and **15** (2:1) was introduced and the mixture was stirred at room temperature for 25 hr. The usual work-up procedure followed by preparative glpc afforded **17** (31%, $n^{25}D$ 1.4332) and **18** (23%, $n^{25}D$ 1.4351).

The nmr spectrum of **17** shows signals at τ 4.18–5.25 (multiplet, vinyl, 3 H), τ 6.69 and 6.73 (singlets, OCH_3, 6 H), and τ 8.53–9.00 (multiplet containing a sharp spike at τ 8.89, 5 H). This spectrum is very similar to that of **14**.

Anal. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 67.50; H, 9.89; parent mass peak, 142.

The nmr spectrum of **18** has signals at τ 4.16–5.17 (multiplet, vinyl, 3 H), τ 6.69 and 6.76 (singlets, OCH_3, 6 H), τ 8.26 (poorly resolved quartet appearing as a triplet, J = 8 cps, allylic cyclopropyl, 1 H), and τ 8.50–9.12 (multiplet, 4 H). The τ 8.26 signal indicates a rather large coupling with the other cyclopropyl hydrogen which is consistent with a *cis* geometry between them. The separation of methoxy singlets in **18** is 4.0 cps while that in **17** is 2.4 cps, as predicted for *cis* and *trans* isomers of this type.

Anal. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 67.35; H, 9.78; parent mass peak, 142.

Reaction of 1,1-Dichloro-2-(1-propenyl)cyclopropane (16) with Potassium Methoxide. Using the procedure described in the preceding experiment, the reaction of 2.9 g (95% pure) of **16** with potassium methoxide derived from 22.4 g of potassium *t*-butoxide gave **19** (57%, $n^{25}D$ 1.4434), **20** (*ca.* 5%, $n^{25}D$ 1.4422), and **21** (*ca.* 5%). The nmr spectrum of **19** has signals at τ 4.00–5.00 (multiplet, vinyl, 2 H), τ 6.75 and 6.88 (singlets, OCH_3, 6 H) superimposed on a multiplet (CHO, 1 H), τ 8.23 (J = 5.8 cps, doublet, allylic methyl, 3 H), and τ 8.70–9.50 (multiplet, cyclopropyl, 2 H).

Anal. Calcd for $C_8H_{14}O_2$: C, 76.57; H, 9.92. Found: C, 76.58; H, 9.91; parent mass peak, 142.

20 [λ_{max} 232 mμ (ϵ 13,300)] gave an nmr spectrum having signals at τ 3.80–4.30 (multiplet, conjugated vinyl, 2 H), τ 5.13 (multiplet, terminal vinyl, 2 H), τ 7.33–8.26 (multiplet, cyclopropyl, 2 H), and τ 8.79 (singlet, O-*t*-Bu, 9 H).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.40; H, 10.40; parent mass peak + 1, 153.

The nmr spectrum of **21** shows signals at τ 4.17–5.00 (multiplet, vinyl, 2 H), τ 6.72 (J = 8.0, 4.6 cps, quartet, CHO, 1 H), τ 6.87 (singlet, OCH_3, 3 H), τ 8.23 (J = 6.0 cps, doublet with secondary splitting, allylic methyl, 3 H), τ 8.83 (singlet, O-*t*-Bu, 9 H), τ 8.98 (J = 8.0, 6.3 cps, quartet, cyclopropyl, 1 H), and τ 9.37 (J = 6.3, 4.6 cps, quartet, cyclopropyl, 1 H).

Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.70; H, 10.94. Found: C, 72.12; H, 10.48.

Reaction of 1,1-Dichloro-2-(1-propenyl)cyclopropane (16) with Potassium *t*-Butoxide. A 9.5-g sample of **16** was stirred with a solution of 10 g of potassium *t*-butoxide in 830 ml of DMSO[10] (nitrogen) for 45 min and then quenched with water. The mixture was worked up by pentane extraction; the extract was filtered through glass wool to remove polymer. Fractional distillation afforded 3.8 g of **20**, bp 31° (20 mm), which was found to be essentially pure by glpc. The product was identical in all respects with material obtained as described in the preceding experiment.

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Kinetics of the Nitric Acid Oxidation of Nitrosobenzene to Nitrobenzene in Aqueous Dioxane

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Abstract: The oxidation of nitrosobenzene to nitrobenzene in aqueous dioxane with dilute ($\leq$1 *M*) nitric acid containing a small amount of nitrous acid has been studied kinetically by means of ultraviolet spectrophotometry. The yield of nitrobenzenes increases with increasing nitric acid concentration and with increasing dioxane content in the solvent. The concentration of nitrous acid in the system increases as the reaction proceeds, and the reaction is autocatalytic. The rate is expressed as $v = kh_0^{0.5}(1 + 0.5h_0)[NO_3^-]^{0.5}[HNO_2]^{0.5}[PhNO]$. The rate increases with increasing content of dioxane in the solvent in spite of decreasing acidity. The reaction is facilitated by electron-releasing groups and retarded by electron-attracting groups. A probable mechanism is discussed which involves an attack of nitrogen dioxide and/or its conjugate acid on the double bond of nitrosobenzene.

Aromatic nitrations are generally retarded by the addition of nitrous acid because of the removal of nitronium ion. However, in more dilute nitric acid, nitrous acid accelerates nitration, and reactive aromatics such as phenol and mesitylene, etc., are subject to nitrosation by nitrous acid. The resulting nitroso compounds