lation counting method previously described.[32] The value given is the average of three separate determinations, each one involving weighing, dilution, and counting. Each sample was counted three to six times. The activity is corrected for background, the usual precautions[32] being taken to minimize instrumental fluctuations by counting background and sample within a short time of each other and by taking background counts before and after a set of counts. Background counts were usually 190–200 dis./min., and sample counts were in the range 2,000–10,000 dis./min. A standard sample was periodically checked to determine instrumental drift. This amounted to only about 1%, but the drift correction was nevertheless applied in comparisons of samples counted at different times.

A sample of 5.2645 g. of optically active 2-bicyclo[2.2.2]-octyl acid phthalate, $[\alpha]D$ +7.75°, +7.72° (c 5 in CHCl₃, two separate determinations), was mixed with 1.0088 g. of the above racemic labeled acid phthalate, the whole was dissolved in ether-ethanol, the solution was evaporated, and the residue dissolved, along with 9.05 g. of brucine, in 35 ml. of hot ethyl acetate. Upon cooling, the solution deposited about 13 g. of salt from which acid phthalate of $[\alpha]D$ +5.48° (CHCl₃) could be regenerated. From the mother liquor, there was obtained 2 g. of salt which gave after the usual work-up a sample of acid phthalate. Recrystallization from benzene–pentane gave 0.7 g. of material

(32) J. A. Berson and W. A. Mueller, J. Am. Chem. Soc., 83, 4940 (1961).

(sample 1), which was recrystallized twice more from benzene–pentane giving samples 2 and 3. These materials had the following properties ([α]D in CHCl₃, c 4; specific radioactivity in c./min./mg.): sample 1, +11.91°, 194; sample 2, +11.49°, 200; sample 3, +11.85°, 199. From these data and eq. 1, it can be calculated that E, the weight of enantiomer in the original optically active sample, is 1.3325 ± 0.17 g. (the uncertainty shown is the experimental average deviation), whence the optical purity is 25.3%. The rotation of optically pure acid phthalate is thus 30.5 ± 3.7° (CHCl₃). The uncertainty shown is that calculated from probability theory as described earlier.[9]

Correlation of 2-Bicyclo[2.2.2]octanol with its Acid Phthalate.— A solution of 5.5 g. of the acid phthalate, $[\alpha]D$ +4.86° (c 8.475 in CHCl₃), and 19 g. of sodium hydroxide in 75 ml. of water was subjected to steam distillation. The distillate was saturated with sodium chloride and extracted with ether. After having been dried over sodium sulfate and evaporated under a Vigreux column, the solution left 2.0 g. (80%) of 2-bicyclo[2.2.2]octanol which was sublimed in vacuo at 130–140°. The resulting material had m.p. 209–211°, infrared spectrum identical with that of the racemate, $[\alpha]D$ +6.20° (c 8.075 in CHCl₃), +6.52° (c 8.34 in CHCl₃). The alcohol thus has 1.31 times the rotatory power of the acid phthalate, and $[\alpha]D$ for optically pure alcohol is 40.0 ± 4.7° (CHCl₃). An indirect correlation[17] gives the ratio 1.18 for the relative rotatory powers; on this basis optically pure alcohol would have $[\alpha]D$ 36°.

Cycloaddition. I. The 1,2-Addition of 1,1-Dichloro-2,2-difluoroethylene to Some Dienes[1]

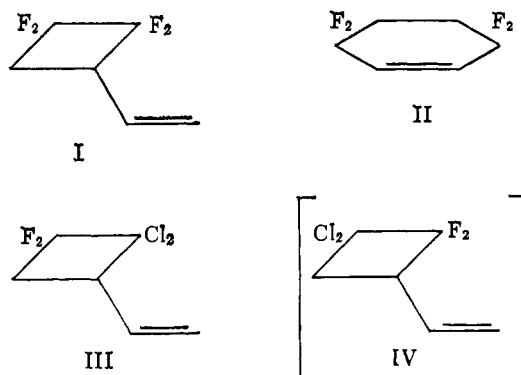By Paul D. Bartlett, Lawrence K. Montgomery, and Bernhard Seidel

In sealed tubes at 80° with 1,1-dichloro-2,2-difluoroethylene in excess and a polymerization inhibitor (hydroquinone or di-n-butylammonium picrate) butadiene, cis-piperylene, and trans-piperylene each yielded a single 1,2-addition product. From isoprene (2-methylbutadiene), 1,2- and 3,4-cycloaddition products were obtained in the ratio of 5.4 to 1; from chloroprene (2-chlorobutadiene) the ratio of 1,2- and 3,4-addition products was 4.0 to 1. Cyclopentadiene and a fourfold excess of 1,1-dichloro-2,2-difluoroethylene yielded a product consisting of the 1,4-adduct 2,2-dichloro-3,3-difluorobicyclo[2.2.1]heptene-5 (44%), the 1,2-adduct 6,6-difluoro-7,7-dichlorobicyclo[3.2.0]heptene-2 (9%), and endo-dicyclopentadiene (47%). The butadiene, isoprene, and chloroprene adducts were degraded by oxidation to the corresponding cyclobutanecarboxylic acids. The structure of 2,2-dichloro-3,3-difluorocyclobutane-1-carboxylic acid was shown by its ease of conversion under acid conditions into 2-chloro-3,3-difluoro-1-cyclobutene-1-carboxylic acid and under basic conditions into 2-chloro-3,3-difluoro-1-cyclobutene. The establishment of these structures provided bases of n.m.r. and infrared comparison from which it is concluded that all the 1,2-cycloadducts have the chlorine atoms adjacent to the unsaturated substituent in the cyclobutane ring. These results are consistent with the hypothesis that a bifunctional ("biradical") intermediate is formed as the first step in 1,2-cycloaddition.

Introduction

Fluorinated olefins generally undergo thermal cycloaddition reactions with 1,3-butadienes to give vinylcyclobutanes.[2] In the present series of papers we report studies of some of the properties of these cycloaddition reactions bearing upon the mechanism of the reaction in the case of 1,1-dichloro-2,2-difluoroethylene.

One of the most remarkable facts about these cycloadditions is the almost complete dichotomy among the known reagents which add to butadiene. With few exceptions a reagent reacts either entirely by 1,4-addition (Diels–Alder reaction), like maleic anhydride, or entirely by 1,2-addition, like tetrafluoroethylene. In the latter case,[3] there is only a single 1,2-addition product (I) and none of the isomeric 1,4-addition product (II).

The use of the less symmetrical reagent, 1,1-dichloro-2,2-difluoroethylene (to be called here "1122" for brevity) introduces the possibility of simple orientation isomerism (III vs. IV). Here, too, existing evidence[2] presents a simple picture: wherever the structures have been established they represent the type III

(1) Presented at the National Organic Symposium, Columbus, Ohio, June 18, 1963.

(2) J. D. Roberts and C. M. Sharts in "Organic Reactions," Vol. 12, John Wiley and Sons, Inc., New York, N. Y., 1962, p. 1.

(3) D. D. Coffman, P. L. Barrick, R. D. Cramer, and M. S. Raasch, J. Am. Chem. Soc., 71, 490 (1949).

and not IV. This fact is covered by the generalization[2,4] that the structure is that which would be formed via the most stable "biradical" intermediate. In the present paper we add something to the existing evidence and find that this rule predicts correctly the orientations in the case of butadiene and 1122.

With 1- and 2-substituted butadienes selectivity between the double bonds gives rise to a further structural variation in the products. In this paper we find that the product from piperylene is entirely V (a or b) with the configuration of the propenyl group being that of the initial piperylene, while isoprene (R = CH₃) and

(4) E. C. Coyner and H. S. Hillman, ibid., 71, 324 (1949).

chloroprene (R = Cl) give mixtures of VI and VII favoring VII.

Va   Vb

VI   VII
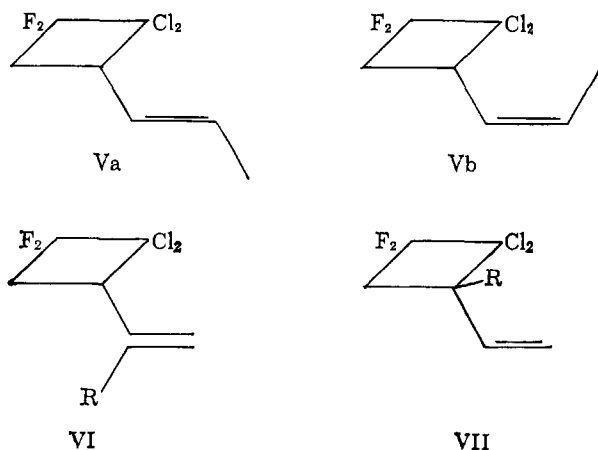
In part II the extension of the study to the geometrical isomers of 2,4-hexadiene reveals two further properties of the 1,2-cycloaddition reagent: (1) its relative reactivities toward *cis* and *trans* double bonds and (2) the stereoequilibration which sets in during addition to a double bond.

In part III we report some kinetic measurements permitting a comparison of the reactivities of dienes and of specific double bonds toward 1,2-cycloaddition, and a comparison of these effects with those observed in the Diels–Alder reaction.

Characterization of Adducts

Butadiene and 1,1-Dichloro-2,2-difluoroethylene.—These two reactants yielded an adduct which was homogeneous to vapor phase chromatography under a variety of experimental conditions. Analogy with the case of tetrafluoroethylene[2] made the vinylcyclobutane structure appear probable while the easy separability of vinylcyclobutanes from cyclohexenes by fractional distillation[5] renders a mixture of products in the present case unlikely. The infrared spectrum of the adduct shows the presence of a vinyl substituent[6] with a double bond stretching frequency at 1646 cm.$^{-1}$. The proton nuclear magnetic resonance spectrum of the adduct consists of four signal groupings whose areas are in the ratio of 1:1.96:1.00:1.92. Figure 1 shows the spectrum together with assignments based upon the vinylcyclobutane structure and consistent with the known behavior of a vinyl system in the n.m.r.[7]

Oxidation of the adduct III with alkaline potassium permanganate gave a 1,2-glycol VIII or mixture of glycols (about 28%), 3,3-difluoro-2,2-dichlorocyclobutanecarboxylic acid (IX, 15%), 2,2-difluorosuccinic acid (X, 30%), and 2,2-difluoromalonic acid (XI, 1.1%). A stepwise degradation proceeding *via* the 1,2-glycol VIII and the aldehyde XII gave in good yield a mixture of the cyclobutanecarboxylic acid (IX, about 23%) and the related unsaturated acid (XIII, about 59%) resulting from the loss of hydrogen chloride. The latter acid was obtained in 79% yield as the sole product of the oxidation of the butadiene–fluoroolefin adduct with chromic acid[8]; the relative ease with which 3,3-di-

(5) J. J. Drysdale, U. S. Patent 2,861,095 (1958); *Chem. Abstr.*, **53**, 9102a (1959).

(6) L. J. Bellamy, "The Infrared Spectrum of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, pp. 4 and 6.

(7) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp. 238–246.

(8) (a) G. N. B. Burch, Ph.D. Thesis, Ohio State University, 1949. (b) The structure of the acid XIII is conclusively shown by its elementary analysis and its proton n.m.r. spectrum, recently determined in carbon tetrachloride by Dr. G. E. H. Wallbillich of this Laboratory. The spectrum con-
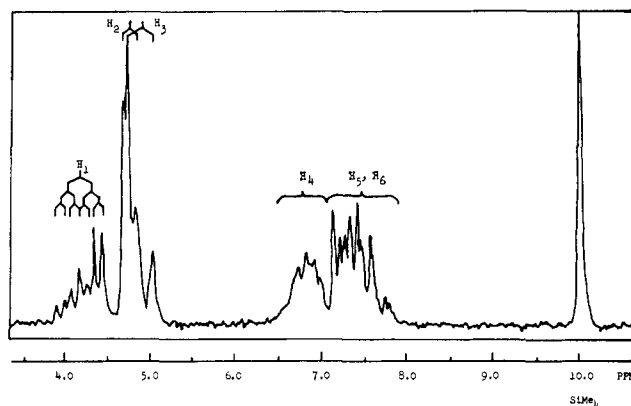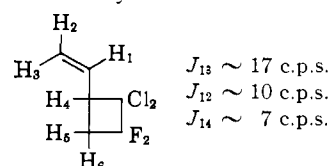
Fig. 1.—60-Mc. n.m.r. spectrum of the adduct of butadiene and 1,1-dichloro-2,2-difluoroethylene

$J_{13} \sim 17$ c.p.s.
$J_{12} \sim 10$ c.p.s.
$J_{14} \sim 7$ c.p.s.

Integration: H_1 1.00:H_2, H_3 1.96:H_4 1.00:H_5, H_6 1.92.

fluoro-2,2-dichlorocyclobutanecarboxylic acid loses hydrogen chloride has been noted previously by Burch,[8a] who obtained the acid from the cycloadduct of methyl acrylate and 1122.

Perhaps the most compelling evidence of the positions of the fluorine and chlorine atoms in the carboxylic acid IX comes from its ready decarboxylative dehydrochlorination typical of β-chloro acids. A small amount of IX was neutralized with sodium hydroxide. The resulting solution was evaporated to dryness and the residue was heated. A low boiling liquid was collected which gave only 2,2-difluorosuccinic acid when
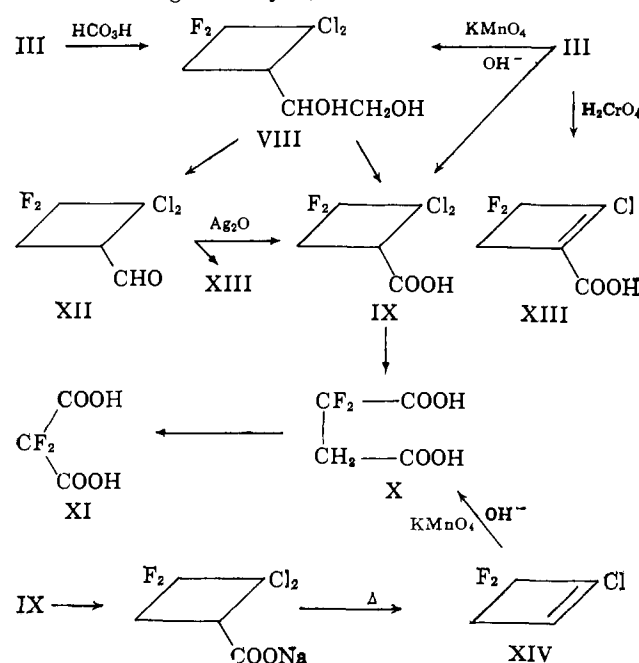
oxidized with alkaline permanganate. About 92% of the theoretical quantity of chloride (based on the formation of 2-chloro-3,3-difluorocyclobutene (XIV)) was liberated. If we accept the v.p.c. evidence that the adduct to the butadiene is homogeneous, these degradations appear consistent only with the adduct structure 1,1-difluoro-2,2-dichloro-3-vinylcyclobutane (III).

sists of a sharp carboxyl singlet at τ −2.32 and a clean two-proton triplet at τ 6.76 with $J \sim 3.7$ cycles.

Fig. 2.—60-Mc. n.m.r. spectrum of the adduct of *trans*-piperylene and 1,1-dichloro-2,2-difluoroethylene.
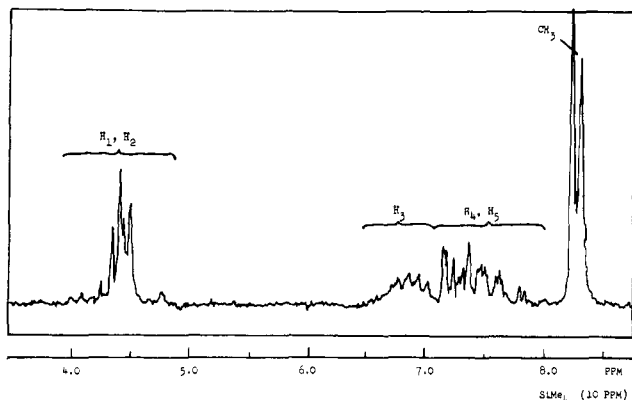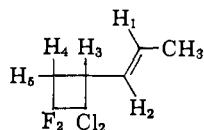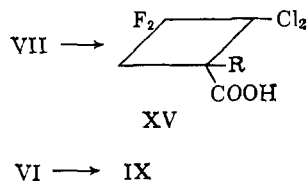

Fig. 3.—60-Mc. n.m.r. spectrum of the adduct of *cis*-piperylene and 1,1-dichloro-2,2-difluoroethylene.

Chloroprene and 1,1-Dichloro-2,2-difluoroethylene.— The reaction of approximately equal molar quantities of chloroprene and 1122 yielded three high boiling products in the ratio of 9.8:1.6:1 according to the v.p.c. analysis. The third component disappeared when a several-mole excess of 1122 was employed. The elementary analysis of the remaining two-component mixture was correct for a 1:1 adduct. The spectra reported here are those for the three-component mixture, the cyclobutane product being accordingly contaminated with 8% of the chloroprene dimer. The infrared spectrum showed the characteristic absorptions for a vinyl substituent, the double bond stretching frequency occurring at 1643 cm.$^{-1}$. A very weak band at 1670 cm.$^{-1}$ is characteristic of a trisubstituted double bond such as might be present in chloroprene dimer. The n.m.r. spectrum is consistent with the major product being 1,2,2-trichloro-3,3-difluoro-1-vinylcyclobutane (VII, R = Cl). The quartet at τ 3.90 is indicative of the nonterminal proton of a vinyl group. At slightly higher fields are the four lines of the terminal vinyl protons. The complexity of the spectrum in the 6.87 τ region indicates proton–fluorine coupling.

The potassium permanganate oxidation of the chloroprene adducts gave a nonacidic product (about 25%), 1,2,2-trichloro-3,3-difluorocyclobutanecarboxylic acid (XV, R = Cl), 2,2-dichloro-3,3-difluorocyclobutanecarboxylic acid (IX, 2.7%), and 2,2-difluorosuccinic acid (X, 8%). The isolation of the cyclobutanecarboxylic acid IX containing only two chlorine atoms clearly indicates the presence of the 3,4-adduct (VI, R = Cl) along with the 1,2-adduct VII.

VI ⟶ IX

Isoprene and 1,1-Dichloro-2,2-difluoroethylene.— The adduct from this reaction shows two poorly resolved peaks on vapor phase chromatography in the ratio of 6.0:1. The n.m.r. spectrum of the mixed isomers shows two methyl peaks at τ 8.13 and 8.59, appropriate for methyl groups attached to vinylic and to saturated carbon atoms, respectively. The integrated ratio of these two signals was 1:5.4, the methyl substituent attached to saturated carbon giving the
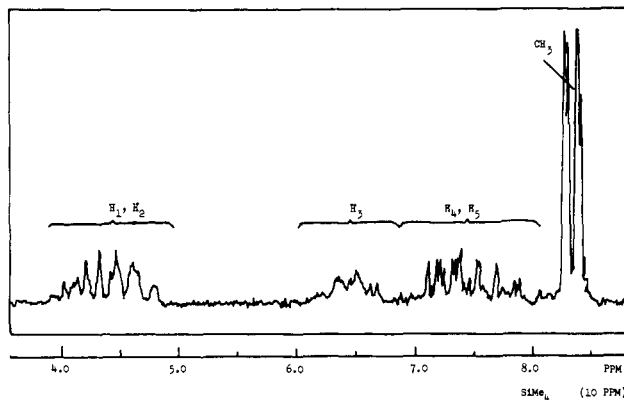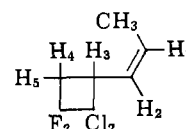
stronger signal. The second isomer in this case might, on the basis of the n.m.r. spectrum, be either the 3,4-adduct of isoprene and 1122 (VI, R = CH₃) or a 1,4-adduct which would also have a methyl group on an unsaturated carbon. However, the absence of infrared absorption by the adduct mixture at 1670 cm.$^{-1}$ speaks against the presence of a cyclohexene in the product.

The only oxidation product of the isoprene adducts to be characterized was 2,2-dichloro-3,3-difluoro-1-methylcyclobutanecarboxylic acid (XV, R = CH₃). This acid was reported previously from the addition of 1122 to methyl methacrylate.[8a]

cis- and trans-Piperylenes and 1,1-Dichloro-2,2-difluoroethylene.— A single 3,4-adduct (Va) was obtained from a thermal cycloaddition of 1122 to *trans*-piperylene. In a similar manner *cis*-piperylene afforded only a single product (Vb) which differed from that of the *trans* isomer. An artificial mixture of the two cycloadducts was cleanly separated by vapor phase chromatography, it being thus established that each isomer was formed to the exclusion of the other. That these are 3,4-cycloaddition products (*cis*- and *trans*-propenylcyclobutanes) is clearly shown by the n.m.r. spectra of the two isomers (Fig. 2 and 3). In each case the methyl peak is appropriately located for methyl on unsaturated carbon and is split into a doublet by the proton on the same carbon atom. In the case of the *cis*-piperylene adduct there is also a small splitting ($J \sim 1.4$ c.p.s.) by the vinyl proton *trans* to the methyl group. There is no detectable absorption corresponding to a methyl group on a saturated carbon atom.

Cyclopentadiene and 1,1-Dichloro-2,2-difluoroethylene.— The product from cyclopentadiene and 1122 gave three peaks on vapor phase chromatography. One of these, representing 47% of the mixture, was the well-known *endo*-dicyclopentadiene. The other two, which were cycloadducts, comprised 8.6 and 44.3% of the product. Spectral evidence is consistent with the minor product being a 1,2- and the major product a 1,4-addition product. This assignment is strongly indicated by the narrow n.m.r. signal at 3.83 τ in the major product and the broad multiplet in the minor product (see Fig. 4). Such a mixture has been observed previously in the addition of tetrafluoroethylene to cyclopentadiene.[9]

(9) J. J. Drysdale, W. W. Gilbert, H. K. Sinclair, and W. H. Sharkey, *J. Am. Chem. Soc.*, **80**, 3672 (1958).

Discussion

These structural studies provide several further examples of the degree to which a two-step mechanism *via* a bifunctional intermediate is able to account for the products of 1,2-cycloaddition.[2] If indeed the first step is the establishment of a single carbon–carbon bond and two ends with some of the character of free radicals, this will, of course, account for the lack of any adduct with the reversed orientation IV, since it is known that a free radical is stabilized by chlorine substitution on the α-carbon atom more than by either hydrogen or fluorine. As one illustration from the chemistry of known free radicals, the concerted decomposition of *t*-butyl trichloroperacetate is 500 times as fast as that of *t*-butyl peracetate.[10] Under similar conditions, *t*-butyl trifluoroperacetate shows no such relative driving force toward production of the trifluoromethyl radical.

With respect to orientation in addition to the substituted butadienes the results are again well rationalized by the picture of a bifunctional intermediate. In the case of isoprene the two possibilities are XVI and XVII.

XVI

XVII
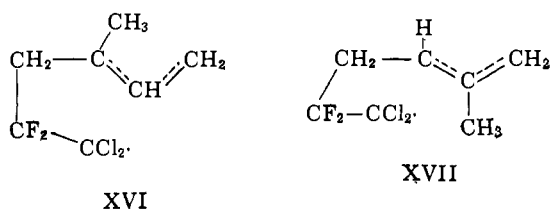
In one of these the methyl group contributes to the stability of the allylic radical by being substituted on one of the loci of the odd electron. In the other the methyl is on the central carbon of the allylic system and makes no such contribution. The preference for 1,2- over 3,4-addition to isoprene is thus predicted by the two-step mechanism. Something similar can be said for chloroprene in view of the radical-stabilizing character of a chlorine atom. The similarity in orienting effect of chlorine and methyl excludes an intermediate with any important amount of dipolar-ion character.

In the case of piperylene it is only in an addition to the terminal double bond that an intermediate radical can occur which the methyl group is in a position to stabilize. If this were the only factor involved, we might expect a mixture of isomers comparable in composition to that obtained from isoprene. However, it is general experience that free radical additions take place with much greater readiness at a terminal double bond than at one which is central in a carbon chain. Practically all the monomers which polymerize well by a free radical mechanism have terminal double bonds. This factor must be as important in *repressing nonterminal* addition to piperylene as is the radical stabilization by the methyl in promoting terminal addition.

The piperylene case illustrates a point which becomes of increased interest as consideration of the two-step mechanism becomes more literal. During addition to *cis*- and *trans*-piperylenes by a biradical mechanism the double bond in whose configuration the two starting materials differ becomes part of an allylic radical in the intermediate. Its configuration can be no more stable than the configuration of the allylic radical itself. Therefore, if a bifunctional intermediate actually occurs, the stereospecificity of cycloaddition to *cis*- and *trans*-piperylenes provides a new illustration of the stereochemical stability of allylic radicals which was observed by Walling and Thaler[11] in a free radical chlorin-

(10) P. D. Bartlett and R. R. Hiatt, *J. Am. Chem. Soc.*, **80**, 1398 (1958).
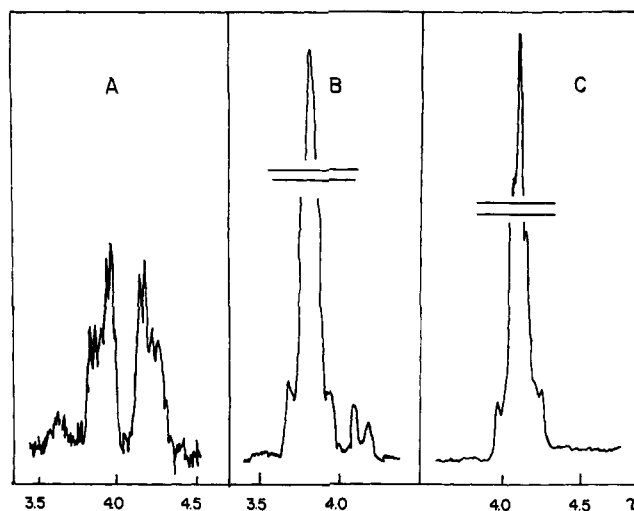(11) C. Walling and W. Thaler, *ibid.*, **83**, 3877 (1961).

Fig. 4.—60-Mc. n.m.r. spectra of 1,1-dichloro-2,2-difluoroethylene adducts in the unsaturation region: A, minor product from cyclopentadiene; B, major product from cyclopentadiene; C, 5-(hydroxymethyl)-norbornene.

ation reaction. This point will be further discussed in Part II where evidence is presented that the two-step mechanism should indeed be taken quite literally.

A suggestion has been made[2] concerning the unique ability of cyclopentadiene to yield both 1,2- and 1,4-addition products with fluorinated olefins. Roberts and Sharts suggest that any diene not constrained to the *cisoid* conformation is so predominantly *transoid* that, once the bifunctional intermediate is formed, the 4-position is too remote in space from the –CCl₂· function to be a likely point of ring closure. The concept of stereochemical stability of an allylic radical can be used to sharpen this viewpoint, for an allylic radical which is formed from a *transoid* diene now has frozen rotation about the C_2C_3 bond no less than about the C_3C_4 bond.[2] Any ring closure, then, which does not allow *cis* and *trans* piperylenes to become equivalent cannot allow 1,4-addition after initial attack upon a diene in the *transoid* conformation. It follows that 1,2-cycloaddition must be the rule in any two-step additions to conjugated dienes which are not constrained to a *cisoid* conformation.

Experimental

Microanalyses were by the Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.

1,1-Dichloro-2,2-difluoroethylene.—Technical grade material, b.p. 19–21°, from Peninsular Chem Research, Inc., Gainesville, Fla., was redistilled through a 4-ft. jacketed column packed with glass helices. The purified material, b.p. 18.9° (758 mm.), was stored at −25°, protected against atmospheric moisture. Various impurities, shown to be present in the crude material by vapor chromatography, were absent in the purified material.

The cycloaddition reactions of 1,3-dienes and 1,1-dichloro-2,2-difluoroethylene were carried out in ampoules prepared from heavy-walled Pyrex tubing. The isoprene, chloroprene, and 1,1-dichloro-2,2-difluoroethylene were freshly distilled. A Dry Ice–acetone mixture was used to cool the ampoules during sealing and opening. The reaction vessels were heated in an oil bath and were agitated by hand periodically.

The opened ampoules were connected to a cold trap and the low boiling materials were collected by distillation. The adducts were distilled through a 25 cm. semimicro column[12] (6 mm. i.d.). All v.p.c. analyses in this paper were best accomplished using diisodecyl phthalate columns (20% liquid phase on 60–80 mesh Chromosorb-P). Estimates of the percentage conversion of the 1,3-dienes to products were obtained by analysis of distilled mixtures. A very small but detectable amount of 1,1-dichloro-2,2-difluoroethylene dimer was formed in all the cycloadditions conducted. All other high-boiling products that were detected by v.p.c. are reported below for each specific diene.

(12) C. W. Gould, Jr., G. Holzmann, and C. Niemann, *Anal. Chem.*, **20**, 361 (1948).

A. Butadiene and 1,1-Dichloro-2,2-difluoroethylene.—In a 100-ml. ampoule were placed 13.5 g. (0.250 mole) of 1,3-butadiene (Matheson Co., Inc., instrument grade), 61.0 g. (0.459 mole) of 1,1-dichloro-2,2-difluoroethylene, b.p. 20° (762 mm.), and 0.200 g. (0.0045 mole) of hydroquinone. The resulting solution was heated at 82 ± 2° for 13.0 hr. About 26 g. of material boiling below 23° was collected. Distillation of the remaining products afforded 32.9 g., b.p. 144.5° (762 mm.), $n^{25.0}$D 1.4346 of butadiene adduct which appeared homogeneous with five different v.p.c. columns (diisodecyl phthalate, UCON LB 550-X, DC silicone Grease, 20 M Carbowax, Apiezon L).

Anal. Calcd. for $C_6H_6Cl_2F_2$: C, 38.53; H, 3.23; Cl, 37.91. Found: C, 39.03; H, 3.43; Cl, 38.46, 38.0,[13] 38.1.[13]

About 3.0 g. of distillation residue remained. The yield of adduct based on 77% conversion was 92%.

B. Isoprene and 1,1-Dichloro-2,2-difluoroethylene.—In a 100-ml. ampoule were placed 17.0 g. (0.250 mole) of isoprene, 101.3 g. (0.764 mole) of 1,1-dichloro-2,2-difluoroethylene, and 0.50 g. (0.0014 mole) of di-*n*-butylammonium picrate (m.p. 64–65°). The resulting solution was heated at 82 ± 2° for 14.1 hr. About 65 g. of 1,1-dichloro-2,2-difluoroethylene was recovered unreacted. Distillation gave 45.4 g. (95% yield based on 95% conversion) of isoprene adduct, b.p. 165° (764 mm.), $n^{25.0}$D 1.4430. The isoprene adduct appeared as a single peak using v.p.c. and employing a number of different columns. With care, however, this peak could be partially resolved into two peaks in the ratio of about 6:1 using an 8-ft. diisodecyl phthalate column, low column temperatures, and a high helium flow rate.

Anal. Calcd. for $C_7H_8Cl_2F_2$: C, 41.82; H, 4.01; Cl, 35.27; F, 18.90. Found: C, 42.13; H, 4.26; Cl, 34.87; F, 18.68.

A residue of 2.4 g. remained in the still pot.

C. Chloroprene and 1,1-Dichloro-2,2-difluoroethylene.—In a 125-ml. ampoule were placed 22.1 g. (0.250 mole) of chloroprene (50% du Pont chloroprene in toluene, stabilized with phenylthiazine) which had been distilled under nitrogen, b.p. 60° (758 mm.), 104.7 g. (0.788 mole) of 1,1-dichloro-2,2-difluoroethylene, and 0.50 g. (0.0014 mole) of di-*n*-butylammonium picrate (m.p. 64–65°). The resulting solution was heated at 82 ± 2° for 23.8 hr. About 70 g. of unreacted starting material was recovered. Distillation at reduced pressure afforded 46.8 g. (89% yield based on 95% conversion) of chloroprene adduct, b.p. 58° (10 mm.), b.p. 182° (760 mm.), n^{25}D 1.4634; v.p.c. analysis of the chloroprene adducts revealed three peaks whose areas were roughly in the ratio of 4.0:0.05:1.00 (order of elution from the diisodecyl phthalate column).

Anal. Calcd. for $C_6H_5Cl_3F_2$: Cl, 48.0. Found[13]: Cl, 48.4, 48.3.

A residue of 5.3 g. remained in the still pot.

Infrared Spectra of the Diene Adducts.—In order to assign frequencies to the weak carbon–hydrogen and carbon–carbon double bond stretching modes in the region 3100–1500 cm.$^{-1}$, measurements were made using 25% solutions (w./v.) of the adducts in carbon tetrachloride. Relative intensities as well as the frequency assignments for the rest of the spectra were obtained from the undiluted adducts using salt plates. All measurements were made with the Perkin–Elmer Model 21 infrared spectrometer. The frequencies are reported in cm.$^{-1}$: (w), weak, less than 10% absorption; (m) medium, 10–30% absorption; (s), strong, 30–80% absorption; (vs), over 80% absorption.

Butadiene adduct (homogeneous to v.p.c.): 3093 (w), 3020 sh, 2995 sh, 2970 (m), 1863 (w), 1646 (m), 1430 (s), 1290 (vs), 1232 (s), 1210 (vs), 1184 (m), 1134 (m), 1067 (w), 1057 (w), 1028 (w), 988 sh, 978 (vs), 939 (vs), 925 (vs), 910 sh, 836 (vs), 796 (s), 713 (w), 690 (s).

Isoprene adduct (two peaks by v.p.c. in the ratio of about 6:1): 3090 (w), 2975 (m), 2960 sh, 2885 sh, 1852 (w), 1645 (m), 1458 (m), 1430 (s), 1382 (m), 1292 (vs), 1220 (vs), 1184 (m), 1168 (m), 1146 (s), 1136 sh, 1091 (m), 1038 (m), 986 (vs), 970 sh, 941 sh, 925 (s), 882 (s), 869 (s), 841 (s), 824 (m), 788 (m), 782 sh, 723 (w), 670 (m).

Chloroprene adduct (three peaks by v.p.c. in the ratio of 9.8: 1.7:1): 3090 (w), 3024 (w), 2965 (m), 1889 (w), 1869 (w), 1670 (w), 1643 (m), 1409 (s), 1352 (m), 1298 (vs), 1230 (vs), 1169 (s), 1137 (s), 1097 (s), 1073 (m), 1062 (m), 1027 sh, 1014 (m), 998 sh, 982 (vs), 939 (vs), 914 (m), 893 (m), 857 (s), 843 sh, 832 (m), 813 (m), 776 (s), 757 (s), 713 (m).

Degradation Studies on the Cycloadduct of Butadiene and 1,1-Dichloro-2,2-difluoroethylene. A. Alkaline Permanganate Oxidation.—In a 1-l., three-necked Morton flask fitted with a mechanical stirrer, a pressure-equalizing dropping funnel, and a thermometer were placed 12.77 g. (0.0683 mole) of butadiene-1,1-dichloro-2,2-difluoroethylene adduct and 75 ml. of water. The reaction flask was cooled with an ice bath. A solution of 43.2 g. (0.273 mole) of potassium permanganate and 6.0 g. (0.150 mole) of sodium hydroxide in 600 ml. of water was added at a rate which kept the temperature of the reaction mixture at 15–20°. The

mixture was stirred for 23.6 hr. after the addition of the permanganate solution was completed. Excess permanganate was destroyed by adding sodium bisulfite. The manganese dioxide was removed by filtration and washed with ether and water. Continuous extraction of the aqueous filtrate with ether and the subsequent removal of the ether through an efficient distillation column yielded 5.58 g. of liquid, nonacidic oxidation products. A white solid crystallized from the liquid upon standing. Addition of pentane to the remaining liquid and cooling gave additional solid. A single recrystallization from pentane gave 4.22 g. of a white solid, m.p. mainly 130–140°. The solid gave a positive qualitative test[14] for 1,2-glycol. The pentane-soluble portion of the nonacidic reaction products, 1.02 g., possessed an infrared spectrum identical with that of the starting material. Acidification of the remaining reaction products with 6 M sulfuric acid and continuous extraction with pentane afforded 2.32 g. of 3,3-difluoro-2,2-dichlorocyclobutanecarboxylic acid, m.p. 65–68°. Recrystallization twice from pentane gave white crystals, m.p. mainly 67.8–68.8° (lit.[8a] m.p. 76.6–76.2°).

Anal. Calcd. for $C_5H_4O_2Cl_2F_2$: C, 29.29; H, 1.96; Cl, 34.59; neut. equiv., 205. Found: C, 29.87; H, 2.17; Cl, 34.61, 34.9,[13] 34.9[13]; neut. equiv., 205, 205.

A total of 3.42 g. of additional acidic products was obtained by continuously extracting with ether. A small fraction of this material, 0.104 g., presumably difluoromalonic acid, was insoluble in methylene chloride and melted quite sharply, m.p. 117–118° (lit.[15] m.p. 118°) without further purification.

Anal. Calcd. for $C_3H_2O_4F_2$: neut. equiv., 70.0. Found: neut. equiv., 70, 70.

Recrystallization of the remaining acid from methylene chloride–pentane gave 3.16 g. of 2,2-difluorosuccinic acid, m.p. 145.1–146.2° (lit.[16] m.p. 145–146°).

Anal. Calcd. for $C_4H_4O_4F_2$: neut. equiv., 77.0. Found: neut. equiv., 77, 76.

B. Stepwise Oxidation.—In a 100-ml., three-necked, round-bottomed flask fitted with a mechanical stirrer and a pressure-equalizing funnel were placed 10.04 g. (0.00536 mole) of butadiene-1,1-dichloro-2,2-difluoroethylene adduct and 35 ml. of 98% formic acid. About 6.0 ml. (0.058 mole) of 30% hydrogen peroxide (Superoxol) was added dropwise over a 10-min. period. The reaction mixture was stirred at 40–45° for about 30 hr. and became homogeneous after 24 hr. The formic acid was removed at reduced pressure through an efficient distillation column. About 20 ml. of ice-cold 30% sodium hydroxide solution was added to the residue and the resulting solution was stirred for 1.0 hr. Continuous extraction with ether gave 11.55 g. of a white, pasty solid.

To a solution of 11.55 g. of the above solid in 50 ml. of water was added 120 ml. (0.0054 mole) of 0.45 M periodic acid. Stirring was continued for 0.8 hr., the solution was neutralized with barium hydroxide, and the precipitated iodate and periodate salts were collected by filtration. The filtrate was continuously extracted with ether, the ether extract was dried over anhydrous sodium sulfate, and the ether was removed through an efficient distillation column. About 9.2 g. of liquid remained.

Silver oxide was prepared by adding a solution of 9.20 g. (0.0542 mole) of silver nitrate in 20 ml. of water to a solution of 4.30 g. (0.108 mole) of sodium hydroxide in 20 ml. of water. The aldehyde obtained above was dissolved in a minimum of water and added slowly to the silver oxide with stirring. The black silver suspension was removed by filtration. The filtrate was acidified and continuously extracted with ether. The ether extract was dried over anhydrous sodium sulfate. Removal of the ether left 7.06 g. of a brown oil. Attempts to obtain crystals from the oil were unsuccessful.

Anal. Found: Cl, 24.9, 25.0; neut. equiv., 178, 178.

C. Oxidation with Potassium Dichromate and Sulfuric Acid. —In a 500-ml. three-necked Morton flask fitted with a mechanical stirrer were placed 44.1 g. (0.150 mole) of potassium dichromate and 225 ml. of 6 M sulfuric acid. The butadiene–1,1-dichloro-2,2-difluoroethylene adduct (13.55 g., 0.0725 mole) was added to the solution, and the mixture was vigorously stirred for about 20 hr., then continuously extracted with ether giving 12.90 g. of a green solid. Dissolving the solid in base, acidifying, and extracting with ether once again removed the green color. The yield of the acid XIII was 9.64 g. (79%), m.p. 125.4–126.2°, after two recrystallizations from pentane–methylene chloride.

Anal. Calcd. for $C_5H_3O_2ClF_2$: Cl, 21.0; neut. equiv., 168.5. Found: Cl, 19.9, 21.2; neut. equiv., 169, 170.

(13) These analyses were obtained using the sodium biphenyl method of L. J. Liggett, *Anal. Chem.*, **26**, 748 (1954).

(14) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd Ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 115.

(15) R. N. Haszeldine, *J. Chem. Soc.*, 4302 (1955).

(16) M. S. Raasch, R. E. Miegel, and J. E. Castle, *J. Am. Chem. Soc.*, **81**, 2678 (1959); **82**, 6427 (1960).

The proton n.m.r. spectrum is uniquely consistent with the structure XIII.[8b]

D. Decarboxylation of Sodium 3,3-Difluoro-2,2-dichlorocyclo-butanecarboxylate.—In a 20 ml., round-bottomed flask was placed 1.103 g. (0.00548 mole) of 3,3-difluoro-2,2-dichlorocyclobutanecarboxylic acid. The acid was dissolved in water, 1 drop of 1% phenolphthalein solution was added, and the acid was neutralized with 40% sodium hydroxide solution. The solution was evaporated to dryness at reduced pressure. The flask was fitted with a microdistillation head and immersed in an oil bath at 200°. The reaction was conducted at reduced pressure (25 mm.). A liquid (0.369 g.) distilled from the flask, b.p. about 80° (760 mm.). The quantity of chloride ion liberated during the reaction was determined by the Volhard procedure (0.00594 mole, 92%).

A second trial was conducted following essentially the same procedure but starting with 0.943 g. (0.00460 mole) of 3,3-difluoro-2,2-dichlorocyclobutanecarboxylic acid. No liquid distilled, but 0.00561 equivalent (122%) of chloride ion was liberated. A significant change in procedure may have been that the salt solution was warmed while evaporating to dryness.

In a 50-ml. erlenmeyer flask were placed 0.185 g. (0.00149 mole) of the 2-chloro-3,3-difluorocyclobutene from the previous decarboxylation, 5 ml. of water, and a magnetic stirring bar. The flask was cooled in an ice bath, and a solution of 0.940 g. (0.00595 mole) of potassium permanganate and 0.125 g. (0.00313 mole) of sodium hydroxide in 15 ml. of water was added dropwise, the reaction temperature being maintained at 15–20°. The reaction was stirred at room temperature for 19.3 hr., excess permanganate was removed by adding sodium bisulfite, and the manganese dioxide was separated by filtration. Continuous extraction with ether yielded a negligible quantity of nonacidic reaction products. Acidification of the filtrate and continuous extraction gave 0.165 g. (72%) of 2,2-difluorosuccinic acid, m.p. 140–145° (lit.[16] 145–146°) which was identified by comparison of its infrared spectrum with that of an authentic sample.

Alkaline Permanganate Oxidation of the Cycloadducts of Isoprene and 1,1-Dichloro-2,2-difluoroethylene.—In 1-l., three-necked Morton flask fitted with a mechanical stirrer, a pressure-equalizing dropping funnel, and a thermometer were placed 12.52 g. (0.0625 mole) of the isoprene–1,1-dichloro-2,2-difluoroethylene adducts and 75 ml. of water. The reaction flask was cooled in an ice bath. A solution of 71.3 g. (0.261 mole) of potassium permanganate and 6.0 g. (0.150 mole) of sodium hydroxide in 600 ml. of water was added at a rate which kept the temperature of the reaction mixture at 15–20°. The reaction was stirred 21.1 hr. after the addition of the permanganate was completed. Excess permanganate was destroyed by adding sodium bisulfite. The manganese dioxide was removed by filtration and washed with ether and water. Continuous extraction of the aqueous filtrate with ether and the subsequent removal of the ether through an efficient distillation column yielded 2.62 g. of a brown oil. The oil was only slightly soluble in pentane and gave a positive qualitative test for a 1,2-glycol. The aqueous solution was acidified with 6 M sulfuric acid and continuously extracted with pentane. A slightly discolored white solid, 7.65 g., was obtained from the pentane extract. Several recrystallizations from pentane and pentane–methylene chloride gave 6.82 g. (50%) of 3,3-difluoro-2,2-dichloro-1-methylcyclobutanecarboxylic acid, m.p. 130.2–130.8° (lit.[8a] m.p. 129.8–130.4°).

Anal. Calcd. for $C_6H_6O_2Cl_2F_2$: Cl, 32.4; neut. equiv., 219. Found: Cl, 32.6,[13] 32.7[13]; neut. equiv., 219, 219.5.

Additional extraction of the oxidation solution with ether gave 2.24 g. of acidic products.

Alkaline Permanganate Oxidation of the Cycloadducts of Chloroprene and 1,1-Dichloro-2,2-difluoroethylene.—In a 1-l., three-necked Morton flask fitted with a mechanical stirrer, a pressure-equalizing dropping funnel, and a thermometer were placed 16.44 g. (0.0738 mole) of chloroprene–1,1-dichloro-2,2-difluoroethylene adducts and 75 ml. of water. The reaction flask was cooled in an ice bath. A solution of 46.6 g. (0.295 mole) of potassium permanganate and 6.0 g. (0.150 mole) of sodium hydroxide in 650 ml. of water was added at a rate which kept the temperature of the reaction mixture at 15–20°. The reaction was stirred for 30.6 hr. after the addition of the permanganate was completed. Unreacted permanganate was converted to manganese dioxide using sodium bisulfite. The manganese dioxide was removed by filtration and washed with ether and water. Continuous extraction of the aqueous filtrate with ether and the subsequent removal of the ether through an efficient distillation column yielded 4.70 g. of an oil which gave a positive qualitative test for a 1,2-glycol. No starting material was recovered. The aqueous solution was acidified with 6 M sulfuric acid and continuously extracted with pentane. A low-melting solid, 5.56 g., was obtained from the pentane extract. Fractional crystallizations from pentane and pentane–methylene chloride gave 3.96 g. (28%) of 3,3-difluoro-1,2,2-trichlorocyclobutanecarboxylic acid, m.p. 125.6–126.6° (lit.[8a] m.p. 124.5–125.8°), and 0.412 g. (2.7%) of 3,3-difluoro-2,2-dichlorocyclobutanecarboxylic acid, m.p. 66–68°.

Anal. Calcd. for $C_5H_3O_2Cl_3F_2$: Cl, 44.4; neut. equiv., 239. Found: Cl, 43.9,[13] 43.9[13]; neut. equiv., 239. Calcd. for $C_5H_4O_2$-Cl_2F_2: Cl, 34.6; neut. equiv., 205. Found: Cl, 34.9,[13] 35.1[13]; neut. equiv., 207, 207.

A total of 1.68 g. of additional acidic products was obtained by continuously extracting the solution of oxidation products with ether. Several recrystallizations from pentane–methylene chloride gave 0.912 g. (8.0%) of 2,2-difluorosuccinic acid, m.p. 144.8–146.2° (lit. m.p. 145–146°).

Anal. Calcd. for $C_4H_4O_4F_2$: neut. equiv., 77.0. Found: neut. equiv., 77.

trans-1,3-Pentadiene (*trans*-piperylene) was prepared from a mixture of the *cis* and *trans* isomers *via* the 1,3-pentadiene–sulfur dioxide adduct.[1b] The mixture of diene isomers used for the preparation was obtained in about 99.7% purity by fractional distillation of commercial 1,3-pentadiene through a 98 cm. (1.0 cm. i.d.) Heli-Pak (1.3 × 2.5 × 2.3 mm.) column.

In a glass-lined, stainless-steel bomb were placed 119 g. (1.75 moles) of 1,3-pentadiene, 5.0 g. of di-*n*-butylammonium picrate, and 170 g. (2.68 moles) of sulfur dioxide. The reactants were heated at 75–85° for 6.8 hr., yielding 190.5 g. of crude sulfone.

In a number of experiments, 85–93% of the crude sulfone decomposed below 150° to yield *trans*-1,3-pentadiene. In a typical experiment 30.82 g. (0.233 mole) of crude sulfone decomposed leaving 3.17 g. of residue (90% decomposition). Sulfur dioxide was removed from the *trans*-1,3-pentadiene by washing with ice water. Distillation gave 8.12 g. (51%) of *trans*-1,3-pentadiene, b.p. 42°, $n^{20}D$ 1.4298 (lit.[18] b.p. 41.7 (745 mm.), $n^{20}D$ 1.4300).

cis-1,3-Pentadiene.—To 50 g. (0.51 mole) of maleic anhydride in 25 ml. of acetone was added 21.00 g. (0.309 mole) of a mixture of *cis*- and *trans*- 1,3-pentadiene (60:40). The temperature of the reactants rose to about 55°, then slowly dropped to room temperature. The mixture was stirred overnight and 100 ml. of water was added. Those products that were volatile with steam were collected. The nonaqueous portion of the steam distillate was washed several times with water, dried over anhydrous calcium chloride, and distilled. *cis*-1,3-Pentadiene (11.48 g., 91%) was obtained, b.p. 44°, $n^{20}D$ 1.4358 (lit.[18] b.p. 43.8° (750 mm.), $n^{20}D$ 1.4360). The *trans*-piperlyene–maleic anhydride adduct was isolated as the diacid (16.79 g., 76%, m.p. 154–156°).

Reaction of *trans*-1,3-Pentadiene and 1,1-Dichloro-2,2-difluoroethylene.—In a glass ampoule were placed 8.38 g. (0.123 mole) of *trans*-1,3-pentadiene, 54.0 g. (0.446 mole) of 1,1-dichloro-2,2-difluoroethylene, and 0.10 g. of di-*n*-butylammonium picrate. The ampoule was heated at 77 ± 2° for 19.0 hr. Distillation through a semimicro column[11] gave 15.74 g. (64%) of a single 1:1 cycloadduct, 1,1-difluoro-2,2-dichloro-3-*trans*-propenylcyclobutane, b.p. 64–68° (40 mm.).

Anal. Calcd. for $C_7H_8Cl_2F_2$: C, 41.82; H, 4.01; Cl, 35.27; F, 18.90. Found: C, 42.18; H, 4.11; Cl, 34.83; F, 18.74.

The n.m.r. spectrum of the adduct is shown in Fig. 2; v.p.c. analysis showed that none of the isomeric *cis*-propenyl adduct was present.

Reaction of *cis*-1,3-Pentadiene and 1,1-Dichloro-2,2-difluoroethylene.—In a glass ampoule were placed 10.80 g. (0.159 mole) of *cis*-1,3-pentadiene, 54.0 g. (0.446 mole) of 1,1-dichloro-2,2-difluoroethylene, and 0.10 g. of di-*n*-butylammonium picrate. The ampoule was heated at 88 ± 2° for 19.0 hr. Distillation through a semimicro column gave about 18 g. (some mechanical loss, 56%) of a single 1:1 cycloadduct, 1,1-difluoro-2,2-dichloro-3-*cis*-propenylcyclobutane, b.p. 91° (55 mm.).

Anal. Calcd. for $C_7H_8Cl_2F_2$: C, 41.82; H, 4.01; Cl, 35.27; F, 18.90. Found: C, 42.20; H, 4.16; Cl, 35.04; F, 18.87.

The n.m.r. spectrum of the adduct is shown in Fig. 3; v.p.c. analysis showed that none of the isomeric *trans*-propenyl adduct was present.

Cyclopentadiene was prepared by thermally cracking dicyclopentadiene. Freshly distilled 1,3-cyclopentadiene, b.p. 42°, $n^{24.8}D$ 1.4419, was used for the preparation of the 1,1-difluoro-2,2-dichloroethylene cycloadducts.

Reaction of Cyclopentadiene and 1,1-Dichloro-2,2-difluoroethylene.—Cyclopentadiene (8.05 g., 0.122 mole) and 65 g. (0.49 mole) of 1,1-dichloro-2,2-difluoroethylene were heated at 80.05° for 20.0 hr. Distillation afforded 9.06 g. of material, b.p. 98–100° (85 mm.), which was shown by v.p.c. analysis (8-ft. tris-cyanoethoxypropane column at 170°) to be composed of three components in the approximate percentages of 47, 9, and 44%. The three components were isolated using v.p.c., and their infrared and n.m.r. spectra were recorded. *endo*-Dicyclopentadiene was identified as the compound comprising 47% of the mixture. The 9 and 44% components have been assigned 1:1 cycloadduct structures, the former possessing a bicyclo[3.2.0]-2-heptene ring system and the latter, a solid of m.p. 91–92.5° (sealed tube), the structure of the Diels–Alder adduct. This structure was assigned on the basis of the similarity of its n.m.r. and infrared spectra to those of related compounds (*endo*- and *exo*-dicyclopent-

(17) D. Craig, *J. Am. Chem. Soc.*, **65**, 1006 (1943).

adiene, norbornene). The n.m.r. spectrum consisted of a sharp signal at τ 3.84 (relative area 1.0) and a complex absorption extending from τ 6.2 to 8.3 (relative area 2.6). The relatively poor integration is reasonably attributed to a contaminant. The most revealing feature of the spectrum was the sharp signal at τ 3.84, which is also observed in all the model compounds of norbornene structure. The n.m.r. spectrum of the other cycloadduct consisted of a complex multiplet centered at τ 4.05 (relative area 1.0), which had the distinct appearance of an AB spin–spin system, and

complex absorptions at τ 6.3 (relative area 1.0) and 7.3 (relative area 1.0). Figure 4 shows the characteristic absorptions of the two products in the unsaturation region, compared to a model norbornene derivative.

Cycloaddition. II. Evidence of a Biradical Intermediate in the Thermal Addition of 1,1-Dichloro-2,2-difluoroethylene to the Geometrical Isomers of 2,4-Hexadiene[1]

BY LAWRENCE K. MONTGOMERY, KATHLEEN SCHUELLER, AND PAUL D. BARTLETT

Under conditions where the geometrical isomers of 2,4-hexadiene, as well as their 1,2-adducts with 1,1-dichloro-2,2-difluoroethylene, undergo no stereoisomerization, the *cis–cis*-diene yields two isomeric adducts, the *trans–trans*-diene yields another two adducts, and the *cis–trans*-diene yields a mixture of all four. It is shown that each addition to a *cis* or *trans* double bond is accompanied by stereochemical isomerization at the site of the addition so as to approach, but not attain, a cyclobutane mixture 82% *trans* and 18% *cis* at the ring at 80°. This nonstereospecific addition shows that the reaction proceeds by way of a bifunctional intermediate. From the quantitative product compositions it is calculated that the internal rotation of this intermediate from a "*cis*" to a "*trans*" conformation occurs 10 times as fast as its ring closure to cyclic product. Since the rate constant for the rotation is estimated to be of the order of 10^{11} sec.$^{-1}$, it follows that the half-life of the bifunctional intermediate is of the order of 10^{-10} sec.

Introduction

Several facts established in part I of this series[2] lend special interest to the cycloaddition of fluorinated olefins to the geometrical isomers of 2,4-hexadiene. First, the general effects of methyl groups and chlorine atoms as substituents in butadiene appear to be uniquely consistent with a two-step addition mechanism by way of a "biradical" intermediate (as opposed to a dipolar ion or a charge-transfer complex). Second, the retention of configuration during addition to *cis*- and *trans*-piperylenes to yield *cis*- and *trans*-propenylcyclobutanes indicated that, if an allylic radical is formed during the addition sequence, it retains its configuration, and the same would be expected to be true of the nonparticipating double bond in the case of 2,4-hexadiene. Third, none of the dienes investigated in part I afforded a test of one of the most obvious possibilities of a "biradical" mechanism, namely, the loss of configuration at the participating double bond through free rotation in the bifunctional intermediate. There is much evidence that cycloaddition of the Diels–Alder type proceeds with complete retention of configuration at the participating double bonds and often with a very striking degree of preference between the *endo* and *exo* configurations in the product.[3]

Similar observations of complete retention of configuration have been made in 1,2-cycloadditions involving reactants which are active dienophiles in Diels–Alder reactions. Thus, in the addition of *cis*- and *trans*-2,3-dicyanohexafluoro-2-butene to the geometrical isomers of propyl propenyl ether, there is complete retention of configuration in both reactants.[4] With reactants of this type in solution, however, there is very little evidence of biradical character in the addition reactions, whether they be of the 1,2- or the 1,4-type, since ionizing power of the solvent is important.[5a,b] The nondienophile

character of 1,1-dichloro-2,2-difluoroethylene ("1122"), observed in part I in its addition to monosubstituted butadienes continues to be emphasized in its reaction with the three geometrical isomers of 2,4-hexadiene.

Isomeric Composition of 2,4-Hexadiene.—2,4-Hexadiene as supplied,[6] was shown by vapor phase chromatography (using an F & M Model 300 instrument with an 8-ft. column packed with β,β'-oxydipropionitrile on 60–80 mesh Chromosorb-P) to be a mixture of three isomers present to the extent of 56.1, 37.8, and 6.0% in the order of their elution. Subsequent evidence is consistent only with the normal assignment of *trans–trans*, *trans–cis*, and *cis–cis* configurations in the order named. It was found that the first and principal component could be fully removed from the mixture by the reaction with excess maleic anhydride at room temperature for 14 hr. The resulting mixture gave just two peaks on vapor chromatography and consisted of 85.8% of the *trans–cis* and 14.2% of the *cis–cis* isomer. When the more powerful dienophile, tetracyanoethylene (TCNE), was allowed to react with the three-component mixture of 2,4-hexadiene isomers at 40° for 22.3 hr., the recovered diene consisted of the *cis–cis* isomer (with the longest retention time) in a purity of 97% and free from its geometrical isomers. Irradiation of a dilute ethanol solution of the three-component mixture with a Hanovia mercury lamp using a Pyrex filter and benzophenone as sensitizer gave a mixture in 85% recovery which now showed 29.6% *trans–trans*, 46.3% *trans–cis*, and 24.1% *cis–cis*. Pure *trans–trans*- and *trans–cis*-2,4-hexadienes were prepared by preparative vapor phase chromatography (Beckman Megachrom using a single 24-ft. stainless steel column packed with tricyanoethoxypropane on 45–60 mesh Chromosorb-P). This procedure easily separated the *trans–trans* isomer from the others, but the pure *trans–cis* was obtained only by a series of careful fraction cuttings on small samples in which the *cis–cis* came out as a shoulder on the *trans–cis* peak. The first two isomers were thus obtained in a purity greater than 99%. The *cis–cis* isomer was freed from the others by means of tetracyanoethylene.

(1) Presented at the National Organic Symposium, Columbus, Ohio, June 18, 1963.

(2) P. D. Bartlett, L. K. Montgomery, and B. Seidel, *J. Am. Chem. Soc.*, **86**, 616 (1964).

(3) K. Alder and M. Schumacher in "Fortschritte der Chemie Organischer Naturstoffe," Vol. X, L. Zechmeister, Ed., Springer Verlag, Vienna, 1953.

(4) S. Proskow, private communication. Compare S. Proskow, H. E. Simmons, and J. L. Cairns, *J. Am. Chem. Soc.*, **85**, 2341 (1963).

(5) (a) C. A. Stewart, Jr., *ibid.*, **84**, 117 (1962); (b) J. A. Berson, Z. Hamlet, and W. A. Mueller, *ibid.*, **84**, 297 (1962).

(6) Donated by the du Pont Co. through the kindness of Dr. Clare Stewart.