

# Organic and Biological Chemistry

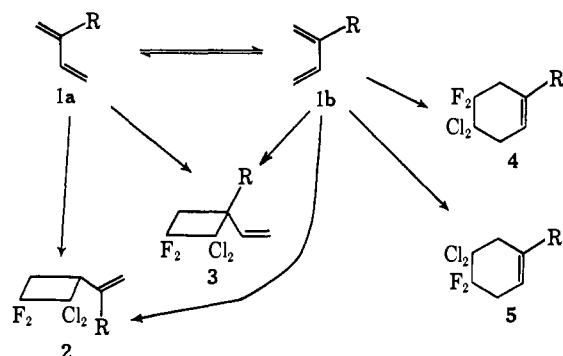
## Cycloaddition. VII. Competitive 1,2 and 1,4 Addition to *cis*-Fixed Cyclic Dienes

Paul D. Bartlett, Alan S. Wingrove, and Raymond Owyang

Contribution from the Converse Memorial Laboratory of Harvard University, Cambridge, Massachusetts 02138. Received April 18, 1968

**Abstract:** 1,1-Dichloro-2,2-difluoroethylene (1122) has been added thermally to 1,2-dimethylenecyclobutane, 1,2-dimethylenecyclopentane, and 1,2-dimethylenecyclohexane. The ratios of 1,2 to 1,4 addition products are >99, 2.3, and 0.78, respectively. The known *cis*-fixed conjugated dienes, including cyclopentadiene, show product ratios varying by a factor of 500. A significant variable in this series is the interatomic distance between the ends of the conjugated system, which affects the ease of 1,4 addition whether by a stepwise or by a concerted mechanism.

It was reported recently<sup>1,2</sup> that the well-known 1,2-cycloaddition to acyclic dienes by 1,1-dichloro-2,2-difluoroethylene ("1122") is accompanied in certain cases by substantial amounts of 1,4 addition as well. Thus as the group R is increased in bulk from hydrogen to *t*-butyl, the fraction of 1,4 addition rises from less than 1 to 44%.



In view of previous demonstrations<sup>3</sup> of a stepwise mechanism in the addition of 1122 to dienes, these results were explained<sup>1,2</sup> in terms of the conformational populations of transoid (1a) and cisoid (1b) dienes. By the biradical mechanism, 1a can lead only to 1,2 addition product (2 or 3)<sup>4,5</sup> while 1b can produce any of the four cycloadducts 2–5.

Comparison of the cycloadduct composition over a range of temperature with thermodynamic estimates of the cisoid population suggested<sup>2</sup> that unsubstituted cisoid butadiene must lead to 1,4 and 1,2 cycloadducts in the ratio of about 1 to 6.<sup>6a</sup> In previously known

(1) Part V: P. D. Bartlett, G. E. H. Wallbillich, A. S. Wingrove, J. S. Swenton, L. K. Montgomery, and B. D. Kramer, *J. Amer. Chem. Soc.*, **90**, 2049 (1968).

(2) Part VI: J. S. Swenton and P. D. Bartlett, *ibid.*, **90**, 2056 (1968).

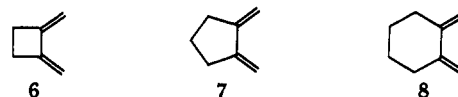
(3) L. K. Montgomery, K. E. Schueller, and P. D. Bartlett, *ibid.*, **86**, 626 (1964).

(4) J. D. Roberts and C. M. Sharts, *Org. Reactions*, **12**, 12 (1962).

(5) C. Walling and W. Thaler, *J. Amer. Chem. Soc.*, **83**, 3877 (1961).

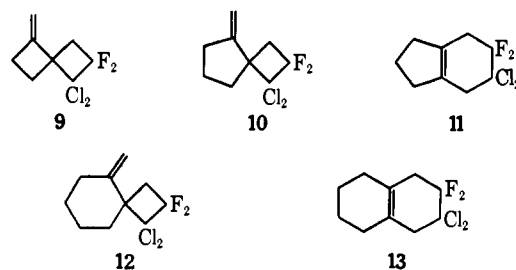
(6) (a) The idea that every butadiene molecule is cisoid or transoid, at best an oversimplification, breaks down completely whenever the steric energy minimum in the skew conformation is deeper than the electronic energy minimum produced by 2,3  $\pi$  overlap in the planar form. Mechanistically, a skew diene may lead to either a *cis* or a *trans* allylic biradical and thus to 1,2 or 1,4 addition just as a cisoid diene can. Recent nmr evidence makes it probable that "cisoid" in the

cases cyclopentadiene and cyclohexadiene, both 100% cisoid, had been found to give (1,2)/(1,4) product ratios of 0.19<sup>6b</sup> and 15.5,<sup>7</sup> respectively. For further understanding of the dependence of this ratio upon structure we have now examined three more cyclic dienes in which the conjugated systems have a permanently cisoid geometry, namely, 1,2-dimethylenecyclobutane (6), 1,2-dimethylenecyclopentane (7), and 1,2-dimethylenecyclohexane (8).



### Results






The dienes were prepared by known methods—6 by dimerization of allene, 7 by the Hofmann method from the appropriate bisquaternary ammonium salt and also, more conveniently, by the Cope method from the bisamine oxide, and 8 by pyrolysis of the diacetate. The cycloadditions were carried out in sealed tubes for 36 hr at 80°. The products were analyzed and isolated by vapor phase chromatography and identified by high-resolution mass spectrometric molecular weights and ir and nmr spectra. Whereas only the 1,2 addition product 9 was identified in the reaction of 6, both 7 and 8 gave mixtures of 1,2 and 1,4 addition products (7 → 10 + 11, 8 → 12 + 13).



discussions of parts V and VI should be largely replaced by "skew" [A. A. Bothner-By and D. Jung, *ibid.*, **90**, 2342 (1968); A. A. Bothner-By and D. F. Koster, *ibid.*, **90**, 2351 (1968)]. (b) P. D. Bartlett, L. K. Montgomery, and B. Seidel, *ibid.*, **86**, 618 (1964).

(7) P. D. Bartlett, G. E. H. Wallbillich, and L. K. Montgomery, *J. Org. Chem.*, **32**, 1290 (1967).

**Table I.** Mode of Cycloaddition of 1,1-Dichloro-2,2-difluoroethylene to *cis*-Fixed Planar Conjugated Dienes at 80°

	Diene	Product compn		Ratio (1,2)/(1,4)
		% 1,2	% 1,4	
6		>99	<1	>99
7		70	30	2.3
8		44	56	0.8
14		16	84	0.19
15		94	6	15.7

**Table II.** Nmr Summary

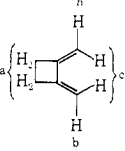
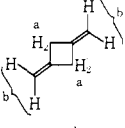
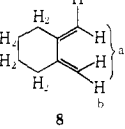
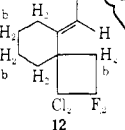
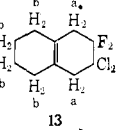
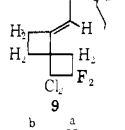
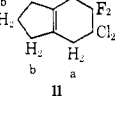
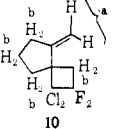
		$\delta$
	6	a, 2.55 (4 H) unresolved multiplet b, 4.60 (2 H) singlet c, 5.08 (2 H) singlet
	7	a, 3.25 (4 H) complex multiplet b, 4.84 (4 H) complex multiplet Typical A <sub>4</sub> B <sub>4</sub> spectra
	8	a, 4.55 (2 H) multiplet b, 4.83 (2 H) multiplet Ring protons: broad singlet at 2.20 and a multiplet at 1.58 (8 H)
	12	a, singlets at 4.68 and 5.01 (2 H) b, broad, unresolved multiplet between 1 and 3.3 (10 H)
	13	a, broad singlets at 2.40, 2.65, and 2.95 (relative intensities 1:2:5) (4 H) b, broad unresolved multiplet between 1.4 and 2.25 (8 H)
	9	a, unresolved multiplet at 5.1 (2 H) All ring protons: complex multiplet appearing between 1.7 and 3.2 (6 H)
	11	a, Three broad singlets at 3.06, 2.74, and 2.5 Integration was not possible because of overlap of b protons with the 2.5 peak. However, the spacing between these peaks corresponds exactly with that in 13 (above), and it seems clear that both compounds have the same general type of structure b, broad, unresolved multiplet between 1.5 and 2.5 Integration not possible due to overlap with other peaks. Spectra show great resemblance with spectra of 13
	10	a, doublet of triplets at 5.02 and 5.11 (2 H) b, complex system of peaks between 1.15 and 3.2 (8.5 H)

Table I summarizes the cross-cycloadducts for **6**, **7**, and **8** as well as for cyclopentadiene and cyclohexadiene,

which have been examined before.<sup>6,7</sup> Table II summarizes the nmr spectra of the dienes and cycloadducts, which afford definitive evidence of their structure.

## Discussion

It is clear at once from Table I that *cis* coplanar geometry does not by itself determine the ratio of 1,2 and 1,4 addition of 1122. The extreme cases of dimethylenecyclobutane and cyclopentadiene, whose product ratios differ by a factor of 500, probably both have energy minima at the *cis* coplanar conformation. Therefore, some property of the diene system other than its mere *cis* coplanarity is important in determining the (1,2)/(1,4) product ratio.

The mechanism of 1,2 cycloaddition of fluorinated olefins to conjugated systems is relatively well understood, and is simplified by the fact that *concerted* 1,2 thermal cycloaddition is forbidden by orbital symmetry considerations.<sup>8</sup> It is obvious that the reagents which afford stepwise 1,2 cycloaddition by way of biradicals are among the inherently poor dienophiles for the Diels–Alder reaction, otherwise the latter reaction would compete with the stepwise process leading to some 1,4 addition. However weak the dienophile, *cis* geometry in the diene can cause the biradical mechanism to branch and lead to a mixture of 1,2 and 1,4 cycloaddition products. But it is not easy to find a general criterion by which to establish, in a particular case, whether the 1,4 addition observed arises entirely by the biradical mechanism involving *cis* intermediates, or whether some or all of it is now the result of *concerted* addition competing with the stepwise.

In the present case we have a series of *cis*-fixed dienes which differ greatly in their predisposition to 1,2 and 1,4 addition, evidently through some property other than their *cis* coplanar geometry.

A property which obviously varies rapidly in the dimethylene-cycloalkane series is the interatomic distance between the ends of the conjugated system, which is estimated as 3.35 Å in **6**, 3.04 Å in **7**, and potentially slightly less in **8**. It also happens that cyclopentadiene, with the highest proportion of 1,4 adduct, has the shortest interterminal distance (~2.44 Å) by a substantial amount.

In the *concerted* 1,4 addition new bonds must be formed by overlap of orbitals on the dienophile, initially 1.34 Å apart, with those at the termini of the diene, at distances from 2.44 to 3.35 Å. Since the Diels–Alder reaction is mildly exothermic (commonly by about 20 kcal),<sup>9</sup> the transition state will involve deformations to bring the geometry intermediate between that of the starting materials and the addition product. A short interterminal distance in the diene is therefore favorable to the *concerted* mechanism of 1,4 cycloaddition, as is in-plane deformability in the diene.

In stepwise 1,4 cycloaddition the product-determining step is the exothermic (by about 50 kcal) combination of the two ends of the biradical intermediate, a type of reaction in which the geometry of the transition state should be relatively close to that of the reactant. By this mechanism also, then, we conclude

(8) R. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.*, **87**, 2046 (1965).

(9) A. Wassermann, "Diels–Alder Reactions," Elsevier Publishing Co., Amsterdam, 1965, p 42.

that a short distance between the ends of the conjugated system should be favorable to 1,4 ring closure, without its having much effect on the ease of 1,2 ring closure.

One other factor which changes significantly in the series of *cis*-fixed dienes is the favorableness of location of the double bond in the 1,2 and 1,4 products, this consideration shifting in favor of the 1,4 product as we go from **6** to **8**. For several reasons this does not appear likely to be a dominant factor. First, the effects are comparatively small. Second, they appear only in the products, and are not likely to reach their full magnitude in the transition states for exothermic reactions. Third, these factors either cancel out in cyclopentadiene and cyclohexadiene, or are actually reversed: despite the strained location of the double bond in norbornene, cyclopentadiene is predisposed to 1,4-cycloaddition compared to cyclohexadiene.

Since the structural factors discussed above seem to apply equally well to 1,4 cycloaddition by any mechanism, it is of interest that the relative rate constants of the Diels-Alder reaction with maleic anhydride for **15**, **8**, and **14** are 1, 57, and 700, respectively,<sup>10</sup> as the relative amount of 1,4 adduct increases. The Diels-Alder reaction is thus somewhat more sensitive, by a factor of 8.5, to the diene structure than is the (1,2)/(1,4) ratio with 1122. The increased differentiation of dienes when an active dienophile is used compared to a less active one is a general characteristic of the Diels-Alder reaction.

In forthcoming papers of this series we shall describe some cases in which identification of the mechanisms of cycloaddition can be achieved.

## Experimental Section

**Proton nmr spectra** were taken with a Varian Associates A-60 analytical nmr spectrometer with a sweep time of 500 sec. Tetramethylsilane was used as an internal standard ( $\delta$  0.00 ppm).

Elementary analyses were performed by Schwarzkopf Micro-analytical Laboratories, Woodside, N. Y. High-resolution molecular weights were determined by Mr. Michael Block on an Associated Electrical Industries Model MS-9 mass spectrometer.

**Acetate and benzoate pyrolyses** were done by passing the substrate through a 1  $\times$  30 cm column (Pyrex) containing 0.5-in. fire-polished pieces of 7-mm glass tubing. Nitrogen gas was used to flush the tube before and during the pyrolysis, and the column was heated with an electric heater.

**Analytical vapor phase chromatography** was done on an F & M Model 300 instrument and occasionally on an F & M Model 609 flame ionization instrument. Preparative vapor phase chromatography was done on a Wilkens Model A 700 Autoprep equipped with columns which are  $\frac{3}{8}$  in. in diameter and 20 ft long and containing 20% by weight of the liquid phase on 60-80 mesh Chromosorb P.

**1,2-Dimethylenecyclobutane (I).**<sup>11</sup> Allene gas (Matheson) was dimerized as follows. A 1  $\times$  30 cm Pyrex tube was filled with  $\frac{1}{8}$  in. i.d. glass helices and was electrically heated to 450°. Allene gas (454 g) was diluted with nitrogen (two volumes of allene to one volume of nitrogen) and passed through the tube at the rate of 75 g/hr. The gases were collected in a Dry Ice-acetone trap, and the unconverted allene was allowed to distill at room temperature through a Vigreux column. The dark residue remaining (90.3 g) was distilled at atmospheric pressure to give 10.3 g of colorless liquid, bp 74-75°. The 80-g sample of dark residue which remained was not volatile up to 180° (pot temperature) and was not kept.

The volatile liquid was analyzed by vpc (with a 0.25 in.  $\times$  6 ft column of 20%  $\gamma$ -methyl- $\gamma$ -nitropimelonitrile on 60-80 mesh Chromosorb P (column 35°, injector 125°, 100 cc of helium/min), and it was found that the dimer mixture contained 27% 1,3-di-

methylenecyclobutane and 73% 1,2-dimethylenecyclobutane (lit.<sup>11</sup> 15:85, respectively). The former had a retention time of 4 min and the latter 7 min under these conditions.

The two dimers were separated by preparative vapor phase chromatography by means of a 20 ft  $\times$   $\frac{3}{8}$  in. column of 20%  $\gamma$ -methyl- $\gamma$ -nitropimelonitrile on 60-80 mesh Chromosorb P (column 35°, injector 125°, detector 150°, flow rate 75 cc of helium/min). The 1,3 isomer had a retention time of 25 min, and the 1,2 isomer was obtained after 40 min. A total of 4.6 g of 1,2-dimethylenecyclobutane was obtained, and 1.5 g of the 1,3 isomer was collected. Each component was shown to be homogeneous on analytical vpc. The nmr spectra of these compounds are reported in Table II.

**Preparation of Materials.** Diethyl  $\alpha,\alpha'$ -dibromopimelate was prepared according to the procedures described by Guha and Sankaran<sup>12</sup> for the conversion of adipic acid to diethyl  $\alpha,\alpha'$ -dibromoadipate. The product was obtained in 95% yield as a pale yellow liquid; bp 164-169° (1.2 mm);  $n^{25}_D$  1.4870 (lit.<sup>13</sup> bp 171-178 (5 mm),  $n^{25}_D$  1.4880).

**Diethyl 1-cyano-1,2-cyclopentanedicarboxylate** was prepared as previously described by Fuson and Cole.<sup>13</sup> The product was obtained in 83% yield as a nearly colorless liquid: bp 126-129° (2 mm),  $n^{25}_D$  1.4540 (lit.<sup>13</sup> bp 126-128° (2 mm),  $n^{25}_D$  1.4560).

**trans-1,2-Cyclopentanedicarboxylic acid** was prepared as previously described by Fuson and coworkers.<sup>14</sup> The *trans*-diacid was obtained in 93% yield as a colorless crystalline solid, mp 161-162° (lit.<sup>14</sup> mp 161°).

**Diethyl trans-1,2-cyclopentanedicarboxylate** was prepared by the procedure described by Mićović.<sup>15</sup> The product was obtained in 96% yield as a colorless liquid: bp 131-132° (16 mm);  $n^{25}_D$  1.4420 (lit.<sup>16</sup> bp 80-88° (0.5-0.7 mm),  $n^{15}_D$  1.4463-1.4468).

**1,2-Bis(dimethylaminomethyl)cyclopentane.** A 158-g (1 mol) sample of *trans*-1,2-cyclopentanedicarboxylic acid was heated under reflux with 700 g of thionyl chloride for 6 hr. The excess thionyl chloride was removed under reduced pressure. The crude acid chloride (C=O at 5.0  $\mu$ ) was dissolved in 500 ml of ether and added dropwise over 30 min to a solution of 500 g of dimethylamine in 2 l. of ether cooled to -20°. The mixture was allowed to warm to room temperature and stirred overnight. The precipitated amine hydrochloride was filtered and washed several times with ether. The combined organic layers were evaporated to give the crude diamide (C=O at 6.15  $\mu$ ). A small sample of the diamide which was evaporatively distilled (120° (0.3 mm)) had  $n^{27}_D$  1.4950.

*Anal.* Calcd for C<sub>11</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>: C, 62.23; H, 9.49; N, 13.20. Found: C, 62.20; H, 9.42; N, 13.75.

Without further purification the remaining crude diamide was reduced with lithium aluminum hydride by the general method described by Mićović and Mihailović.<sup>17</sup> On distillation through a Claisen head the diamine was obtained in 82% yield (over-all from diacid) as a colorless liquid: bp 73-75° (2.6 mm);  $n^{25}_D$  1.4540. Vpc analysis on an FFAP column at 275° showed one component at 13.0 min.

**1,2-Dimethylenecyclopentane.** A solution of 92.0 g (0.5 mol) of 1,2-bis(dimethylaminomethyl)cyclopentane and 270 ml of 30% hydrogen peroxide (Merck) was stirred at 20-30° for 20 hr.<sup>18</sup> The excess hydrogen peroxide was then decomposed by stirring the reaction mixture with a small amount of platinum black for 4 hr. The mixture was filtered and concentrated under reduced pressure (1-2 mm) at 50-60° in two portions. Each portion of amine oxide was mixed with ca. 0.5 g of hydroquinone and heated in an oil bath maintained at 170-180° (150 mm). The pyrolysate was collected in three Dry Ice-acetone traps. The combined pyrolysates from the two portions of amine oxide were washed with water, cold dilute hydrochloric acid, water (until neutral to litmus), and saturated brine. The diene was then cooled in a Dry Ice-acetone bath and decanted from water which had frozen to give 37.4 g (80% yield) of the diene,  $n^{25}_D$  1.4750 (lit.<sup>16</sup>  $n^{25}_D$  1.4732). This diene was used in subsequent steps without further purification. It was homogeneous

(12) P. C. Guha and D. F. Sankaran, *Org. Syn.*, **26**, 57 (1946).

(13) R. C. Fuson and W. Cole, *J. Amer. Chem. Soc.*, **60**, 1237 (1938).

(14) R. C. Fuson, C. L. Fleming, P. F. Warfield, and D. E. Wolf, *J. Org. Chem.*, **10**, 121 (1945).

(15) V. M. Mićović, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 264.

(16) A. T. Blomquist, J. Wolinsky, Y. C. Meinwald, and D. T. Longone, *J. Amer. Chem. Soc.*, **78**, 6057 (1956).

(17) V. M. Mićović and M. W. Mihailović, *J. Org. Chem.*, **18**, 1190 (1953).

(18) Cf. A. C. Cope and E. R. Trumbull, *Org. Reactions*, **11**, 317 (1960).

(10) J. Sauer, D. Lang, and A. Mielert, *Angew. Chem.*, **74**, 352 (1962).

(11) (a) A. T. Blomquist and J. A. Verdol, *J. Amer. Chem. Soc.*, **78**, 109 (1956); (b) J. K. Williams and W. H. Sharkey, *ibid.*, **81**, 4269 (1959).

on a 35% Apiezon N column and had an infrared spectrum identical with that reported<sup>16</sup> for the known material.

***cis*-1,2-Dihydroxymethylcyclohexane.** *cis*-1,2-Cyclohexanedicarboxylic anhydride (154.0 g, 1.0 mol, from Matheson Coleman and Bell Co.) was dissolved in about 500 ml of anhydrous ether (distilled from lithium aluminum anhydride before use). In the meantime, 50.0 g (1.2 mol) of lithium aluminum anhydride and 750 ml of dry ether were placed in a 5-l. flask (equipped with a stirrer, condenser, dropping funnel, and nitrogen bubbler). The flask was cooled with an ice bath, and the anhydride-ether solution was added dropwise over a period of 1 hr. The ice bath was removed, and the mixture was refluxed for 90 min. The mixture was then cooled with an ice bath, and hydrolyzed with excess 10% hydrochloric acid, at which time all the solids had dissolved. The ether layer was removed, and the aqueous layer was then extracted with four 500-ml portions of dichloromethane (each extraction was done by stirring the dichloromethane and aqueous solutions together for 1 hr followed by removal of the dichloromethane). All of the organic extracts were combined together and dried over anhydrous sodium carbonate and magnesium sulfate, followed by removal of the solvent. Vacuum distillation gave 24.4 g of lactone VI, bp 88–90° (3 mm), and 88.6 g (61.5% yield) of diol, bp 102–103° (1 mm) (lit.<sup>19</sup> 134–136° (3 mm)). The structure of the diol was confirmed by nmr and ir spectroscopy.

**1,2-Dimethylenecyclohexane (8).** The above diol (99.6 g, 0.62 mol) was converted to its diacetate by 157.0 g (1.54 mol) of acetic anhydride and 5 ml of pyridine according to reported procedures.<sup>19</sup> From this 133.9 g (95% yield) of diacetate was obtained: bp 87–88° (1 mm);  $n_D^{25}$  1.4589 (lit.<sup>19</sup> bp 152–153° (10 mm) and  $n_D^{25}$  1.4578). Infrared and nmr spectra confirmed the structure of the product.

The diacetate (133.0 g) was pyrolyzed at 520–530° at the rate of 2 g/min. Nitrogen gas was used as a carrier, and the pyrolysate was collected in a flask cooled by a Dry Ice-acetone bath. The pyrolysate was washed exhaustively with water to remove the acetic acid and then dried over a mixture of anhydrous magnesium sulfate and sodium bicarbonate. The organic material was removed by filtration and distilled with a small amount of di-*n*-butylammonium picrate (added to inhibit polymerization). At 95 mm pressure and 60–65°, 15.1 g (25% yield) of the desired diene (8) was obtained. At 23 mm and 107°, 19.7 g of monoacetate was collected. Unconverted diacetate (39.2 g) was also recovered, bp 91° (1 mm).

The diene 8 contained a small amount of impurity which was removed by preparative vpc on a 20 ft × 3/8 in. column of 20%  $\gamma$ -methyl- $\gamma$ -nitropimelonitrile on 60–80 mesh Chromosorb P (95° column, 200° injector, 205° detector, 140 cc of helium/min). The desired product had a retention time of 13 min. A total of 10.2 g of pure diene was collected, and its structure was confirmed by nmr (see Table II).

**Reaction of 1,2-Dimethylenecyclobutane (6) with 1,1-Dichloro-2,2-difluoroethylene.** 1,2-Dimethylenecyclobutane (3.8 g, 0.0475 mol) was sealed in a dry, heavy-walled ampoule at –80° along with 0.1 g of di-*n*-butylammonium picrate and 20 ml of 1122. The ampoule was then heated at 80° for 36 hr, at the end of which time the ampoule was cooled to –80° and opened. The dark contents were transferred to a round-bottomed flask, and the excess 1122 was removed by distillation through a Vigreux column. The adduct was then vacuum distilled to give 6.7 g (67% yield), bp 87–88° (28 mm).

(19) W. J. Bailey and H. R. Golden, *J. Amer. Chem. Soc.*, 75, 4780 (1953).

This adduct was analyzed on a variety of vpc columns and was found to be 99% pure. However, a sample of this product was further purified by preparative vpc, using a 20 ft × 3/8 in. column of  $\gamma$ -methyl- $\gamma$ -nitropimelonitrile on 60–80 mesh Chromosorb P (column 115°, injector 225°, detector 195°, flow rate 20 cc of helium/min). The main peak had a retention time of 65 min, mol wt (calcd) 211.9953.

**Reaction of 1,2-Dimethylenecyclopentane (7) with 1,1-Dichloro-2,2-difluoroethylene.** 1,2-Dimethylenecyclopentane (2.25 g, 0.024 mol) was placed in a heavy-walled ampoule along with 0.1 g of di-*n*-butylammonium picrate and 12 ml of pure 1,1-dichloro-2,2-difluoroethylene. The tube was sealed at –80°, brought to room temperature, and then heated at 80° for 36 hr. The ampoule was cooled to –80° and opened. The black contents were transferred to a round-bottomed flask where the excess 1122 was removed through a Vigreux column. The residue was then subjected to vacuum distillation to give 3.4 g (63% yield) of the adduct mixture, bp 104–105° (27 mm).

The adduct mixture was analyzed on a 6 ft × 0.25 in. column of  $\gamma$ -methyl- $\gamma$ -nitropimelonitrile on 60–80 mesh Chromosorb P (column 125°, injector 200°, detector 280°, 54 cc of helium/min) and found to contain 70% of adduct 10 and 30% of adduct 11 retention times 13 and 21 min, respectively.

Preparative vpc afforded the two adducts in pure state. On a 20 ft × 3/8 in. column of  $\gamma$ -methyl- $\gamma$ -nitropimelonitrile on 60–80 mesh Chromosorb P (column 125°, injector 205°, detector 210°, 140 cc of helium/min), the two adducts had retention times of 135 and 217 min, respectively. These adducts were identified by nmr spectroscopy (Table II), mol wt (10) 226.0100, (11) 226.0100 (calcd 226.0128).

**Reaction of 1,2-Dimethylenecyclohexane (8) with 1,1-Dichloro-2,2-difluoroethylene.** 1,2-Dimethylenecyclohexane (4.2 g, 0.039 mol, autoprep pure) was placed in a dry, heavy-walled tube along with 0.1 g of di-*n*-butylammonium picrate, and the ampoule was cooled to –80° (Dry Ice-acetone bath). 1,1-Dichloro-2,2-difluoroethylene (20 ml) was added. The ampoule was sealed and was then heated at 80° for 36 hr. At the end of this time, the ampoule was cooled to –80° and opened. The contents were placed in a round-bottomed flask, and the excess 1122 was removed at room temperature through a short Vigreux column. The residual brown-black oil was vacuum distilled to give 6.3 g (67% yield) of a colorless, camphoraceous smelling product, bp 130–139° (26 mm).

The adduct mixture was analyzed on a 1/8 in. × 10 ft column of FS-1265 (100° column, 200° detector, and 180° injector, flow rate of 30 cc of helium/min). Under these conditions the mixture was found to contain 44% of 12, and 56% of 13, with retention times of 32 and 60 min, respectively. These two compounds were isolated on the Autoprep A-700 using a 20 ft × 3/8 in. column of 20%  $\gamma$ -nitro- $\gamma$ -methylpimelonitrile (115° column, 175° injector, 200° detector, flow rate 200 cc of helium/min). Under these conditions, the retention times were 195 and 250 min, respectively, for adducts 12 and 13. The nmr spectra of these compounds are summarized in Table II, mol wt (12) 240.0214, (13) 240.0225 (calcd 240.0284).

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