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REACTION OF DIFLUOROCARBENE WITH SMALL BICYCLIC MOLECULES[†1,2]

James E. Jackson,* Ulf Misslitz, Maitland Jones, Jr.* and A. de Meijere[+]
Department of Chemistry, Princeton University, Princeton, NJ 08544

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Abstract - Difluorocarbene reacts with 1,2,2-trimethylbicyclo[1.1.0]butane to give the product of two bond cleavage, 1,1-difluoro-3,3,4-trimethyl-1,4-pentadiene in 3% yield. Bicyclo[2.1.0]pentane is even less reactive, yielding 1,1-difluorohexa-1,5-diene in ca. 0.5% yield. Bicyclo[3.1.0]hexane does not react with difluorocarbene. Theoretical descriptions of these reactions are discussed.

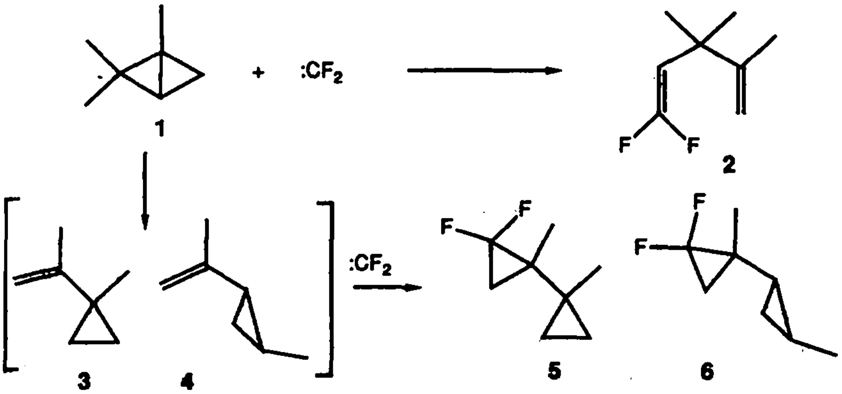
Introduction

Over the last several years we have communicated a number of papers on the reactions of carbenes with carbon-carbon single bonds contained in highly strained rings.[2,3] With one exception[3c] experimental details have been lacking and a variety of carbenes reacting with the various hydrocarbons has been described. Here we report the details of the reaction of a single carbene, difluorocarbene, with a spectrum of compounds containing small rings.

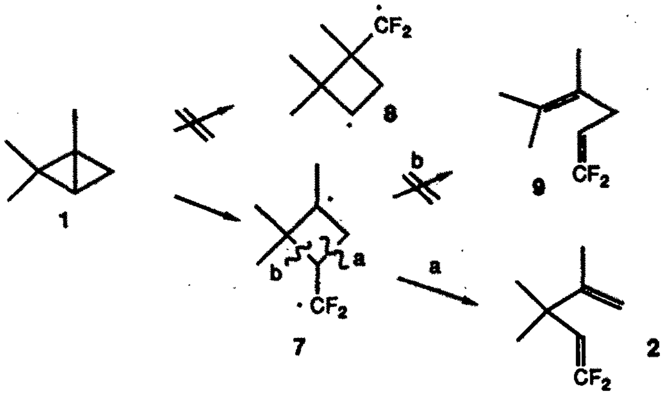
Little previous work has been reported on the reaction of carbenes with carbon-carbon single bonds and for good reason: the reaction almost doesn't occur! "Normal" C-C bonds do not react[3c,4] and for the reaction to occur at all activation must be present. Thus molecules containing exotic kinds of bonding are required and even in such cases yields are low. We are operating at the limits of reactivity even for such voracious electrophiles as carbenes.

Reaction of Difluorocarbene with Bicyclobutane

Like methylene and dicarbomethoxycarbene,[3a,c] difluorocarbene reacts with bicyclobutanes by two bond cleavage. Thus CF_2 combines with 1,2,2-trimethylbicyclo[1.1.0]butane (1) to give 1,1-difluoro-3,3,4-trimethyl-1,4-pentadiene (2) in 3% yield. Difluorocarbene was generated by the method of Burton,[5] under which conditions 1 was apparently converted to vinylcyclopropanes 3 and 4 as substantial amounts of 5 and 6 were isolated along with 2.[3] Diene 2 was independently synthesized by a sequence starting from pivalolactone.[6,7] Questions of mechanism are reduced to the classic "is there an intermediate or not?" We have remarked before[3a,3c] that formation of dienes such as 2 argues strongly against a mechanism involving a two-step reaction in which an intermediate diradical is formed, only to suffer cleavage to the diene. For both steric and electronic reasons



diradical 7 should be favored over 8. Intermediate 7 has two possible cleavages leading to dienes 2 and 9. It seems inevitable that in the transition state for this second step in diene formation some of the increased thermodynamic stability of 9 over 2 would be felt. As we are unable to detect 9 (or any other diene products besides 2), it seems highly probable to us that the reaction is not two-step, but rather a concerted one in which the central and one side bond of 1 are cleaved. This notion, as well as further details of a number of possible concerted paths is revealed by a theoretical investigation of the reaction at the MNDO level.[8]



We have previously reported a theoretical description of the reaction of $:CH_2$ with bicyclobutane.[3c] For purposes of comparison we will summarize our findings here. Aside from carbon-hydrogen insertion pathways, we find three transition structures (TS) for the reaction. One, (TS "C") involves a non-symmetrical top-side attack and leads to bicyclo[1.1.1]pentane without the intervention of an intermediate [see figure 1]. As the central carbon-carbon bond in bicyclobutane is constructed of two essentially pure 2p orbitals,[9] it comes as no surprise that this addition resembles closely the best theoretical picture of the addition of methylene to a carbon-carbon double bond.[10] In this picture,[10] reaction begins with a carbene oriented so as to best overlap its empty 2p orbital (the Lowest Unoccupied Molecular Orbital, or LUMO) with a filled π orbital (Highest Occupied M.O., or HOMO) of the olefin. The planes of the carbene and the olefin are essentially parallel at this early electrophilic stage. At a closer approach, the carbene pitches down as its filled sp^2 orbital begins to interact favorably with the now somewhat distorted π^* orbital of the olefin. Ultimately, the carbene rotates to the orientation found in the product cyclopropane.

The computed paths to diene products are quite different, arising by carbene attack from outside and below the bridgehead. In transition structure "A" [figure 2] methylene approaches the side of bicyclobutane, the empty 2p orbital (carbene LUMO) overlapping with the rear of one of the 2p orbitals making up the HOMO of bicyclobutane, and the carbene's filled hybrid orbital overlapping with σ^* of one of the bicyclobutane's side bonds. This leads, again without an intermediate, to 1,4-pentadiene. The C1-C4 bond of "A", situated anti-planar to the carbene's lone pair in the TS, is uniformly the side bond broken, so product regioselectivity is already determined at the point of cresting the activation barrier. A third transition structure "B" [figure 2] involves a more symmetrical side approach. This TS is nearly degenerate in energy with "A" but quickly breaks symmetry, converting to A-like structures as the carbene continues to approach bicyclobutane along this path. We interpret the energetic degeneracy of TS's "A" and "B" to mean that in the transition structure the methylene-bicyclobutane interaction is purely electrophilic. As yet the bicyclobutane "feels" no difference between the carbene's lone-pair and C-H bond pair electrons.

Qualitatively, addition of $:CF_2$ is similar [figure 1,2]. However, in the top approach (TS "F") addition is substantially less symmetrical, with the electrophilic stage of the reaction more advanced than for the addition of methylene, as evidenced by the shortening of the carbene-C3 distance. The onset of the nucleophilic stage is also apparent as difluorocarbene has tilted over substantially farther in the transition state than has methylene. Similarly, the H-C3-C1 angle has opened and is now nearly 180°. Bond making and breaking has progressed further than in the analogous reaction of the much more reactive methylene where the fragments are barely distorted from their starting geometries. The more stable carbene (CF_2) is participating in a less exothermic addition[11] and thus the transition state comes relatively late and naturally has a substantially higher activation energy [tables 1,2], in this case 44.1 vs. 17.9 kcal/mol.

Table 1. Heats of Formation and Activation Energies

T.S.	Description	ΔH_f	E_a	Figure
1 + $^{1}CH_{2}$ (A)	Unsymmetrical side approach	182.5	11.1	2
1 + $^{1}CH_{2}$ (B)	Symmetrical side approach	182.6	11.2	2
1 + $^{1}CH_{2}$ (C)	Top approach	189.3	17.9	1
1 + $^{1}CF_{2}$ (D)	Unsymmetrical side approach	25.58	26.7	2
1 + $^{1}CF_{2}$ (E)[a]	Symmetrical side approach	27.26	28.4	2
1 + $^{1}CF_{2}$ (F)	Top approach	43.01	44.1	1
10 + $^{1}CH_{2}$ (G)	Bisector-C_5 side approach[b]	155.99	18.4	4
10 + $^{1}CH_{2}$ (H)	Bisector-C_2 side approach[b]	159.54	22.0	4
10 + $^{1}CH_{2}$ (I)	Bisector-H_1 side approach[b]	156.76	19.2	4
10 + $^{1}CH_{2}$ (J)	Top approach	161.70	24.0	3
10 + $^{1}CF_{2}$ (K)	Bisector-C_5 side approach[b]	7.98	43.0	4
10 + $^{1}CF_{2}$ (L)	Bisector-C_2 side approach[b]	12.55	47.5	4
10 + $^{1}CF_{2}$	Bisector-H_1 side approach[b]	No TS - collapses to "K" or "L"		
10 + $^{1}CF_{2}$ (M)	Top approach	19.70	54.7	3

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[a] A second-order stationary point or "hilltop", showing 2 negative eigenvalues of the second derivative matrix. In this case, when unconstrained, this structure collapses toward structure type "A".

[b] The H-C-H or F-C-F angle bisector of the carbene is approximately eclipsing the bond from C_1 to the indicated atom, as shown by the Newman projections in the figures. In general, this is the side bond which is cleaved.

Table 2. Heats of Formation of Starting Materials and Products

	MNDO ΔH_f	Exp. ΔH_f
$CH_2(^1A_1)$	107.4	-102.0[13]
CF_2 $(^1A_1)$	-65.2	-44.5[14]
Bicyclo[1.1.0]butane	64.1	51.9[15]
Bicyclo[2.1.0]pentane	30.2	37.7[15]
1,4-Pentadiene	24.3	25.3[15]
Bicyclo[1.1.1]pentane	58.3	49.6[15]
1,1-Difluoro-1,4-pentadiene	-74.3	-58.5[16]
2,2-Difluorobicyclo[1.1.1]pentane	-33.6	-42.5[16]
1,5-Hexadiene	19.9	20.1[17]
Bicyclo[2.1.1]hexane	19.3	15.3[15]
1,1-Difluoro-1,5-hexadiene	-79.0	-63.7[16]
5,5-Difluorobicyclo[2.1.1]hexane	-71.6	-76.8[16]

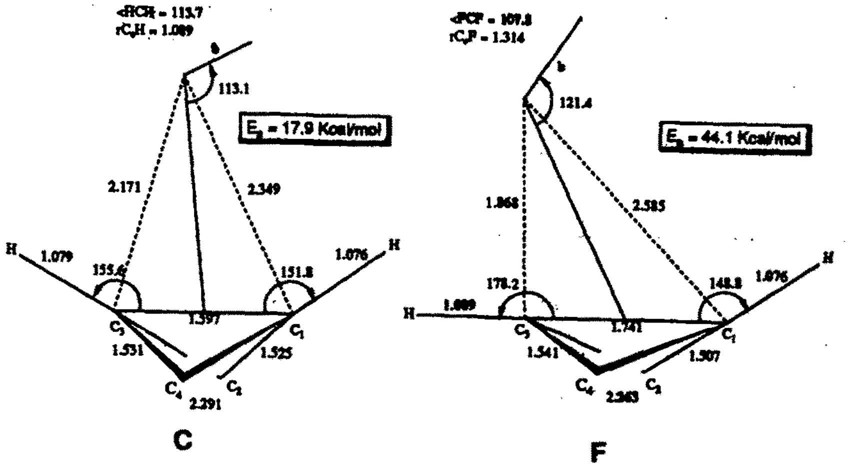


Figure 1. The MNDO TS "C" for top approach of :CH$_2$ to bicyclobutane, compared with the corresponding structure "F" for attack of :CF$_2$.

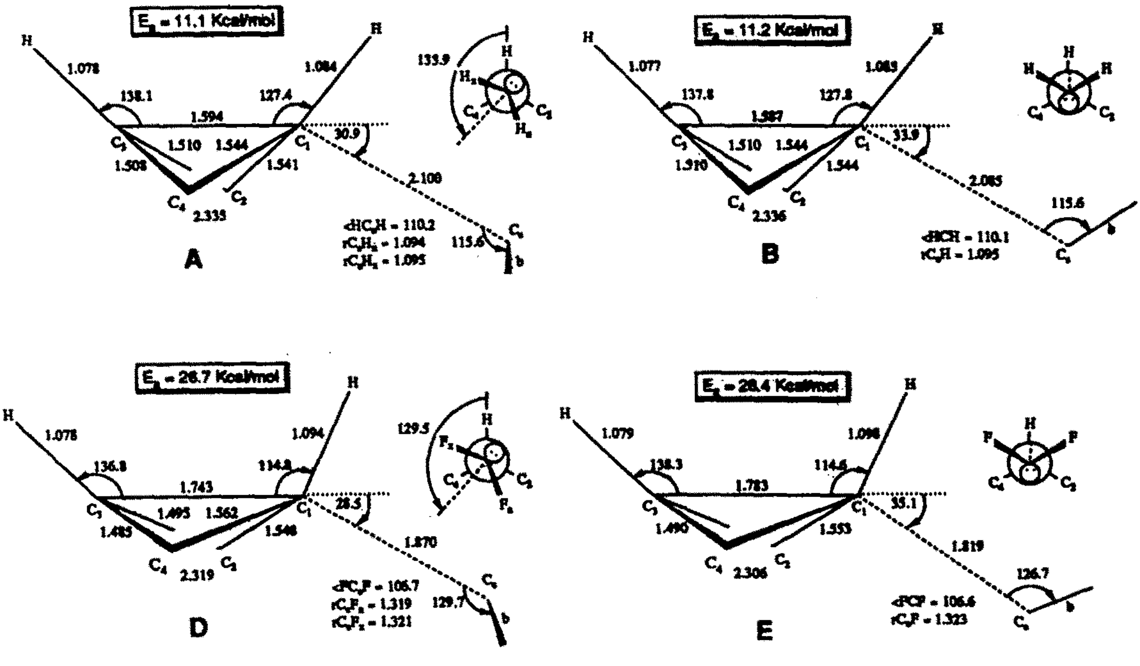
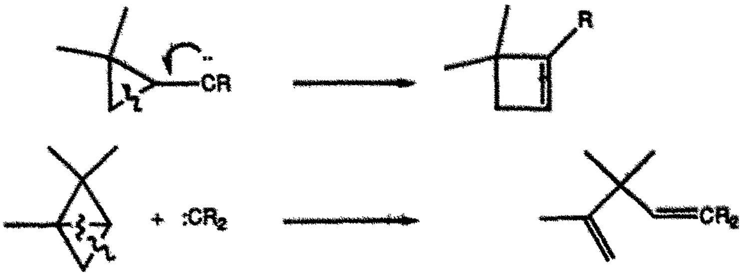


Figure 2. The MNDO TS's "A" and "B" for side approach of :CH$_2$ to bicyclobutane, compared with the corresponding structures "D" and "E" for attack of :CF$_2$.

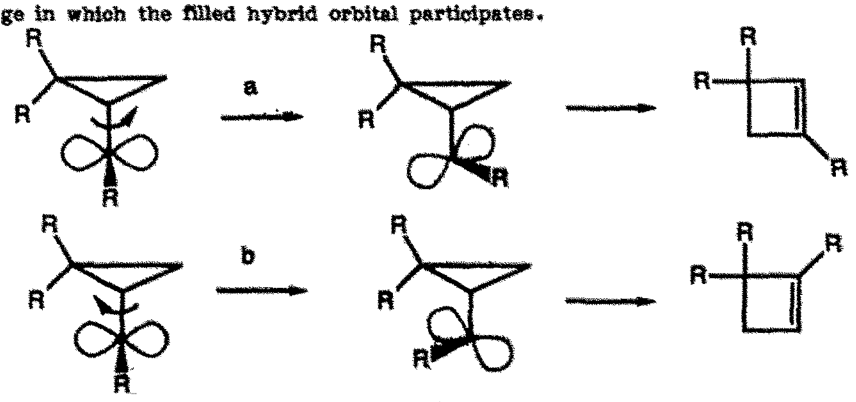
Side approach offers a similar comparison. The distance between the carbene and C1 is shorter [figure 2] and the breaking bonds C1-C3 and C1-C4 are longer than their counterparts in the methylene reaction. The carbene itself is further along in the nucleophilic phase, the flattening process which brings it to its position in the final diene. Again the activation energy is more than double that of the methylene reaction (26.7 vs. 11.1 kcal/mol, see table 1). Unlike the methylene case, the zero-gradient structure for symmetrical side approach, "E" (1.7 kcal/mol higher in energy than "D") is found to be a second order stationary point, an energetic hilltop, which collapses to the less symmetrical "D" without barrier when symmetry constraints are relaxed.

For bicyclobutane the top approach (TS "C") of methylene was calculated to be 5-7 kcal/mol higher in energy than either approach to the side (TS "A" and "B"). For difluorocarbene the analogous energy difference is roughly threefold larger [table 1], ca. 17 kcal/mol. It is therefore no surprise that no bicyclo[1.1.1]pentanes are observed from reaction of 1 and difluorocarbene.

All reactions of singlet carbenes with 1 studied so far have shown that 2 is the sole isolable diene. What is the source of this specificity? We have considered the stepwise mechanism and found it to predict the opposite result, that is, predominant formation of 9, not 2. There are harbingers of this effect lurking in the literature. As early as 1967 it was noted that in the ring expansion of cyclopropylcarbenes, the intramolecular version of this reaction, it was the stronger, i.e. less substituted bond that migrated.[18,19] Here we see exactly the same effect: it is the less substituted side bond of bicyclobutane that is broken.



The regioselectivity of the intramolecular reaction was rationalized reasonably as early as 1968 by Frey and his collaborators[19] who pointed out the evident influence of steric factors on the course of the reaction. Rotation must occur in either mode "a" or "b" in order to form the cyclobutene. Rotation in the direction which minimizes the steric interaction between substituents goes far towards explaining the preference for migration of the less substituted bond. Schoeller[20] later reported MINDO/3 calculations and discussed the reaction in terms of the by now familiar sequence of an early electrophilic interaction between the carbene's 2p orbital and a ring bond followed by a nucleophilic stage in which the filled hybrid orbital participates.



Our calculations show the intermolecular reaction with bicyclobutanes to be similar. There are two orientations possible (10 and 11) as the bond begins to strengthen between the carbene's empty 2p orbital and the HOMO of the bicyclobutane. Structure 10 is surely favored on steric grounds and it is this structure in which the carbene HOMO better overlaps with the back lobe of σ^* of the side bond of bicyclobutane that breaks to give the observed product, diene 2.

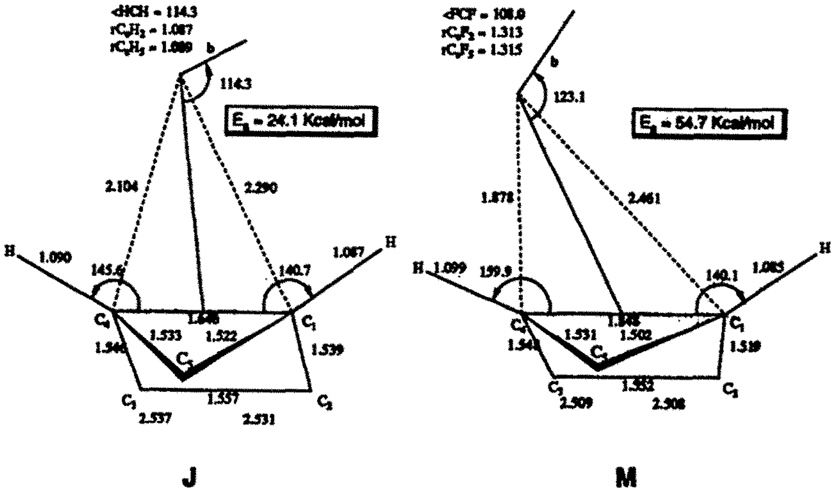


Figure 3. The MNDO TS "J" for top approach of $:CH_2$ to bicyclo[2.1.0]pentane, compared with the corresponding structure "M" for attack of $:CF_2$.

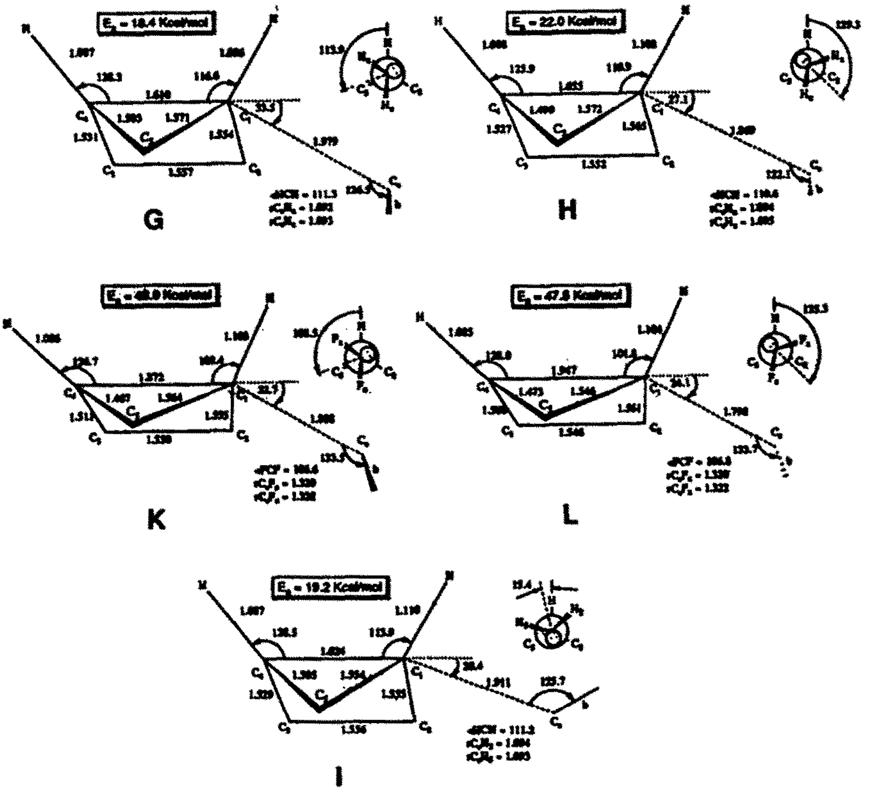
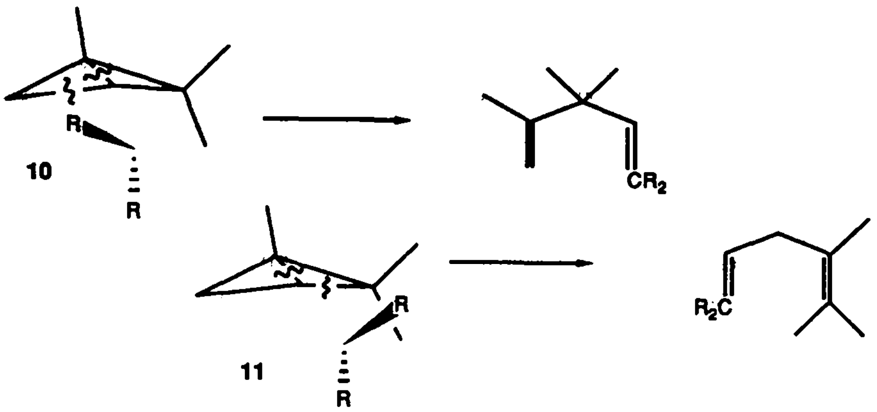


Figure 4. The MNDO TS's "G", "H", and "I" for side approach of $:CH_2$ to bicyclo[2.1.0]pentane, compared with the corresponding structures "K" and "L" for attack of $:CF_2$. As noted in the text there is no $:CF_2$ analogue for the $:CH_2$ + bicyclo[2.1.0]pentane transition structure "I".



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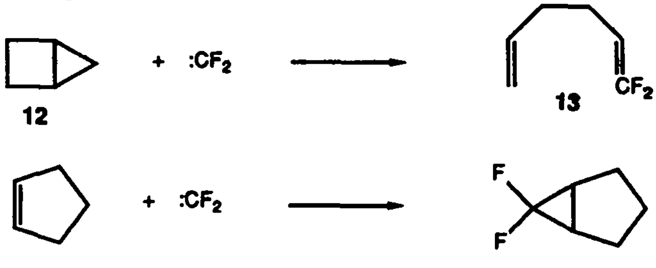
Reaction of Difluorocarbene with Bicyclo[2.1.0]pentane

Although neither dicarbomethoxycarbene nor phenylcarbene reacts with the carbon-carbon bonds of bicyclo[2.1.0]pentane (12),[2] difluorocarbene does, although the cleavage product is formed in only 0.5% yield. Generation[5] of difluorocarbene in 12 led to 1,1-difluorohexa-1,5-diene (13) and 6,6-difluorobicyclo[3.1.0]hexane (14) in approximately equal amounts. Authentic syntheses of both products established their structures.[21-25] Unfortunately the presence of 14 cannot be regarded as significant. Despite our best efforts, we were unable to obtain bicyclopentane better than 99.7% pure. It seems very likely that the residual 0.3% cyclopentene reacted rapidly with difluorocarbene to generate the small amounts of 14. It is also possible that small amounts of cyclopentene are formed from 12 during the reaction.



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We have compared the calculated reactions of difluorocarbene with calculations for the reaction of bicyclopentane with methylene itself [figures 3,4]. Top approach by difluorocarbene to the more stable bicyclopentane (TS "M") is even more difficult than is top approach to bicyclobutane [compare figures 1,3]. Our calculations at the MNDO level give an activation energy of nearly 55 kcal/mol compared to 24 kcal/mol for the analogous attack of methylene on bicyclopentane (TS "J", figure 3) and 43 kcal/mol for top approach of difluorocarbene to bicyclobutane [table 1].

For both methylene and difluorocarbene side approach with the R-C-R angle bisected by the C1-C5 bond (TS "G", "K", figure 4) is better by 3-4 kcal/mol than the analogous approach with the C1-C2 bond on the carbene's bisector [TS's "H", "L", figure 4, table 1]. This is necessary for the second, nucleophilic stage of the reaction to proceed as the filled carbene hybrid orbital overlaps with the empty σ^* orbital of the C1-C5 bond, and is in accord with the formation of hexadiene in the difluorocarbene reaction. It does suggest that formation of allyl cyclopropanes (TS "L", figure 4) might be achievable under some circumstances should a way be found to disfavor the cleavage to hexadienes.

Many of the features apparent in the reaction with bicyclobutane also appear in the bicyclopentane reaction. In the computed transition structure "K" difluorocarbene is closer than is methylene (TS "G") to its final position, as the difluorocarbene transition state comes later in the process. The C1-C5 bond has lengthened compared to its neighbor, C4-C5, which will eventually become a double bond. Meanwhile, the carbene carbon is flattening towards its final position in the diene product.

In the case of difluorocarbene, searches for transition structures like "I" (figure 4), in which the bicyclopentane's C1-H bond lies near the carbene's bisector plane, invariably led to carbene rotation, giving conformations like "K" or "L" where the C1-C5 or C1-C2 bonds of the bicyclopentane are on the bisector instead. This result is consistent with the observation that structure "E" (C_s symmetry) for CF_2 attack on bicyclobutane is in fact a second-order stationary point as noted above. Thus in the lower symmetry CF_2 + bicyclopentane case, no structure of this sort could be found.

Reaction of Difluorocarbene wtih Bicyclo[3.1.0]hexane

Generation of difluorocarbene in bicyclo[3.1.0]hexane (15) by the same method[5] led to no products incorporating 15 and the carbene. Thus we have reached the limits of reactivity of difluorocarbene. Compound 15 fits firmly into the category of "normal" hydrocarbons.

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EXPERIMENTAL

General Data. NMR spectra were recorded on an IBM/Brüker spectrometer WM 250 (250 MHz) or a General Electric/Nicolet spectrometer GE/NT 300 (300 MHz) with tetramethylsilane as internal standard (δ 0.00 ppm). ^{13}C-NMR spectra were recorded on an IBM/Brüker WM 250 spectrometer operated at 62.89 MHz or a General Electric/Nicolet GE/NT 300 spectrometer operated at 75.47 MHz with deuteriochloroform as internal standard (δ 77.0 ppm). ^{19}F-NMR spectra were recorded on a General Electric/Nicolet GE/NT 300 spectrometer operated at 282.32 MHz or an IBM/Brüker NR 80 spectrometer operated at 75.29 MHz with trichlorofluoromethane or hexafluorobenzene as internal standard.

IR spectra were recorded on a Perkin Elmer model 283B spectrometer.

A Hewlett Packard 5992 B GC/MS (electron impact, 70 eV) was used for routine mass spectra. High resolution mass spectra were recorded on an AEI-MS 9 (electron impact, 70 eV) or by the Midwest Center for Mass Spectrographic Analysis, Lincoln, Nebraska.

Preparative gas chromatographic separations were performed on a Varian A90P gas chromatograph equipped with a 10'x1/4" stainless steel column packed with 10% FFAP on Chromosorb W-AW-DMCS, 60-80 mesh (column A) or with a 11'x1/4" stainless steel column packed with 10% $AgNO_3$/30% benzylcyanide on Chromosorb P-NAW, 45-60 mesh (column B) with helium as carrier gas. Column temperatures and flow rates are specified for each separation.

Starting Hydrocarbons. 1,2,2-Trimethylbicyclo[1.1.0]butane. (99.0% as measured by ^1H-NMR. Major impurity: 1-methyl-1-*iso*-propenylcyclopropane), bicyclo[2.1.0]pentane (99.7% by ^1H-NMR, major impurity: cyclopentene) and bicyclo[3.1.0]hexane (98.0% by ^1H-NMR, major impurity: cyclopentene) were obtained by published methods.[3c,a,b] Triglyme, triphenylphosphine, dibromodifluoromethane and potassium fluoride were purified as previously described by Jefford et al.[26]

General Procedure. All carbene reactions were performed under argon in flame-dried glassware. Pre-cooled dibromodifluoromethane (2.09 g, 10.0 mmol) was injected into a solution of 2.62 g (10.0 mmol) of trimethylphosphine and 10 mL of triglyme. After 1 min a white precipitate of (bromodifluoromethyl)triphenylphosphonium bromide had formed. After 30 min 8.0-10.0 mmol of the hydrocarbon and 2.32 g (40.0 mmol) of potassium fluoride were added. Stirring was continued for 48-72 h at room temperature. Then all volatile products were flash distilled at room temperature under high vacuum. Absolute and relative yields of the difluorocarbene adducts were determined by integration of the ^{19}F-NMR signals with hexafluorobenzene as internal integration standard.

Reaction of 1,2,2-Trimethylbicyclo[1.1.0]butane (1) with Difluorocarbene

As described in the general procedure, 0.80 g (8.3 mmol) of 1 were stirred under the reaction conditions for 72 h. Isolation yielded 1.00 g of a very volatile, colorless liquid. The total yield of difluorocarbene adducts was 21.9% by ^{19}F-NMR spectroscopy. The adducts were separated by preparative VPC (column B, column temperature: 40°C, flow: 60 mL/min) and collected by increasing retention times as solutions in deuteriochloroform.

I. 1,1-Difluoro-3,3,4-trimethyl-1,4-pentadiene (2, 3.1%): ^1H-NMR (250 MHz, $CDCl_3$): δ 1.26 (bs, 6H), 1.76 (bs, 3H), 4.14 (dd, 1H), 4.74 (mc, 1H), 4.87 ppm (bs, 1H). ^{19}F-NMR (75.29 MHz, $CDCl_3$): δ -92.0 ppm (AB, 2F).

II. 2,2-Difluoro-1-methyl-1-(1'-methylcyclopropyl)cyclopropane (5, 16.6%): ^{1}H-NMR (250 MHz, $CDCl_3$): δ 0.38 (bs, 4H), 0.72 (ddd, 1H), 0.86 (ddd, 1H), 1.17 (s, 3H), 1.28 ppm (t, 3H). ^{19}F-NMR (75.29 MHz, $CDCl_3$): δ -139.1 ppm (AB, 2F).

III. trans-2,2-Difluoro-1-methyl-1-(2'-methylcyclopropyl)cyclopropane (6, 2.2%): ^{1}H-NMR (250 MHz, $CDCl_3$): δ 0.25 (mc, 2H), 0.60 (mc, 2H), 0.84 (mc, 2H), 1.07 (d, 3H), 1.17 ppm (t, 3H). ^{19}F-NMR (75.29 MHz, $CDCl_3$): δ -139.3 ppm (AB, 2F).

Independent Synthesis of 1,1-Difluoro-3,3,4-trimethyl-1,4-pentadiene. 2,2,3-Trimethyl-3-buten-1-al

To a vigorously mechanically stirred suspension of 12.3 g (57.1 mmol) of pyridinium chlorochromate and 0.93 g (11.3 mmol) of sodium acetate in 50 mL of dry dichloromethane was added 4.34 g (38.0 mmol) of 2,2,3-trimethyl-3-buten-1-ol in 50 mL of dry dichloromethane in one portion at room temperature under an atmosphere of argon. After 1 h the mixture was diluted with 100 mL of dry diethyl ether. The organic layer was decanted and the residual black gum washed with three 50-mL portions of dry diethyl ether. The combined organic layers were filtered through Florisil. Fractional distillation at atmospheric pressure yielded 2.46 g (58%) of 2,2,3-trimethyl-3-buten-1-al bp. 108°C (lit.[27]) 72-5 °C/138 torr).

1,1-Difluoro-3,3,4-trimethyl-1,4-pentadiene (2)

A solution of 0.48 g (4.53 mmol) of lithium diisopropylamide in 5.0 mL of dry tetrahydrofuran was added dropwise to a mixture of 0.85 g (4.52 mmole) of (diethylphosphinyl)-difluoromethane[27] in 2.5 mL of dry tetrahydrofuran at -78°C under an atmosphere of argon. After 1 h, 0.50 g (4.46 mmol) of 2,2,3-trimethyl-3-buten-1-al was added. The mixture was stirred at -78°C for another hour and was then allowed to warm up to room temperature in about 1 h. Finally the dark brown solution was refluxed for 12 h. Then all volatile products were flash distilled at room temperature under reduced pressure. The distillate was diluted with 5.0 mL of n-pentane. This solution was washed with 5.0 mL of water, 50 mL 5% hydrochloric acid and 50 mL water. The residual liquid was dried over 4 Å molecular sieves and purified by preparative VPC (column B, column temperature: 50°C, flow: 250/mL/min). 1,1-Difluoro-3,3,4-trimethyl-1,4-pentadiene (2, 110 mg, 17%): IR (neat): 1750 ($C=CF_2$), 1625 cm^{-1} (C=C). ^{1}H-NMR (250 MHz, $CDCl_3$): δ 1.26 (bs, 6H), 1.76 (bs, 3H), 4.14 (dd, 1H), 4.74 (mc, 1H), 4.87 ppm (bs, 1H). ^{13}C-NMR (75.47 MHz, $CDCl_3$): δ 19.5 (s), 27.5 (s), 37.4 (s), 86.8 (dd, $^{2}J_{C,F}$ = 19.6 Hz, $^{2}J_{C,F}$ = 15.1 Hz), 109.0 (s), 151.1 (s), 155.2 ppm (dd, $^{1}J_{C,F}$ = 292.9 Hz, $^{1}J_{C,F}$ = 286.1 Hz). ^{19}F-NMR (75.29 MHz, $CDCl_3$): δ -92.0 ppm (AB, 2F). MS (70 eV): m/e = 146 (43), 131 (100), 111 (23), 109 (12), 105 (57), 91 (21), 89 (10), 85 (13), 83 (10), 77 (45), 67 (19), 65 (17), 53 (13), 51 (17). Precise mass. Calculated for 2, $C_8H_{12}F_2$: 146.0907. Found: 146.0905 ± 0.0012.

Reaction of Bicyclo[2.1.0]pentane (12) with Difluorocarbene

As described in the general procedure, 0.68 g (10.0 mmol) of 12 were stirred for 70 h to yield 1.34 g of a very volatile, colorless liquid. The total yield of difluorocarbene adducts was 1.1% as determined by ^{19}F-NMR spectroscopy. The adducts were separated by preparative VPC (column B, column temperature: 40°C, flow: 120 mL/min).

I. 6,6-Difluorobicyclo[3.1.0]hexane (14, ca. 0.5%). ^{1}H-NMR (250 MHz, $CDCl_3$): δ 1.51 (mc, 1H), 1.72 (mc, 1H), 1.81-2.08 ppm (m, 6H). ^{19}F-NMR (75.29 MHz, $CDCl_3$): δ 125.9 (d, $^{2}J_{F,F}$ 156.1 Hz, 1F), -149.3 ppm (d, $^{2}J_{F,F}$ = 156.1 Hz, 1F). Precise mass. Calculated for 14, $C_6H_8F_2$: 118.0594. Found: 118.0594 ± 0.0012.

II. 1,1-Difluorohexa-1,5-diene (13, ca. 0.5%).[28]

Bicyclo[3.1.0]hexane

A mixture of 41.0 g (0.62 mol) of zinc-copper couple and a crystal of iodine was stirred under 250 mL of dry ether under argon until the brown color disappeared. A mixture of 38.8 g (0.57 mol) of cyclopentene (dried over 4 Å molecular sieves) and 166.5 g (0.62 mol) methylene iodide was added in one portion. The mixture was refluxed for 6 h, cooled for 3 h and then refluxed again for 15 h. The mixture was filtered through Celite and poured into 100 mL of a cooled saturated NH_4Cl solution. The organic layer was separated and washed with 3 x 100 mL portions of saturated NH_4Cl, 3 x 100 mL saturated $NaHCO_3$, 1 x 300 mL saturated $Na_2S_2O_3$ and 1 x 100 mL H_2O. After drying over $MgSO_4$, the solvent was completely removed by distillation through a 20-inch Vigreaux column. Fractionation of the residue yielded 14 g (30%) of bicyclo[3.1.0]hexane.[29,30]

Reaction of Bicyclo[3.1.0]hexane (15) with Difluorocarbene

As described in the general procedure, 0.80 g (9.8 mmol) of bicyclo[3.1.0]hexane were stirred for 72 h to yield 1.50 g of a very volatile colorless liquid. Inspection by ^1H- and ^{19}F-NMR spectroscopy showed no difluorocarbene adducts.

Computational Details

MNDO calculations were carried out by using a slightly modified version of the MOPAC package (QCPE #455, version 2.08) running on a VAX 11/780 minicomputer. All structures were computed by the restricted Hartree-Fock (RHF) method. In some cases, transition structures were further examined by using the open-shell 3x3 configuration interaction option available in the MOPAC program which, in addition to the closed shell ground state, includes the two configurations resulting from single and double HOMO to LUMO excitations. All stationary points were fully characterized by vibrational analysis. Using the resultant vibrational frequencies, correction for zero-point energy (ZPE) differences between the starting fragments and transition structures did not change the relative calculated barriers by more than ca. 1 kcal/mol (absolute corrections were never > 2.5 kcal/mol). Given the much larger uncertainties inherent in the application to transition structures of a method calibrated to reproduce the properties of ground-state minima, such relatively subtle adjustments as ZPE differences and thermal energy corrections were considered insignificant and are not reported.

REFERENCES AND NOTES

† Dedicated to Professors Johannes and Hildegard Padelt on the occasions of their 80th birthdays.

\+ Permanent address: Institut für Organische Chemie und Biochemie, Universität Hamburg, Federal Republic of Germany.

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