for 1.5 h and refluxed for 30 min. Chlorotrimethylsilane (1.00 g) was added and the mixture was refluxed for 3 h. Skelly F was then added and a standard aqueous workup followed. The organic phase was washed with cold dilute $KHSO_4$ and dried over $MgSO_4$. The solvent was removed by rotary evaporation. Distillation of the residue gave, after a small forerun, 0.55 g (95%) of silyl enol ether **37**: ^1H NMR (CCl_4) δ 3.48 (3 H, s), 1.17 (18 H, s), 0.28 (9 H, s); mass spectroscopic mol wt 258.2004 (calcd for $C_{14}H_{30}O_2Si$ 258.2015).

Preparation of Bromo Ketone 38. A solution of 0.30 g of silyl enol ether **13** in 2 mL of CCl_4 was cooled to −30 °C and 0.21 g of bromine in 0.5 mL of CCl_4 was added. Solvent was removed by aspirator and the residue was distilled, giving 0.25 g (82%) of bromo ketone **38**, bp 63 °C (1.1 mm). Previously reported[26b] bromo ketone **38** had the following: NMR (CCl_4) δ 4.40 (1 H, s), 1.25 (9 H, s), 1.14 (9 H, s).

Reaction of LiTMP with Bromo Ketone 38. LiTMP was prepared from 0.29 g of tetramethylpiperidine and 1.46 mL of 1.4 M methyllithium. The mixture was cooled to −60 °C and 158 mg of bromo ketone **38** was added. The mixture was warmed to room temperature and stirring was continued for 50 min. A standard aqueous workup followed. After solvent removal by distillation through a Vigreux column, the residue was distilled to give 93 mg (88%) of ketone **9** which was identified by IR and NMR comparison with an authentic sample.

Reaction of Triflate 7 with Potassium *tert*-Butoxide. A 0.51 M solution of potassium *tert*-butoxide in *tert*-butyl alcohol (2.6 mL, prepared by dissolving 0.40 g of potassium in 20 mL of anhydrous *tert*-butyl alcohol) was cooled to 15 °C and 0.20 g of triflate **7** was added. After 2.5 h at room temperature, a standard aqueous workup followed. Gas-chromatographic analysis showed diketone **8** along with about 10% pivaloin. After distillation of the solvent through a Vigreux column, the residue was distilled, giving 0.05 g (45%) of diketone **8** which was identified by IR and NMR spectral comparison with an authentic sample.[27b]

Reaction of Tosylate 30 with Potassium *tert*-Butoxide. Tosylate **30** (0.25 g) was added to 3 mL of a 0.51 M solution of potassium *tert*-butoxide in *tert*-butyl alcohol. The mixture was refluxed for 1 h and a standard aqueous workup followed. Gas chromatographic analysis showed diketone **8** along with about 10% pivaloin. Distillation gave 0.044 g (34%) of diketone **8** which was identified by IR and NMR spectral comparison with an authentic sample.[27b]

Preparation of Alcohols 41. A solution of 490 mg of silyl enol ether **39**[29] in 5 mL of methylene chloride was cooled to −78 °C and ozonized until a blue color appeared. Gas-chromatographic analysis showed the presence of siloxy ketones **40** as well as camphoric anhydride (**41**). Solvent was removed by rotary evaporation. The NMR of the residue shows an *exo*-siloxy:*endo*-siloxy ratio of 1.5 in the mixture. The exo proton of **40** appears as a doublet, $J = 5$ Hz, at δ 4.08. The endo proton in **40** appears as a broad singlet at δ 3.58. The crude residue was dissolved in 5 mL of methanol and after 5 min, the solvent was removed by rotary evaporation. The residue was taken up into Skelly F. Camphoric anhydride (**41**), which did not dissolve, was separated by decanting the liquid. The yield of **41** was 40 mg (10%). Anhydride **41** was identified by spectral comparison with an authentic sample. After evaporation of the Skelly F by rotary evaporation, the residue was further purified by sublimation at 1 mm. The NMR of **42** showed an *exo*-hydroxy:*endo*-hydroxy ratio of 1.5. The exo proton of **42** appears as a doublet (after exchange of the hydroxyl proton with D_2O), $J = 5$ Hz, at δ 4.17. The endo proton of **42** appears as a broad singlet at δ 3.70. The preparation of hydroxy ketones **42** by alternate routes has been reported.[30]

Preparation of Triflates 43. Triflic anhydride (2.20 g) was dissolved in 8 mL of pyridine at 0 °C and a solution of 1.00 g of the mixture of alcohols **42** in 4 mL of pyridine was added at 0 °C. After 18 min at 0 °C, the mixture was taken up into ether and extracted with cold water. After a standard aqueous workup with HCl washing to remove pyridine, the solution was dried over $MgSO_4$. About one-half of the solvent was removed by a steam bath and the remainder of the ether was removed by rotary evaporation. The crude mixture of triflates **43**, 1.33 g (74%), was used directly in the next reaction. The NMR of the triflate mixture showed an exo-triflate:endo-triflate ratio of 0.7. The exo proton (α to the carbonyl group) in the mixture appeared as a doublet, $J = 5$ Hz, at δ 5.06. The endo proton appeared as a broad singlet at δ 4.62.

Reaction of Triflate 43 with Potassium *tert*-Butoxide. A 0.42 M solution of potassium *tert*-butoxide in *tert*-butyl alcohol (6.3 mL) was cooled to about 15 °C and 0.51 g of triflates **43** was added. After 5 min at room temperature, a standard aqueous workup followed. The organic extract was dried over $MgSO_4$ and solvents were removed by rotary evaporation, leaving 0.26 g (92%) of crude camphorquinone, mp 194–196 °C, which was identified by spectral comparison with an authentic sample.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No. 7, 71341-17-8; **7**-*d*, 73333-50-3; **8**, 4388-88-9; **9**, 868-91-7; **12**, 815-66-7; **12**-d_2, 73333-51-4; **13**, 73333-52-5; **13**-*d*, 73333-53-6; **16**, 68505-99-7; **17**, 20859-13-6; **18**, 29569-89-9; **19**, 73333-54-7; **26**, 73333-55-8; **27**, 73333-56-9; **28**, 73333-57-0; **29**, 73333-58-1; **30**, 14775-42-9; **31**, 73333-60-5; **36**, 73333-61-6; **37**, 73333-62-7; **38**, 55073-87-5; **39**, 56613-17-3; *endo*-**40**, 68546-51-0; *exo*-**40**, 68546-50-9; **41**, 76-32-4; *endo*-**42**, 21488-68-6; *exo*-**42**, 22759-33-7; *endo*-**43**, 73333-63-8; *exo*-**43**, 73333-64-9; **44**, 465-29-2; LiTMP, 38227-87-1; 2,2,5,5-tetramethyl-3-hexanol, 55073-86-4.

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(29) Joshi, G. C.; Pande, L. M. *Synthesis* **1975**, 450–1.

(30) (a) Rupe, H.; Müller, F. *Helv. Chim. Acta* **1941**, *24*, 265E–82E. (b) Rupe, H.; Thommen, W. *Ibid.* **1947**, *30*, 933–47. (c) Pfrunder, B.; Tamm, Ch. *Ibid.* **1969**, *52*, 1630–43. (d) Coulombeau, C.; Rassat, A. *Bull. Soc. Chim. Fr.* **1971**, 505–16. (e) Kreiser, W. *Justus Liebigs Ann. Chem.* **1971**, *745*, 164–8.

(31) For a recent discussion of ortho metalations of activated aromatic substrates using butyllithium, see: (a) Beak, P.; Brown, R. A. *J. Org. Chem.* **1979**, *44*, 4463–4. (b) Meyers, A. I.; Lutomski, K. *Ibid.* **1979**, *44*, 4464–6, and references therein.

Reaction of Diphenyl- and Difluorocarbenes with 3,7-Dimethylenebicyclo[3.3.1]nonane[1]

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Received October 23, 1979

Both difluorocarbene and diphenylcarbene add to 3,7-dimethylenebicyclo[3.3.1]nonane to give mono- and diadducts. Products of abstraction–recombination are produced from diphenylcarbene, but neither carbene gives products of conjugate addition.

Attempts to find conjugate or 1,4-addition reactions of carbenes almost invariably fail.[3] We know of only three successes: one is the addition of triplet dicyanocarbene to cyclooctatetraene;[4] another involves the general class

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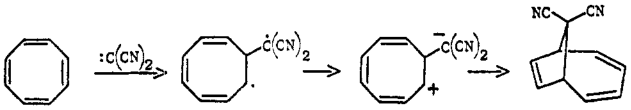
Table I. NMR Spectra and Analyses

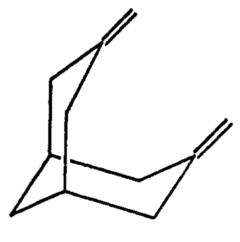
compd	^{1}H NMR[a]	^{19}F NMR[b]	analysis
2	1 H, 0.42 (s);[c] 1 H, 0.61 (s);[c] 2 H, 1.20 (s); 2 H, 1.62 (s); 8 H, 1.85-2.60 (m); 2 H, 4.62 (s); 10 H, 6.92-7.50 (m)		calcd: C, 91.67; H, 8.33 found: C, 91.77; H, 8.20
3	2 H, 0.84 (t); 2 H, 1.29 (s); 10 H, 1.4-2.4 (m); 2 H, 4.87 (s); 10 H, 7.0-7.6 (m)		calcd: C, 91.67; H, 8.33 found: C, 91.44; H, 8.39
4	2 H, 1.60 (s); 1 H, 1.76 (br s); 7 H, 1.9-2.5 (m); 2 H, 2.64 (d); 1 H, 4.06 (t); 1 H, 4.31 (s); 1 H, 4.54 (s); 1 H, 5.23 (d); 10 H, 6.95-7.5 (m)		calcd: C, 91.67; H, 8.33 found: C, 91.29; H, 8.28
6	2 H, 0.45 (br d); 10 H, 0.95-2.30 (m); ~3 H, 1.51 (s); 1 H, 5.20 (d); 10 H, 6.7-7.4 (m)		calcd: C, 91.67; H, 8.33 found: C, 91.39; H, 8.17
7	4 H, 0.85 (br d); 6 H, 1.82 (s); 6 H, 2.1-2.4 (m); 20 H, 6.9-7.7 (m)		calcd: C, 92.45; H, 7.55 found: C, 92.32; H, 7.65
10	2 H, 0.88 (t); 12 H, 1.0-2.60 (m); 2 H, 4.59 (br s)	−141.3 (t)	calcd: C, 72.70; H, 8.14 found: C, 72.61; H, 8.21
11[e]	12 H, 0.60-2.52 (m); 3 H, 1.62 (s); 1 H, 5.40 (d)	−141.7 (q)	calcd: C, 72.70; H, 8.14 found: C, 68.96; H, 7.97
12[d]	1.15 (t); 1.40 (br s); 1.62 (br s); 1.85-2.3 (m)	−141.9 (t)	calcd: C, 62.89; H, 6.50 found: C, 62.51; H, 6.22

[a] 90 MHz in $CDCl_3$, Me_4Si as internal standard. [b] 94.1 MHz in $CDCl_3$, $CFCl_3$ as internal standard. [c] These apparent singlets may be the internal peaks of an AB system. [d] Integration of the overlapping peaks of ^{1}H NMR was very difficult. [e] Mass spectrum, m/e 198.

of 1,4-additions of dihalocarbenes to norbornadienes discovered by the groups of Jefford and Klumpp;[5] finally, there is the remarkable example of Burger and Gandillon in which an intramolecular example was found.[8] The first case is unique—that is, both partners must be present. Dicyanocarbene does not generally add to dienes to give 1,4-addition, and cyclooctatetraene gives exclusively 1,2-addition with other triplet carbenes.[3] The only cogent explanation of this singular behavior comes from Hendrick, who suggested that electron transfer may occur in the originally formed diradical intermediate to give a zwitterion containing both a homotropylium ion and a well-stabilized carbanion.[9]



The second example indicates that formally unconjugated dienes, in which orbital overlap is nonetheless strong,[10] might be apt substrates for unusual addition reactions. We have examined the reactions of one such diene, 3,7-dimethylenebicyclo[3.3.1]nonane (1), with an archetypal triplet, diphenylcarbene, and with the most efficient of the halocarbenes in reaction with norbornadiene, difluorocarbene.



1

That the formally separated double bonds in 1 are in fact substantially interacting is borne out by the photoelectron[11] and ultraviolet spectra (220 nm, ε 1860). Abundant examples of the radical and cationic ring closures of 1 exist.[12] As triplet carbenes exhibit radical-like properties[13] and singlets are often powerful electrophiles,[13] our two choices of triplet diphenylcarbene and singlet difluorocarbene seem to us to provide likely sources of conjugate addition.

The reaction of diphenylcarbene with 1 seemed likely to be complex, as stereoisomeric products of both cycloaddition and abstraction reactions were to be expected. In addition, as 1 contains two potential sites for reaction,

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(1) Support by the National Science Foundation in the form of Grant CHE77-24625 is gratefully acknowledged. P.A.K. is indebted to the International Research and Exchanges Board for a fellowship.

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(3) (a) For a summary of several failures see: Jones, M., Jr.; Ando, W.; Hendrick, M. E.; Kulczycki, A., Jr.; Howley, P. M.; Hummel, K. F.; Malament, D. S. *J. Am. Chem. Soc.* **1972**, *94*, 7469. (b) Recent work is reviewed in: "Reactive Intermediates"; Jones, M., Jr., Moss, R. A., Eds.; Wiley-Interscience: New York, 1978; Vol. 1, Chapter 3.

(4) Anastassiou, A. G.; Cellura, R. P. *Tetrahedron Lett.* **1970**, 5267.

(5) For a summary see ref 3b. The recent discoveries of possible 1,4-additions of nucleophilic carbenes to 2,3-dicyanobicyclo[2.2.2]octatriene[6] and tetraarylcyclopentadienones[7] are other possible examples. However, stepwise reactions are by no means excluded.

(6) Saito, K.; Yamashita, Y.; Mukai, T. *J. Chem. Soc., Chem. Commun.* **1974**, 58.

(7) Mitsuhashi, T.; Jones, W. M. *J. Chem. Soc., Chem. Commun.* **1974**, 103.

(8) Burger, U.; Gandillon, G. *Tetrahedron Lett.* **1979**, 4281. We thank Professor Burger for communication of his work prior to publication.

(9) Hendrick, M. E., private communication, 1971. If Hendrick is correct, the stabilization afforded the carbanionic end of the dipole by the cyano groups is crucial. Thus bis(carbomethoxy)carbene fails to give the reaction [pK_a(CH_2CN_2) = 11.2, pK_a($(ROOC)_2CH_2$) = 13.5] but diacetylcarbene might [pK_a($CH_3COCH_2COCH_3$) = 9.0].

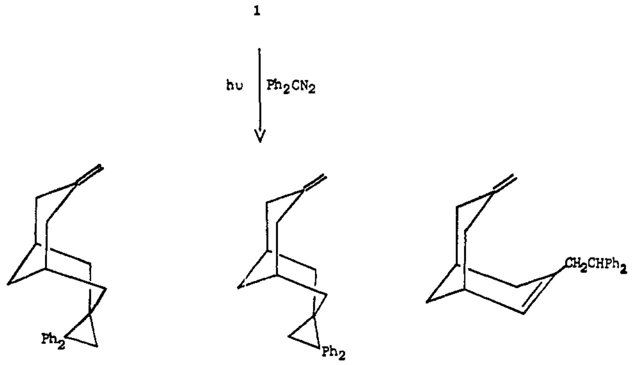
(10) Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1. Bischof, P.; Hashmall, J. A.; Heilbronner, E.; Hornung, V. *Helv. Chim. Acta* **1969**, *52*, 1745.

(11) We are grateful to Professor R. Gleiter for measuring this spectrum. Details will be forthcoming in a paper on the structure of 1 and its Ag^+ complex. Gleiter, R.; Krasutksy, P. A.; Jones, M., Jr., to be submitted for publication.

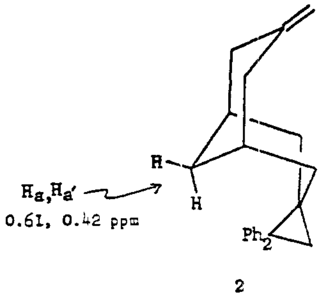
(12) Stepanov, F. N.; Krasutsky, P. A.; Yurchenko, A. G. *J. Org. Chem. USSR* (*Engl. Transl.*) **1972**, *12*, 1192. Stepanov, F. N.; Krasutsky, P. A.; Rudenok, L. I. *Ibid.* **1972**, *12*, 2667. Yurchenko, A. G.; Zosim, L. A.; Dovgan, N. L.; Verpovsky, N. S. *Tetrahedron Lett.* **1976**, 4843.

(13) (a) Kirmse, W. "Carbene Chemistry"; Academic Press: New York, 1971; Vol. 2. (b) "Carbenes"; Jones, M., Jr., Moss, R. A., Eds.; Wiley-Interscience: New York, 1973; Vol. I. (c) *Ibid.* Vol. II.

both mono- and diadducts could appear. Both these expectations were borne out. Irradiation through Pyrex of a benzene solution of 1 and diphenyldiazomethane (3:1 ratio) for 15 h led to a colorless solution from which a series of products could be isolated by crystallization and chromatography on silica gel (see Experimental Section for details). Compounds 2, 3, and 4 are produced in 48.4% yield in the ratio of 58:9:33. Mass spectrometry and elemental analyis established the three compounds as 1:1 adducts. Analysis of the ^{1}H NMR spectra of 2 and 3 allows their identification as the isomeric cyclopropanes formed by cycloaddition of diphenylcarbene to one of the double bonds. Close scrutiny permits a detailed structural analysis. In 2 a pair of one-proton signals appears at unusually high field (δ 0.61 and 0.42). The symmetry of the two possible adducts differentiates only the bridge hydrogens—*all* others must appear in pairs. Thus the high-field signals must belong to H_a and $H_{a'}$. The extraordinary shift to high field of these bridge protons allows us to identify 2 as the isomer in which the diphenylcarbene has entered syn to the one-carbon bridge. By default the isomer of 2 must be 3. Here, as in 2, the assignment of structure to the boat–chair arrangement seems reasonable, as steric considerations render the chair–chair isomer untenable. In 3 as in 2 there is a two-proton high-field signal, this time a triplet at δ 0.84 (*J* = 10 Hz). Although this time we cannot be as certain as with 2, a reasonable assignment is the proton pair H_b. Compound 4 contains three vinyl hydrogens, two of the terminal methylene type appearing as two broad singlets at δ 4.31 and 4.54 and a third, also a doublet (*J* = 6 Hz), assigned to H_c at δ 5.23. A single proton appears as a triplet at δ 4.06 (H_d) and is clearly coupled to a two-proton doublet at δ 2.64 (H_e). Compound 4 is the product of hydrogen abstraction and recombination.



2 3 4



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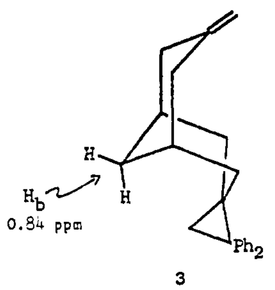

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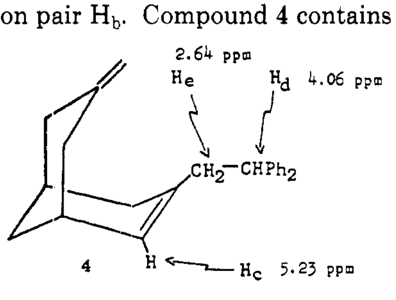
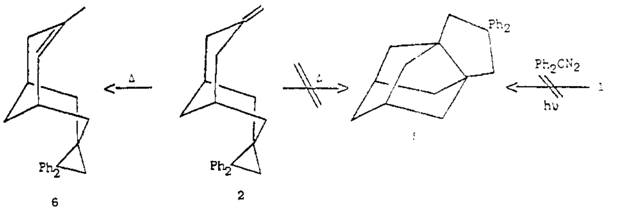
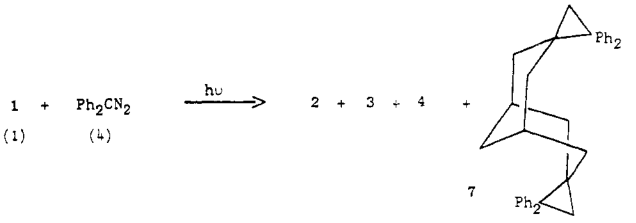


4

The reaction of diphenylcarbene and simple olefins has been investigated,[14] and although many substituted alkenes give overwhelmingly the hydrogen abstraction–recombination process, terminal olefins react predominantly by addition. The most appropriate model for 1 is methylenecyclohexane, and here the addition/abstraction ratio is 73:27. This compares remarkably well to a (2 + 3)/4 ratio of 67:33. Thus the simple 1:1 adducts do not include substantial amounts of the product of hypothetical "conjugate" addition, 5, nor are we able to rearrange the simple adduct 2 to 5. Neither heating in degassed diglyme nor acid-catalyzed isomerization led to 5. Instead an excellent yield of a new isomer, 6, was obtained. The new compound 6 retains the two upfield one-proton singlets of 2, but the signal for the terminal methylene protons has been replaced by a single proton resonating at δ 5.20. Compound 6 absorbs 1 mol of hydrogen on catalytic hydrogenation to give a new compound lacking simple carbon–carbon double bonds.



For better isolation of the diadducts, a photolysis was run in which the ratio of 1 to diphenyldiazomethane was 1:4. Once more, a series of crystallizations and chromatographic separations led to 2, 3, and 4 (12.5%, ratio 58:16:26), but substantial amounts of diadducts could also be obtained (26% yield of a mixture of isomers). From this a pure isomer, 7, could be isolated. Although elemental analysis, mass spectroscopy, and the absence of olefinic protons clearly establishes 7 as a dicyclopropane, the stereochemistry is not certain. Analysis of the ^{1}H NMR spectrum makes the structure shown the most likely. Other isomers remain in the mother liquors from which 7 was isolated, but as little appeared to be gained from a further analysis, the question of their structures was not pursued beyond an examination of the ^{1}H NMR spectra which indicated that the remaining isomers were predominantly formed by abstraction–recombination.



Thus no evidence of unusual addition processes was obtained in the reaction of diphenylcarbene with 1. Compound 1 behaves as a normal olefin in reactions with this carbene.

We wondered if the same would be true for difluorocarbene, a species known to add efficiently to norbornadiene to give 8.[3b,5] As in norbornadiene,[10] the double bonds in 1 are interacting,[11] and we hoped that formation of 9 might be observed.

We chose as a difluorocarbene source the reagent produced by the action of fluoride ion and triphenyl(bromo-

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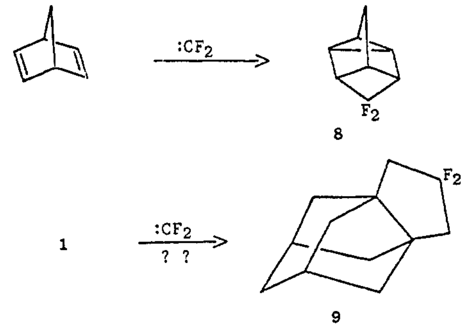
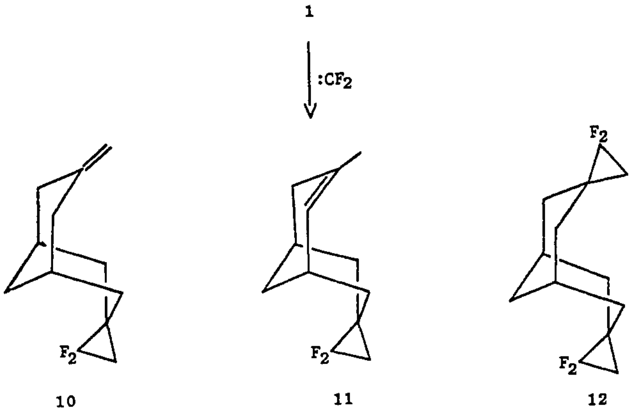
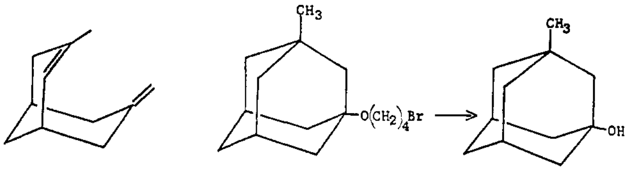
[14] Baron, W. J.; Hendrick, M. E.; Jones, M., Jr. *J. Am. Chem. Soc.* 1973, *95*, 6286.



difluoromethyl)phosphonium bromide.[15] Reaction of this reagent with 1 in either tetrahydrofuran or acetonitrile resulted in two 1:1 adducts (10 and 11) and a single diadduct (12) as revealed by gas chromatography.



In tetrahydrofuran, for which only normal drying precautions were taken, ca. 40% of ether cleavage products 13 and 14 and substantially isomerized starting material (15, 35%) were obtained.[16] Compound 14 was shown to be a product of hydrolysis of 13. When extraordinary precautions were taken to prepare superdry reagents and to exclude moisture (see Experimental Section), the amounts of 13 and 14 were substantially reduced although isomerization to 15 still occurred (ca. 14%). Under dry conditions the ratio of 10/11/12 was 56:1:11 in an overall yield of 61%.



Compound 10 showed only a two-proton signal in the ^{1}H NMR spectrum for the exocyclic methylene protons (δ 4.59) and thus is a monocyclopropane. A high-field triplet integrating for two protons (J = 9 Hz) centered at δ 0.88 was matched in the ^{19}F NMR spectrum by a broadened triplet at −141.3 ppm from CFCl$_3$ (J = 9 Hz) and is thus assigned tentatively to the cyclopropyl hydrogens. A pair of one-proton singlets emerges from a broad multiplet at δ 1.12 and 1.28. If these represent the bridge hydrogens, then a boat–chair form for 10 is indicated as with 2, but we cannot be certain of the details of this structure.

Compound 11 shows but a single doublet proton signal at δ 5.40. In addition, a sharp three-proton signal appears at δ 1.62, an appropriate position for a methyl group on a double bond.

Diadduct 12 shows no vinyl protons, and symmetry is implied by a four-proton triplet (J = 9 Hz) centered at δ 1.15 and assigned to the cyclopropyl protons. The ^{19}F NMR spectrum shows a corresponding triplet (J = 9 Hz) centered at −141.9 ppm from CFCl$_3$. The NMR spectra argue for a symmetrical structure, and we think the "exo–exo" compound shown is more likely than the "endo–endo". Although assignment as a symmetrical diadduct is safe, we cannot absolutely eliminate this last structure.

We have examined >95% of the volatile products of this reaction, and clearly, no substantial amount of 9 is produced. Thus, 1 behaves once more as a typical olefin and does not take part in special addition reactions.

Experimental Section

General Methods. Elemental analyses were performed by Atlantic Microlab, Inc. Infrared spectra were obtained on a Perkin-Elmer Model 238B spectrometer, ^{19}F NMR spectra were recorded on a Varian XL-100 spectrometer, and ^{1}H NMR spectra were recorded on a Perkin-Elmer R32 spectrometer. Melting points were recorded on a Thomas-Hoover apparatus in capillary tubes.

Irradiation of Diphenyldiazomethane in a Benzene Solution of 3,7-Dimethylenebicyclo[3.3.1]nonane (3:1 Ratio). A solution of 6.9 g of 3,7-dimethylenebicyclo[3.3.1]nonane (1) and 2.9 g of diphenyldiazomethane in 40 mL of benzene was irradiated for 15 h through Pyrex with a 450-W medium-pressure Hanovia lamp. After the irradiation was complete, the benzene was removed and 50 mL of hexane added to the slightly yellow oily residue. When the mixture was allowed to stand for 4 h in a refrigerator, 0.6 g of azine precipitated (mp 164–165 °C). Unreacted starting olefin (3.25 g) was recovered by evaporation at 0.05 torr and 50 °C. The residue (4.31 g) was chromatographed on silica gel with pentane–2% ether as eluent. From the silica gel column the last residues of unreacted 1 were collected as a first fraction. The second fraction (2.44 g) contained a mixture of 2 (28%), 3 (4.4%), and 4 (16%). A third fraction (1.1 g) contained a mixture of diadduct, tetraphenylethane, and azine. A further fraction containing 0.17 g of polymeric material was obtained by washing the silica gel column with pure ether.

The monoadducts (2, 3, and 4) can be separated by chromatography on a column containing silica gel impregnated with 5% AgNO$_3$. Pentane–2% ether eluted 1.6 g of oily crystals which was shown by ^{1}H NMR spectroscopy to contain 87% 2 and 13% 3. Recrystallization of 1.6 g of this mixture from 5 mL of hexane yielded 1.05 g of pure 2 as white rhombic crystals (mp 146–147 °C). The mother liquors (0.55 g) contained 2 and 3 in the ratio 62:38. Repeated chromatography using a column containing 5% AgNO$_3$ on silica gel and alumina yielded a mixture of 2 and 3 in the ratio 20:80. Recrystallization from hexane yielded pure 3 (mp 140–142 °C).

Compound 4 was obtained from the original chromatography on 5% AgNO$_3$-impregnated silica by elution with benzene–methanol (2:1). After evaporation of solvent, 1.4 g of white crystals were obtained. This was a mixture of a AgNO$_3$ complex of 4 and AgNO$_3$. Stirring with 30 mL of 5% NH$_4$OH for 0.5 h, followed by extraction with ether, yielded 0.7 g of pure 4 as a colorless oil.

Irradiation of Diphenyldiazomethane in a Benzene Solution of 3,7-Dimethylenebicyclo[3.3.1]nonane (1:4 Ratio). A solution of 3.8 g of 1 and 17.3 g of diphenyldiazomethane in 70 mL of benzene was irradiated through Pyrex as before for 42 h at which time the color had changed from red to yellow. The benzene was evaporated and 80 mL of hexane added. The mixture was allowed to stand in a refrigerator for 4 h and was filtered to yield 12.9 g of azine. Chromatography on silica gel of the 6.9 g of residue with heptane–2% ether as eluent yielded several fractions. The first fraction contained 0.34 g of unreacted 1. The second fraction (1.76 g) contained the products of monoaddition 2, 3, and 4 in the ratio 58:16:26. A mixture of diadducts (4.3 g) was obtained as a third fraction along with tetraphenylethane and tetraphenylethylene by further elution. A last fraction (0.4

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(15) Seyferth, D., Chapter 3 in ref 13c.

(16) We hope to report separately on these compounds.

g) of polymeric material was obtained by elution with pure ether.

The third fraction is further chromatographed on silica gel impregnated with 5% $AgNO_3$ with pentane-benzene (3:2) as eluent. A first fraction (1.1 g) was recrystallized twice from hexane to give 0.25 g of pure **7** (mp 200-202 °C). A second fraction (0.6 g) of tetraphenylethane was obtained followed by 2.2 g of slightly yellow crystals which could be shown to be a mixture of diadducts.

Thermal Rearrangement of 2. A solution of 0.25 g of **2** in 10 mL of diglyme was sealed in a Pyrex tube after degassing by the freeze-thaw method. After being heated to 220 °C for 30 h, the tube was cooled and opened, and the contents were poured into 40 mL of water. The structure was extracted with 60 mL of benzene and the benzene solution washed several times with water. Crystallization from this benzene solution yielded 0.22 g of **6** (mp 103-106 °C).

Acid-Catalyzed Isomerization of 2. A solution of 0.1 g of **2** in 15 mL of CCl_4 with 0.1 mL of CF_3COOH was refluxed for 0.5 h. The solvent was washed with water and dried over sodium sulfate. Crystallization yielded 0.04 g of **6** (mp 103-106 °C).

Hydrogenation of 6. A solution of 0.1 g of **6** in 15 mL of heptane was hydrogenated at 3 atm of H_2 over 0.1 g of PtO for 15 h. Filtration and evaporation of solvent yielded 0.09 g of oily crystals from which 0.05 g of hydrogenated product could be obtained after crystallization from hexane (mp 133-134 °C).

Reaction of 1 with Triphenyl(bromodifluoromethyl)phosphonium Bromide in Tetrahydrofuran at Room Temperature. To a solution of 2.7 g of triphenylphosphine in 15 mL of absolute tetrahydrofuran was added 2.7 g of dibromodifluoromethane. After the rapid exothermic formation of the phosphonium salt ceased, stirring was continued for 40 min, at which point 1.6 g of **1** was added rapidly, followed by 2.6 g of KF. Stirring was maintained at room temperature for 120 h, and the mixture was filtered and washed with fresh tetrahydrofuran. The solvents were evaporated at reduced pressure, 30 mL of pentane was added, and the mixture was allowed to stay in a refrigerator for 1 h. The mixture was then filtered and evaporated to yield 2.25 g of an oily material which could be chromatographed on silica gel with heptane as eluent. The first fraction contained 0.32 g of recovered **1** and isomerized **1** (**15**) in the ratio 35:65. Gas chromatography on a 3-ft SE-30 column at 105 °C separated the components. A second fraction contained a mixture of **10** and **11** in the ratio 88:12 as revealed by gas chromatography on a 10-ft, 5% Dexil column operated at 180 °C. Further elution of the column with pentane-ether (80:20) yielded **13** and **14.**

Reaction of 1 with Triphenyl(bromodifluoromethyl)phosphonium Bromide in Tetrahydrofuran under "Superdry" Conditions. Before the reaction, triphenylphosphine was dried at 60 °C and 0.5 torr for 4 h. KF was dried at 250 °C and 2 torr for 4 h, and tetrahydrofuran was freshly distilled. The reaction was carried out in a carefully closed vessel.

To a solution of 1.1 g of triphenylphosphine in 10 mL of THF freshly distilled from LAH was added 0.9 g dibromodifluoromethane. After the rapid exothermic formation of phosphonium salt, the stirring was continued for 40 min, at which time 0.47 g of **1** followed by 0.93 g of KF was added. Stirring was maintained at room temperature for 200 h. Analysis by gas chromatography on a 10-ft, 5% Dexil column at 180 °C showed **15** (14%), **1** (18%), **11** (1%), **10** (56%), and diadduct **12** (11%).

Reaction of 1 with Triphenyl(bromodifluoromethyl)phosphonium Bromide in Acetonitrile at Room Temperature. To a solution of 2.2 g of triphenylphosphine in 25 mL of freshly distilled acetonitrile was added 1.8 g of dibromodifluoromethane. After rapid formation of the phosphonium salt, stirring was continued for 30 min, and 1.0 g of **1** and 1.8 g of KF were added. Stirring was maintained in the carefully closed flask for 30 h. Gas chromatography on a 10-ft, 5% Dexil column at 180 °C showed **1** (17%), **10** (59%), **12** (19%), and 5% of an unknown compound.

Acknowledgment. Our thanks go to Mary W. Baum, who was most helpful in determining NMR spectra.

Registry No. **1**, 770-14-9; **2**, 73367-56-3; **3**, 73395-34-3; **4**, 73367-57-4; **6**, 73367-58-5; **7**, 73367-59-6; **10**, 73367-60-9; **11**, 73367-61-0; **12**, 73367-62-1; **13**, 73367-63-2; **14**, 702-81-8; **15**, 59039-27-9; diphenyldiazomethane, 883-40-9; triphenyl(bromodifluoromethyl)phosphonium bromide, 58201-66-4.

Nonadditive Carbon-13 Nuclear Magnetic Resonance Substituent Shifts in 1,4-Disubstituted Benzenes. Nonlinear Resonance and Shift-Charge Ratio Effects[1]

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Received February 5, 1980

Meta and para carbon-13 substituent chemical shifts are reported for fourteen series of para-disubstituted benzenes (p-C_6H_4Y) at high dilution in deuteriochloroform. Series with one substituent (Y) fixed and the other one variable (p-X) have been examined for each of the following substituents: NMe_2, NH_2, OMe, F, Cl, Br, Me, H, CF_3, CN, CO_2Et, COMe, CHO, and NO_2. The substituent effects are strongly nonadditive; the fixed group Y substantially changes the para carbon substituent chemical shifts (C_p-SCS). The results are interpreted in terms of the local π-electron density at the para carbon. Through the use of theoretical calculations of π electronic charges and dual substituent parameter methods, the common Y group is shown to exert two major influences on C_p-SCS values. First, the Y group gives rise to a characteristic sensitivity effect, called the shift-charge ratio (SCR), which is the C_p-SCS value divided by the corresponding para X substituent induced π charge at carbon. Values of the SCR are found to range from ~125 to 250 ppm/e. Second, the π-electron delocalization of the para X substituent may be either enhanced (conjugative effect) or reduced (repulsive π-electron saturation), depending upon the "electron demand" exerted by the Y group. These resonance effects are accurately described by a nonlinear relationship with the $\sigma_R{}^0$ value of the para substituent, involving an "electron-demand" parameter, ϵ, for the Y group. The meta carbon C_m-SCS data offer further confirmation of these effects as well as show that small resonance effects operate at the meta positions which are of opposite sign to those for the corresponding para positions. The detailed analysis obtained with the present results was made possible through the use of a broad range of substituent electronic properties, the relatively high sensitivity of the C_p-SCS measurements, and the use of very dilute solutions of a relatively inert solvent, $CDCl_3$.

Carbon-13 chemical shift measurements have been used extensively for studying the electronic properties of aromatic systems.[3] Since ^{13}C substituent chemical shifts (SCSs) for fixed distant sites are related to electronic ef-

0022-3263/80/1945-2429$01.00/0 © 1980 American Chemical Society