The Reactions of Tetrafluorohydrazine with Some Cyclic Polyolefins

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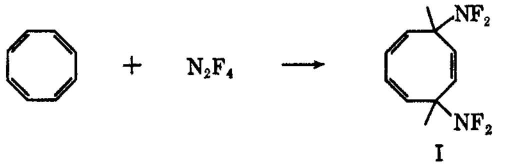
Tetrafluorohydrazine undergoes addition to cyclooctatetraene to give 5,8-bis(difluoramino)-1,3,6-cyclooctatriene, the product of 1,4 addition. Likewise, reaction of tetrafluorohydrazine with 6,6-diphenylfulvene gives the two 1,4 adducts, *cis*- and *trans*-3,5-bis(difluoramino)-4-benzhydrylidenecyclopentene. Addition to acenaphthylene affords the *cis*- and *trans*-1,2-bis(difluoramino)acenaphthenes and 1,3-cyclooctadiene gives a mixture of 1,2 and 1,4 adducts. The evidence from which the structures were deduced is presented, and the stereochemistry of the addition processes is commented upon.

Recently Cerfontain has reported that tetrafluorohydrazine undergoes symmetrical addition, in solution or in the gas phase, to stilbene, styrene, and anthracene to give bis(difluoroamines).[2a] Trotman-Dickenson, Kerr, and Dijkstra have observed the addition of tetrafluorohydrazine to ethylene, propylene, and several other simple substituted olefins to give 1,2-bis(difluoramino)alkanes and have studied the kinetics of the addition process.[2b] The known dissociation of tetrafluorohydrazine to difluoramino radicals at ordinary temperatures,[3] the ease with which the addition reaction proceeds in the gas phase,[2a] the acceleration of the reaction by common free-radical initiators,[2b] and the results of kinetic studies[2b] leave little doubt that the addition proceeds by a free-radical mechanism. Difluoramino radicals have recently been shown to be capable of intercepting triphenylmethyl and 2-cyano-2-propyl radicals[4] as well as α-alkoxyalkyl radicals produced by hydrogen abstraction from ethers.[5]

We have been interested for some time in the reactions of free radicals with nonbenzenoid aromatic compounds such as cyclooctatetraene and the fulvenes. While cyclooctatetraene does not possess aromatic character to a significant extent, it is usually included in discussions of nonbenzenoid aromatic compounds[6a] and, moreover, is prone to undergo interesting rearrangements in its reactions with most reagents.[6b] Previous investigations of the reaction of cyclooctatetraene with common radical sources led to addition and rearrangement products, albeit in low yield,[7] and the relatively high concentration of radicals present in tetrafluorohydrazine appeared to provide a convenient new system for study. Also the reactions of cyclooctatetraene,[8a] 6,6-diphenylfulvene,[8a] and acenaphthylene[8b] with dinitrogen tetroxide have recently been investigated and in view of the similarities of N_2O_4 to N_2F_4 (in particular dissociation to radicals under mild conditions) it seemed of interest to compare the results of the two reagents in these systems. The present report concerns the products of the reactions of tetrafluorohydrazine with the three above-mentioned hydrocarbons.

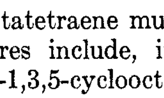
Cyclooctatetraene.—It has presently been found that cyclooctatetraene and tetrafluorohydrazine react in chlorobenzene solution at 60–70° to give 5,8-bis(difluoramino)-1,3,6-cyclooctatriene (I, eq 1) in 65–70% yield. The product was purified by trap-to-trap distillation; although it decomposes readily on warming in the presence of air or moisture, it could be stored at −20° under nitrogen for extended periods.



I

(1)

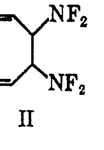
From its elemental analysis and spectral properties the product of reaction of tetrafluorohydrazine with cyclooctatetraene must be a 1:1 adduct. Its possible structures include, in addition to I, 7,8-bis(difluoramino)-1,3,5-cyclooctatriene (II), 1,8-bis(difluoramino)-octatetraene (III), derivatives of bicyclo[4.2.0]octadiene (IV and V), and those containing benzene or cycloheptatriene groups.[9] The ultraviolet spectrum of the present adduct exhibits a shallow maximum at 261 mμ (ε ~2500), most consistent with structures I or II.[10] The nmr spectrum of the adduct strongly suggests that structure I is correct. The spectrum consists of a doublet of area 2 at τ 3.63 (J = 9.9 cps), a singlet of area 2 at 4.11, a pair of doublets of total area 2 at 4.46 (J = 9.9 cps, J' = 6.8 cps), and a broadened triplet of doublets of area 2 at 5.25 (J = 26.4 cps, J' =



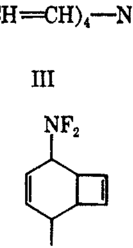
II

$F_2N—(CH{=}CH)_4—NF_2$

III



IV



V

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[1] Department of Chemistry, Rice University, Houston, Texas 77001.

[2] (a) H. Cerfontain, *J. Chem. Soc.*, 6602 (1965); (b) A. F. Trotman-Dickenson, J. Kerr, and A. J. Dijkstra, *ibid., A*, 582 (1966).

[3] (a) F. A. Johnson and C. B. Colburn, *J. Am. Chem. Soc.*, **83**, 3043 (1961); (b) F. A. Johnson and C. B. Colburn, *J. Chem. Phys.*, **33**, 1869 (1960); (c) L. H. Piette, F. A. Johnson, K. A. Booman, and C. B. Colburn, *ibid.*, **35**, 1481 (1961).

[4] R. C. Petry and J. P. Freeman, *J. Am. Chem. Soc.*, **83**, 3912 (1961).

[5] M. J. Cziesla, K. F. Mueller, and O. Jones, *Tetrahedron Letters*, 813 (1966).

[6] (a) See, for example, D. Ginsburg, Ed., "Nonbenzenoid Aromatic Compounds," Interscience Publishers, Inc., New York, N. Y., 1959; (b) G. Schröder, "Cyclooctatetraen," Springer Verlag, Berlin, 1964.

[7] J. L. Kice and T. S. Cantrell, *J. Am. Chem. Soc.*, **85**, 2298 (1963).

[8] (a) H. Shechter, J. J. Gardikes, T. S. Cantrell, and G. V. D. Tiers, *ibid.*, in press; (b) H. Shechter and T. S. Cantrell, *J. Org. Chem.*, in press.

[9] For a summary of the types of structures produced by addition of various reagents to cyclooctatetraene, see R. A. Raphael, ref 6a, Chapter X.

[10] Bicyclo[4.2.0]octadiene and cycloheptatriene chromophores possess strong absorption maxima in the 265–275-mμ region. See M. Kamlet and H. E. Ungnade, Ed., "Organic Electronic Spectral Data," Interscience Publishers, Inc., New York, N. Y., 1960: Vol I, p 203; Vol II, p 102.

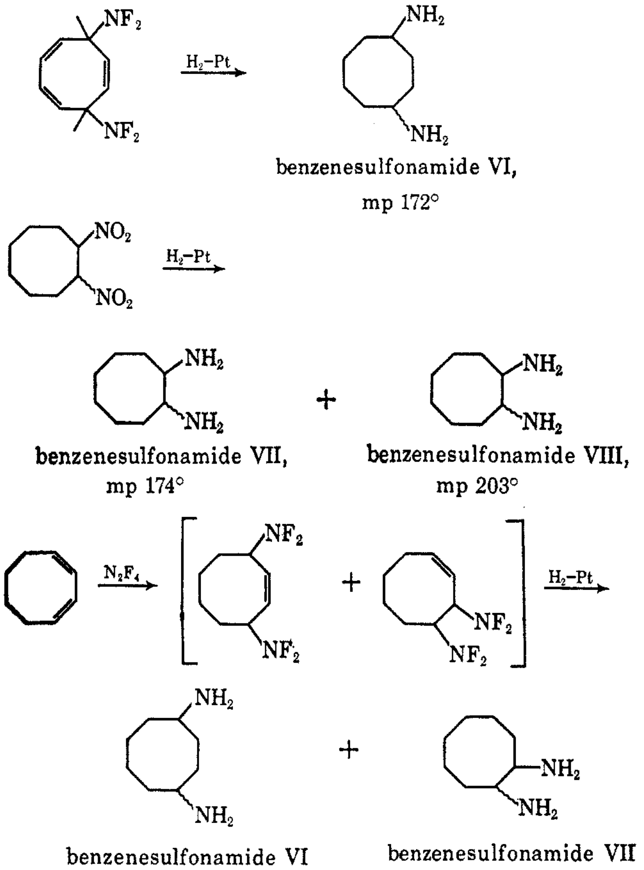
6.8 cps). This spectrum clearly excludes benzenoid, cycloheptatriene, and bicyclo[4.2.0]octadiene structures; the absence of aryl hydrogen signals at τ 2.0–3.5 eliminates the presence of a benzene ring, and the lack of signals in the 5.5–7.5 region indicates the absence of tertiary hydrogens on carbon atoms which do not bear difluoramino groups, thus ruling out any bicyclooctadiene or cycloheptatriene structural possibilities. The pattern of vinyl hydrogen signals observed is quite similar, except for small differences in the magnitude of the coupling constants, to the vinyl region of the spectrum of 5,8-bis(2-cyano-2-propyl)1,3,6-cyclooctatriene, the product of 1,4-homolytic addition of 2-cyano-2-propyl radicals and cyclooctatetraene.[7] The tertiary hydrogens of I give rise to a triplet of doublets since they are each coupled to the two fluorine atoms on the adjacent nitrogen as well as to the neighboring hydrogens on C-1 and C-4; as in the case of the previously reported cyclooctatriene mentioned above, little or no coupling is observed with the hydrogens on C-6 and C-7 since the dihedral angle in question is probably about 80°.[11]

Chemical proof of the correctness of structure I was obtained by characterization of the product of catalytic reduction. Hydrogenation of I over platinum in acetic acid resulted in the rapid uptake of 7 mole equiv of hydrogen. The hydrogenolysis of each difluoramino group of I to an amino group and two molecules of HF requires 2 moles of hydrogen, or 4 moles for two NF_2 groups, and thus a total of 7 moles for complete reduction of I to a diaminocyclooctane.

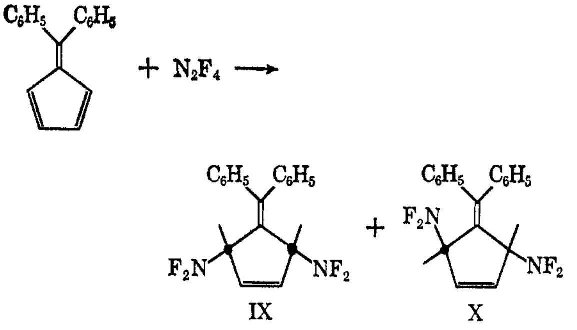
The oily diamine obtained by work-up of the reaction mixture was converted to a dihydrochloride, mp 290–296° dec, and to a bis(benzenesulfonamide), mp 172–173° (VI). That this bis(benzenesulfonamide) is a derivative of one of the stereoisomeric 1,4-diaminocyclooctanes was shown in the following way. Reduction of the mixture of 1,2-dinitrocyclooctanes obtained by addition of dinitrogen tetroxide to cyclooctene gave the two isomeric 1,2-diaminocyclooctanes. These were converted to bis(benzenesulfonamides) of mp 174–175° (VII) and 203–204° (VIII). Both of these derivatives were different from VI, the bis(benzenesulfonamide) obtained by degradation of I (Chart I). Addition of tetrafluorohydrazine to 1,3-cyclooctadiene gave a mixture of bis(difluoramino)cyclooctenes resulting from 1,2 and 1,4 addition. These were reduced to the diamines and converted to the benzenesulfonamides. There were thus obtained two diamines: (1) a diamine whose bis(benzenesulfonamide) was identical with VII, obtained previously as described above and which must be one of the 1,2-diaminocyclooctanes; (2) a diamine whose dihydrochloride and bis(benzenesulfonamide) were identical with the derivatives of the diamine obtained by degradation of I. Since this benzenesulfonamide (VI) and hydrochloride are not derived from either of the two 1,2-diaminocyclooctanes, they must be derivatives of one of the 1,4-diaminocyclooctanes; thus the cyclooctatetraene–tetrafluorohydrazine adduct must have the gross structure I.

No direct experimental evidence is available on the stereochemistry of I; however, it appears more likely that the difluoramino groups have the *trans* orientation since examination of models reveals that in a *cis*-5,8-disubstituted 1,3,6-cyclooctatriene one substituent must occupy a quasi-axial position and would be subject to serious steric interference with the atoms on the opposite side of the ring as well as with the π-electron clouds of the transannular double bonds.[11]

CHART I



6,6-Diphenylfulvene.—Reaction of tetrafluorohydrazine with 6,6-diphenylfulvene in chlorobenzene solution proceeded rapidly at 40° to give the adducts 4-benzhydrylidene-*cis*-3,5-bis(difluoramino)cyclopentene (IX, 29%) and 4-benzhydrylidene-*trans*-3,5-bis(difluoramino)cyclopentene (X, 7%, eq 2). Isomer X is converted to the *cis* compound IX on heating in benzene solution. Both compounds are stable indefinitely in the solid state at room temperature.



(2)

The elemental analyses, molecular weights, and absorption spectra of IX and X support the assigned structures. The infrared spectra of IX and X show strong bands at 11–13 μ, characteristic of difluoramines. Compound IX shows an ultraviolet absorption maximum at 250 mμ (ϵ 10,200); the spectrum of X shows a

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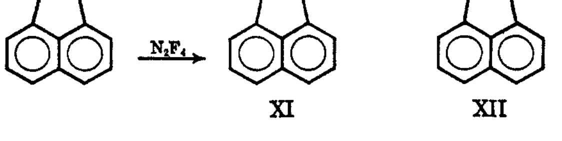
(11) See ref 7 for a discussion of this point.

maximum at 251 mμ (ϵ 10,000). These spectra are similar to that of 1,1-diphenylethylene [$\lambda_{\max}$ 251 mμ (ϵ 12,000)][12a] but quite different from that of 3-benzhydrylidenecyclopentene [$\lambda_{\max}$ 290 mμ (ϵ 19,000)].[12b] It is thus apparent that IX and X possess the 1,1-diphenylethylene chromophore and are the stereoisomers resulting from 1,4 addition of tetrafluorohydrazine across the five-membered ring of diphenylfulvene. The stereochemistries of IX and X were assigned on the basis of dipole moments. The experimentally determined dipole moments of IX and X were 4.7 and 1.3 D., respectively. The group moment of the difluoramino group has not appeared in the literature. However, the isomer of 3,5-bis(difluoramino)-4-benzhydrylidenecyclopentene with the difluoramino groups *cis* would certainly have a higher dipole moment than the corresponding *trans* isomer; hence, isomer IX is assigned the *cis* configuration and isomer X is given the *trans* structure. From these data it can be calculated, using bond angles derived from measurements of Dreiding models, that the group moment of the difluoramino group is *ca.* 2.7 D.

The predominantly *cis* addition of tetrafluorohydrazine is not surprising in view of the isolation of a good yield of the *cis* adduct, but no *trans* from the addition of dinitrogen tetroxide to diphenylfulvene.[8a] The stereochemical course of the latter reaction could be reasonably explained by the postulation of an initially formed charge-transfer complex of dinitrogen tetroxide with the electron-rich ring of the fulvene; this complex undergoes electronic reorganization to yield the *cis* adduct. In support of this explanation are reports of the existence of complexes of N_2O_4 with electron-rich aromatic compounds.[13] It would seem plausible that tetrafluorohydrazine might behave as an electron-deficient species in many reactions, and thus react in the same manner as dinitrogen tetroxide since the fluorine atoms are even more electronegative than oxygen. The *trans* isomer isolated may be formed by a different, stepwise mechanism, or alternatively, from isomerization of the *cis* isomer to an equilibrium mixture of the *cis* and *trans* forms.

Acenaphthylene.—The reaction of tetrafluorohydrazine with acenaphthylene in chlorobenzene solution proceeded rapidly at 50–55° to give a mixture of *cis*-1,2-bis(difluoramino)acenaphthene (XI, 30–34%, mp 106–107°), and *trans*-1,2-bis(difluoramino)acenaphthene (XII, 40–47%, mp 49–50°, eq. 3). The gross structure of XI and XII is apparent from their analytical and molecular weight data, and from their ultraviolet spectra ($\lambda_{\max}$ 293 and 296 mμ, respectively (ϵ *ca.* 6000). The lower melting isomer (XII) was tentatively assigned the *trans* structure, since in the case of 1,2-disubstituted acenaphthene isomer pairs of firmly established stereochemistry, the *cis* compounds melt 48–60° higher than the corresponding *trans* isomers.[14]



XI XII (3)

Insufficient material was available for a standard dipole moment determination, but preliminary measurements of the dielectric constants and refractive indices of solutions of XI and XII gave larger values for the solutions of XI, indicating that it is indeed the *cis* isomer. Attempts at catalytic hydrogenolysis of XI and XII to the corresponding 1,2-diaminoacenaphthenes, whose configuration could be confirmed by chemical means, gave only intractable tars.

Experimental Section

All melting points were determined on a Fisher-Johns block and are corrected. The infrared spectra were obtained on a Perkin-Elmer Model 137 Infracord. The nmr spectra were obtained on a Varian HR-60 (F^{19} nuclei) or on a Varian A-60 (protons). Tetrafluorohydrazine was manufactured by the Air Products Co. and stated to be of 97% purity was used as received.

Reaction of Cyclooctatetraene with Tetrafluorohydrazine.—A solution of freshly distilled cyclooctatetraene (3.41 g, 0.033 mole) and azobis(isobutyronitrile) (0.02 g, 0.15 mmole) in dry chlorobenzene (15 ml) in a 1-l., round-bottom flask was cooled to −78° and degassed at 10^{-4} mm by three freeze–pump–thaw cycles on a vacuum line. The flask was warmed to 75–80° under *ca.* 1 atm of tetrafluorohydrazine and the contents were stirred magnetically until consumption of N_2F_4 had ceased (*ca.* 2 hr). The flask was cooled to room temperature and the reaction mixture was fractionated by trap-to-trap distillation. Unchanged N_2F_4 was retained by the −196° trap, while the chlorobenzene and a trace of unreacted cyclooctatetraene were found in the −78° traps. The 0° trap contained the adduct 5,8-bis(difluoramino)-1,3,6-cyclooctatriene (I, 4.32 g, 68%) as a faintly yellow oil. I could be distilled in a conventional apparatus at 0.01 mm (bath temperture 35–40°) with considerable losses owing to resinification. Repeated trap-to-trap distillation on the vacuum line gave a sample of colorless material whose infrared spectrum, however, was identical with that of the sample of I after one distillation.

Anal. Calcd for $C_8H_8F_4N_2$: C, 46.15; H, 3.85; N, 13.46. Found: C, 45.78; H, 3.85; N, 12.72.

The infrared spectrum of I exhibited strong N–F absorption at 10.5–12.3 μ; other significant bands were at 3.28, 6.11, 6.30, and 6.76, 14.1, and 14.43 μ. The ultraviolet spectrum showed $\lambda_{\max}$ 261 mμ (ϵ 2400) and $\lambda_{\min}$ 241 mμ (ϵ 2100). The nmr spectrum consisted of signals at τ 3.63 (2 H doublet, J = 9.9 cps), 4.01 (2 H singlet), 4.46 (2 H pair of doublets, J = 9.9 cps, J' = 6.8 cps), and 5.25 (2 H broadened triplet of doublets, J = 26.4 cps, J' = 6.8 cps).

Reaction of Cyclooctene with Tetrafluorohydrazine.—Cyclooctene (5.3 g, 0.050 mole) was treated with tetrafluorohydrazine in the manner described for cyclooctatetraene, except that the reaction mixture was heated at 85–90° for 4 hr. The material collected in the 0° trap was redistilled at 0.01 mm (bath temperature 40–45°) to give 7.5 g (0.036 mole, 72%) of 1,2-bis(difluoramino)cyclooctane as a colorless oil, n^{25}_{D} 1.4367.

Anal. Calcd for $C_8H_{14}F_4N_2$: N, 13.09. Found: N, 12.88.

Reaction of 1,3-Cyclooctadiene with Tetrafluorohydrazine.—The reaction between 1,3-cyclooctadiene (6.2 g, 0.06 mole) and tetrafluorohydrazine was carried out as described above. The reaction mixture was heated at 55–60° for 1.5 hr. Fractionation on the vacuum line and redistillation gave a mixture of 3,8-bis(difluoramino)cyclooctene and 3,4-bis(difluoramino)cyclooctene as a colorless oil, bp 38–45° (bath temperature) (0.01 mm), n^{25}_{D} 1.4419.

Anal. Calcd for $C_8H_{12}N_2F_4$: C, 45.28; H, 5.34; N, 12.63. Found: C, 45.25; H, 5.65; N, 13.02.

The nmr spectrum of the mixture exhibited a series of complex overlapping multiplets for olefinic hydrogens at τ 3.8–4.5; no estimate of the composition of the mixture was possible.

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(12) (a) E. A. Braude and W. F. Forbes, *J. Chem. Soc.*, 2014 (1950); (b) J. L. Kice and F. M. Parham, *J. Am. Chem. Soc.*, **80**, 3792 (1958).

(13) C. C. Addison and J. C. Sheldon, *J. Chem. Soc.*, 1941 (1956).

(14) The known isomer pairs follow: *cis*- and *trans*-1,2-dichloroacenaphthene, mp 116 and 58°, respectively [S. J. Cristol, F. R. Stermitz, and P. S. Ramey, *J. Am. Chem. Soc.*, **78**, 4939 (1956)]; *cis*- and *trans*-1,2-difluoroacenaphthene, mp 104 and 43° [R. F. Merritt and F. A. Johnson, *J. Org. Chem.*, **31**, 1859 (1966)]; *cis*- and *trans*-1,2-acenaphthenediol, mp 209 and 149° [R. Criegee, L. Kraft, and B. Rank, *Ann.*, **507**, 159 (1936)].

Hydrogenation of 5,8-Bis(difluoramino)-1,3,6-cyclooctatriene.—A solution of I (0.099 g, 0.48 mmole) in acetic acid (11 ml) was shaken with platinum oxide under 1 atm of hydrogen. Absorption had ceased after 2 hr, when a total of 82.5 ml or 6.9 mole equiv (98.5%) had been taken up. After filtering, the acetic acid was evaporated under reduced pressure. *n*-Propyl alcohol (10 ml) was added to the residue and the resulting mixture was evaporated to dryness; a second portion of *n*-propyl alcohol was added and then evaporated. Finally, 5 ml of concentrated hydrochloric acid was added and the solution was once more evaporated to dryness. Trituration of the residue with ethanol and filtration gave the dihydrochloride of one of the isomers of 1,4-diaminocyclooctane as a white powder, mp 290–296° dec (0.091 g, 81%).

Anal. Calcd for $C_8H_{20}Cl_2N_2$: N, 13.04. Found: N, 12.64.

Preparation of the Bis(benzenesulfonamide) of a 1,4-Diaminocyclooctane.—Benzenesulfonyl chloride (1.5 g) was added to a mixture of the dihydrochloride of 1,4-diaminocyclooctane (0.4 g) and 4 ml of 10% sodium hydroxide. The mixture was shaken vigorously for 5 min, filtered, acidified, and filtered again. The white solid was washed with water and recrystallized from 95% ethanol to give VI, the bis(benzenesulfonamide) of 1,4-diaminocyclooctane as white needles, mp 172–173°.

Anal. Calcd for $C_{20}H_{26}N_2O_4S_2$: N, 6.63. Found: N, 6.40.

This material was identical (infrared spectra and mixture melting point) with one of the bis(benzenesulfonamides) of the diamines obtained by reduction of the adduct of N_2F_4 and 1,3-cyclooctadiene (*vide infra*).

Hydrogenation of 1,2-Bis(difluoramino)cyclooctane.—The adduct from cyclooctene and N_2F_4 was hydrogenated over platinum oxide in the manner described above to give the 1,2-cyclooctanediamine dihydrochloride as white crystals, mp 276–279° dec. This material was converted to the bis(benzenesulfonamide) as described above; there was thus obtained VII, 1,2-bis(benzenesulfonamido)cyclooctane as stout white needles, mp 174–175°.

Anal. Found: N, 6.58.

A mixture of VI and VII had mp 156–158°.

Reaction of Cyclooctene with Dinitrogen Tetroxide in Ethyl Ether.—To a solution of cyclooctene (22 g, 0.20 mole) in dry ether (400 ml) was added a solution of dinitrogen tetroxide (18 g, 0.20 mole) in ether (80 ml) at 0°, with stirring, over 45 min. The solution was stirred for 1 additional hr at 0° and filtered. The white solid was washed with cold ether and air dried. The filtrate and washings were combined, washed four times with water, dried, and cooled to −20° overnight. Filtration and washing with ether gave additional white solid. Concentration to *ca.* 150 ml and cooling gave a third crop of the white solid. Recrystallization from chloroform gave the dimer of 1-nitro-2-nitrosocyclooctane as white needles, mp 131–132° (2.6 g, 7%).

Anal. Calcd for $C_{16}H_{28}N_4O_6$: C, 51.61; H, 7.54; N, 15.05; mol wt, 372. Found: C, 51.83; H, 7.78; N, 14.89; mol wt, 379 (osmometric).

A portion (6.0 g) of the yellow oil remaining after evaporation of the ether from the filtrates was chromatographed on a 30 × 300 mm column of silica gel. The column was eluted with 300 ml each of 5:1 hexane–methylene chloride, 3:1 hexane–methylene chloride, 1:1 hexane–methylene chloride, and pure methylene chloride. The first 500 ml of eluate gave on evaporation 3.2 g of a yellow oil which showed a strong infrared absorption band at 6.45 μ (NO_2) but no band attributable to hydroxyl, and was taken to be a mixture of *cis-* and *trans*-1,2-dinitrocyclooctane. No attempt was made to separate this mixture; it was instead reduced directly to the corresponding diamine mixture.

Hydrogenation of the Mixture of *cis-* and *trans*-1,2-Dinitrocyclooctane.—A solution of the oily mixture of 1,2-dinitrocyclooctanes (2.00 g, 0.010 mole) in acetic acid (50 ml) was hydrogenated over 0.2 g of platinum oxide at 40 psig for 14 hr. Evaporation of the acetic acid under reduced pressure gave a viscous oil which was dissolved in 15 ml of xylene and again evaporated to dryness. Concentrated hydrochloric acid (10 ml) was added and the mixture was evaporated to dryness once more. The semisolid residue thus obtained was triturated with cold ethanol and filtered to give as a white solid one of the isomers of 1,2 diaminocyclooctane dihydrochloride (1.0 g, 52%), mp 276–280° dec. Reaction with benzenesulfonyl chloride by the procedure described previously gave bis(benzenesulfonamide) VII, mp and mmp 173–174°.

The ethanol filtrate from filtration of the amine hydrochloride mixture was evaporated nearly to dryness and filtered to give the second isomeric 1,2-diaminocyclooctane dihydrochloride. Conversion to the benzenesulfonamide as before and recrystallization from ethanol gave bis(benzenesulfonamide) VIII as shiny white prisms, mp 203–204°.

Anal. Calcd for $C_{20}H_{26}N_2O_4S_2$: N, 6.63. Found: N, 6.64.

Hydrogenation of 1-Nitro-2-nitrosocyclooctane Dimer.—The dimer of 1-nitro-2-nitrosocyclooctane (1.40 g, 0.004 mole) was hydrogenated at 40 psig of hydrogen over platinum oxide (0.30 g) in acetic acid (40 ml) during 10 hr. The acetic acid was evaporated and the residue was dissolved in 10 ml of hydrochloric acid and reevaporated. The white solid thus obtained was recrystallized from ethanol to give white needles of one of the isomers of 1,2-diaminocyclooctane dihydrochloride, mp 278–280° dec; conversion to the bis(benzenesulfonamide) by the procedure described above gave stout, white needles of VII, mp 174–174.5°. This material was identical (infrared spectrum and mixture melting point) with the sample obtained from the dinitrocyclooctane mixture.

Anal. Found: N, 6.46.

Hydrogenation of the 1,3-Cyclooctadiene–Tetrafluorohydrazine Adduct Mixture.—A solution in acetic acid of the mixture of 3,4-bis(difluoramino)cyclooctene and 3,8-bis(difluoramino)cyclooctene was reduced over platinum and converted to a mixture of bis(benzenesulfonamides) as described above. Fractional crystallization from ethanol gave as the less soluble benzenesulfonamide (VI), mp 172–173°, identical with VI obtained from the cyclooctatetraene–N_2F_4 adduct.

The more soluble bis(benzenesulfonamide) obtained from the mother liquor proved to be VII, shown to be one of the 1,2 isomers.

Reaction of 6,6-Diphenylfulvene with Tetrafluorohydrazine.—A solution of 6,6-diphenylfulvene (4.60 g, 0.020 mole) in dry chlorobenzene (15 ml) contained in a 1-l., round-bottom flask was degassed on a vacuum line by three freeze–pump–thaw cycles at 10^{-4} mm. Tetrafluorohydrazine (3.1 g, 0.03 mole) was distilled into the vessel. The solution was stirred magnetically while the vessel was warmed to 40–45°. After 1 hr, uptake of N_2F_4 had ceased and the red fulvene color had faded to a pale orange; the total amount of N_2F_4 consumed was 1.82 g (0.018 mole). Excess N_2F_4 and solvent were removed by trap-to-trap distillation on the vacuum line. The semisolid residue was dissolved in warm chloroform and the solution was treated with charcoal. Concentration of the solution, cooling, and filtration gave 4-benzhydrylidene-*cis*-3,5-bis(difluoramino)cyclopentene (IX) as chunky, transparent prisms, mp 183–185° (1.74 g, 0.0052 mole, 29%). Recrystallization from benzene gave the analytical sample as transparent prisms, mp 185–186° dec.

Anal. Calcd for $C_{18}H_{14}N_2F_4$: C, 64.67; H, 4.19; N, 8.39. Found: C, 64.69; H, 3.68; N, 8.58.

The infrared spectrum of IX had significant maxima at 6.05 (m), 6.65 (m), 6.91 (s), 9.25 (s), 10.05 (m), and 11.2–13.3 (s, br) μ. The ultraviolet spectrum consisted of a maximum at 250 mμ (ϵ 10,200). The nmr spectrum exhibited signals at τ 2.54 (10 H, singlet, phenyl hydrogens), 3.40 (2 H, doublet, J = 1.0 cps, olefinic hydrogens), and 4.74 (2 H, broad triplet, J_{HF} = 31 cps, allylic hydrogens).

Concentration of the chloroform mother liquors and cooling gave a crop of 4-benzhydrylidene-*trans*-3,5-bis(difluoramino)-cyclopentene (X) as off-white needles, mp 136–137° (0.40 g, 0.0012 mole, 7%). Recrystallization from benzene gave pure X as white needles, mp 137–138°.

Anal. Found: C, 64.87; H, 4.62.

The ultraviolet spectrum of X showed a maximum at 251 mμ (ϵ 10,000). The nmr spectrum exhibited signals at τ 2.68 (10 H, singlet, phenyl hydrogens) and 3.37 (2 H, singlet, olefinic hydrogens); the allylic hydrogen signals appeared as a very broad multiplet centered at *ca.* τ 4.1.

Attempts to obtain additional crystalline material from the mother liquors were fruitless. Chromatography of a portion of the residue on neutral alumina caused decomposition on the column.

The Reaction of Acenaphthylene with Tetrafluorohydrazine.—A solution of acenaphthylene (5.07 g, 0.033 mole) in dry chlorobenzene (20 ml) was degassed on the vacuum line by three freeze–pump–thaw cycles at 10^{-4} mm. Tetrafluorohydrazine (4.1 g, 0.040 mole) was condensed into the vessel, which was then warmed to room temperature. The temperature was raised to 50–55° with magnetic stirring of the reaction mixture. After 1.5 hr, consumption of N_2F_4 had ceased; the total uptake was 3.2 g (0.031 mole). The excess N_2F_4 and the chlorobenzene were removed by trap-to-trap distillation; the reaction vessel was evacuated to 10^{-4} mm at 50°. The dark semisolid residue was triturated with cold hexane and filtered. The resulting tan solid was dissolved in hot 2:1 hexane–benzene and cooled. Two crops of *cis*-1,2-bis(difluoramino)acenaphthene (XI) were obtained, totaling 3.41 g (0.0133 mole, 38% based on unrecovered N_2F_4). Further recrystallization from benzene–hexane gave the analytical sample of XI as white needles, mp 107–108°.

Anal. Calcd for $C_{12}H_8F_4N_2$: C, 51.72; H, 3.44; N, 12.07. Found: C, 51.83; H, 3.65; N, 12.16.

The infrared spectrum of XI exhibited significant maxima at 6.68 (m), 8.30 (m, br), 10.36, 10.60 (s), 11.39 (vs), and 12.02 (m) μ. The nmr spectrum consisted of signals at τ 2.4–2.6 (6 H, multiplet, aryl hydrogens) and 5.24 (2 H, triplet, J_{HF} = 32 cps, aliphatic hydrogens).

Further concentration and cooling of the mother liquors gave a total of three crops of *trans*-1,2-bis(difluoramino)acenaphthene (XII, 4.02 g, 0.0157 mole, 46%), mp 46–48°. Two recrystallizations from hexane–benzene gave the analytical sample as white prisms, mp 49–50°.

Anal. Found: C, 51.46; H, 3.68; N, 11.90.

Compound XII showed infrared maxima at 6.69 (m), 8.52 (m), 9.70 (m), 10.66 (s), 10.89 (s), 11.37 (vs), and 12.26 (s) μ. The nmr spectrum consisted of signals at τ 2.4–2.65 (6 H, multiplets, aryl hydrogens) and 4.71 (2 H, broad triplet, J = cps, aliphatic hydrogens).

Dipole Moment Measurements.—Measurements of the electrical properties and refractive indices of solutions of IX and X in benzene were made at 30°. A General Radio Corp. Model 1610-A capacitance bridge was used for the electrical measurements and the dielectric constants of the solutions were caculated using the directions of the manufacturer.

The method used for calculating the dipole moments from the above data was that of Everard, Hill, and Sutton.[15] There were thus obtained values of 4.7 ± 0.2 D. for IX and 1.3 ± 0.3 D. for X.

Registry No.—Tetrafluorohydrazine, 10036-47-2; I, 10083-79-1; 1,2-bis(difluoramino)cyclooctane, 10076-43-4; 3,8-bis(difluoramino)cyclooctene, 10095-57-5; 3,4-bis(difluoramino)cyclooctene, 10095-58-6; VI, 10095-59-7; VII, 10095-60-0; dimer of 1-nitro-2-nitrosocyclooctane, 10102-91-7; IX, 10095-61-1; X, 10095-62-2; XI, 10095-63-3; XII, 10095-64-4; 1,4-diaminocyclooctane dihydrochloride, 10095-65-5.

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Bridgehead Substituted Bicyclo[2.1.0]pentanes

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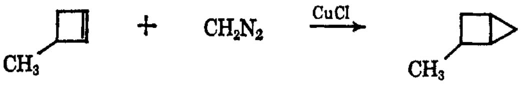
Previously unknown bridgehead substituted bicyclo[2.1.0]pentanes have been synthesized by a variety of methods including intramolecular displacement of *p*-toluenesulfonic acid from butyl *cis*-(2-tosyloxymethyl)-cyclobutanecarboxylate, methylene transfer to methyl cyclobutene-1-carboxylate, metalation of bicyclo[2.1.0]-pentane with amylsodium, and subsequent carbonation, and pyrolysis, and photolysis of the pyrazoline obtained *via* reaction of methyl cyclobutene-1-carboxylate with diazomethane. The preferred routes involve either the metalation of bicyclo[2.1.0]pentane or photolysis of the above-mentioned pyrazoline.

In connection with our continuing work on the cycloaddition reactions of acetylenes with bicyclo[2.1.0]-pentane[2] we desired a variety of bridgehead substituted derivatives of **1**. It was desired that these compounds should differ considerably in the nature of the substituent group such that both strongly electron-withdrawing and electron-inducing groups were present. Since the first preparation of bicyclo[2.1.0]pentane (**1**) was published by Criegee and Rimmelin[3] in 1957, several derivatives of **1** have been synthesized.[4] Unfortunately, methyl[4e,f] and isopropyl[4c] were the only known bridgehead substituents. In view of this lack of bridgehead substituted bicyclo[2.1.0]pentanes, it was decided to synthesize methyl bicyclo[2.1.0]-pentane-1-carboxylate (**2**). The ester function was chosen because simple chemical transformations could readily convert this group into substituents having considerably different electronic effects.

Five alternate pathways to 1-substituted bicyclo-[2.1.0]pentane were envisioned. These were (a) methylene transfer to the appropriately substituted cyclobutene, (b) intramolecular displacement of a sulfonic acid from a simple functionalized cyclobutylcarbonyl derivative, (c) metalation and subsequent carbonation of bicyclo[2.1.0]pentane, (d) pyrolytic loss of nitrogen from the pyrazoline obtained from the reaction of methyl cyclobutene-1-carboxylate with diazomethane, and (e) photolysis of the above-mentioned pyrazoline.

Precedent for the formation of a bicyclo[2.1.0]pentane *via* methylene addition to a cyclobutene derivative was provided by the work of Chesick[4a] who treated **3** with diazomethane in the presence of cuprous chloride[5] to obtain **4** in unspecified yield (eq 1). We



3 **4** (1)

attempted to apply the diazomethane–cuprous chloride procedure to 1-carbomethoxycyclobutene (**5**) but none of the desired bicyclo[2.1.0]pentane derivative was obtained. Since the Simmons–Smith reaction was

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