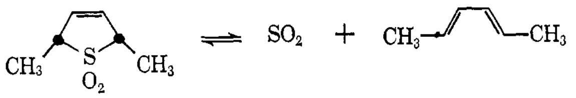
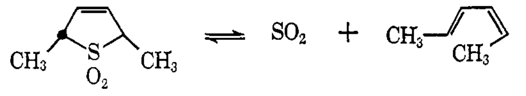
and **4** possess the *cis* and *trans* configuration, respectively; it follows that *these sulfolenes interconvert with their components in the disrotatory manner.*[10] The high thermal stability of sulfolene **4** relative to **3** is traceable primarily to repulsion in the transition state between the methyl and hydrogen which overlap so greatly in the *s-cis* conformation of the product.[11]



3



4

N-Nitroso-3-pyrroline (**1**, Y = >N—N=O, mp 34.5–36°, mol wt found, 100) was less than half decomposed by heating for 1 hr at 200° in benzene solution. Of the fraction destroyed roughly one-third was accounted for as pyrrole, and polymer was formed in considerable amount. Thus fragmentation to butadiene and nitrous oxide is a sluggish reaction if it occurs at all.[12]

Were heat of reaction the determining factor, N-nitroso-3-pyrroline would be expected to dissociate more readily than the labile 3-sulfolene ($t_{1/2}$ = 43 min. at 125°).[13,14] We attribute its reluctance to fragment chiefly to the fact that disrotation is symmetry forbidden.[2c] Compared with this pathway, the conrotatory counterpart suffers from these disadvantages: (1) C–N orbital overlap decreases to low values before the new C–C bonds are well developed; (2) the ring twists strongly, reducing π overlap between C-3 and C-4; and (3) the leaving group interferes sterically with the hydrogens which come to occupy the "inside" positions at the termini of the diene. In certain larger rings the severity of these effects is sharply diminished, so the possibility of observing conrotatory fragmentations remains an attractive one.

Acknowledgment. We wish to thank Professors R. Hoffmann, R. B. Woodward, and J. E. Baldwin for making unpublished information available to us. We are also grateful for the financial support generously provided by the National Science Foundation and the National Institutes of Health.

[10] The same conclusion has been reached independently by W. L. Mock, *J. Am. Chem. Soc.*, **88**, 2857 (1966).

[11] In principle, disrotatory fragmentation of **3** could have given *cis,cis* diene as well as *trans,trans*. The fearful methyl–methyl repulsion which blocks approach to the transition state for formation of the *cis,cis* isomer explains its absence.

[12] No more than a trace of butadiene was present, though some may have polymerized under the reaction conditions. In another pyrolysis (neat at 212°, 1 hr) nitrous oxide was detected, but the yield was very low and, in fact, its origin is equivocal.

[13] O. Grummitt, ref 3.

[14] This statement is based on the model compounds dimethyl nitrosamine and dimethyl sulfone, for which $(\Delta H^\circ_{\mathrm{N_2O}} - \Delta H^\circ_{\mathrm{(CH_3)_2N_2O}}) = (\Delta H^\circ_{\mathrm{SO_2}} - \Delta H^\circ_{\mathrm{(CH_3)_2SO_2}}) - 16$, where the ΔH°'s are standard heats of formation in kcal/mole at 25°. The value for dimethyl sulfone (crystalline) is not corrected for heat of fusion. ("Selected Values of Chemical Thermodynamic Properties," Circular 500 of the National Bureau of Standards, U. S. Government Printing Office, Washington, D. C., 1952, pp 37, 53, 139, and 144.)

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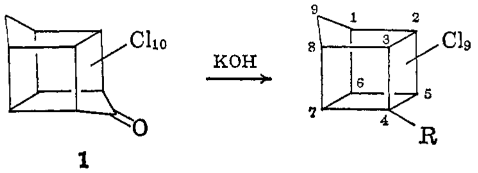
Received March 17, 1966

Bridgehead Reactivity in a Perchlorinated Cage Compound[1]

Sir:

Studies of reactions at or adjacent to bridgehead carbon have been instrumental in establishing the preferred geometry of trivalent carbon species,[2] in illuminating the mechanisms of reactions,[3] and in preserving for study otherwise fleeting intermediates.[4] We wish to call attention to the ready availability and favorable properties of a new bridgehead system and to make a preliminary report of its transformations.



1

2, R = COOH
3, R = $CO_2C_2H_5$
4, R = $C(CH_3)_2OH$
5, R = H
6, R = Cl
7, R = Br
8, R = NH_2
9, R = OH

Nonachloropentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane-4-carboxylic acid[5] (**2**), the precurser of all the compounds to be described, may be prepared in 80–90% yield by the Favorskii rearrangement of decachloropentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decan-10-one (**1**).[6] Dissolving the hydrated **1** in xylene (1 l./100 g), azeotropically removing water, adding powdered 85% potassium hydroxide (50 g/100 g of **1**) in portions to the refluxing solution, and refluxing the mixture with efficient stirring for 12–18 hr conveniently effect rearrangement. The potassium salt of **2**, collected by filtration, was converted to **2** by acidification. Crude product may be freed of the unchanged weakly acidic[1b] **1** hydrate by digesting it with aqueous ammonia, filtering, and reacidifying the filtrate.

The chlorinated pentacyclic cage skeleton of **2–8** confers on its simple derivatives several properties useful in physicochemical studies, in particular good solubility in organic solvents, nonabsorption through the ultraviolet, visible, nmr, and much of the infrared spectral regions, and sufficient volatility and thermal stability to allow gas chromatographic analysis.[7]

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[1] (a) Presented in part at the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965. (b) Transformations of Cage Chlorocarbons. II; for paper I see *Tetrahedron Letters*, 1199 (1965). (c) Supported in part by Public Health Service Research Grant No. GM-12731 from the National Institute of General Medical Sciences and by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

[2] (a) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, Chapter 13; (b) U. Schöllkopf, *Angew. Chem.*, **72**, 147 (1960); (c) P. von R. Schleyer and R. D. Nicholas, *J. Am. Chem. Soc.*, **83**, 2700 (1961); (d) D. E. Applequist and L. Kaplan, *ibid.*, **87**, 2194 (1965).

[3] (a) P. D. Bartlett and L. H. Knox, *ibid.*, **61**, 3184 (1939); (b) P. T. Lansbury, V. A. Pattison, and J. W. Diehl, *Chem. Ind.* (London), 653 (1962); (c) P. T. Lansbury and J. D. Sidler, *Tetrahedron Letters*, 691 (1965).

[4] J. C. Kauer and W. W. Henderson, *J. Am. Chem. Soc.*, **86**, 4732 (1964).

[5] In our initial report on the formation of this substance[1b] the pentacyclic skeleton was incorrectly numbered.

[6] (a) J. S. Newcomer and E. T. McBee, *J. Am. Chem. Soc.*, **71**, 946 (1949); (b) E. T. McBee, C. W. Roberts, J. D. Idol, Jr., and R. H. Earle, Jr., *ibid.*, **78**, 1511 (1956); (c) E. E. Gilbert and S. L. Giolito, U. S. Patent 2,616,928 (1952); *Chem. Abstr.*, **47**, 2424 (1953); U. S. Reissue Patent 24,435 (1958); (d) G. W. Griffin and A. K. Price, *J. Org. Chem.*, **29**, 3192 (1964); (e) available as H-1 ketone monohydrate from Hooker Chemical Corp., Niagara Falls, N. Y.

[7] Typically at 200° on a 5 to 20 ft column packed with 5% SE-30 or Dow-11 on Chromosorb W.

We initially expected the carboxyl group of **2** to be severely hindered, by analogy with the notoriously hindered 2,6-disubstituted benzoic acids,[8] but find that it is esterified readily by ethanolic sulfuric acid, giving a 66% yield of ester **3**,[9] mp 100.5–101.5°, after several days at room temperature. The ester, in turn, undergoes ready hydrazinolysis and also reacts normally with methylmagnesium iodide in refluxing ether to give an 88% yield of the bridgehead dimethylcarbinol **4**,[9] 225–280° dec without melting, $\nu_{\mathrm{OH}}^{\mathrm{C_2Cl_4}}$ 3598 cm^{-1}.

A bridgehead carbanion at C-4 should be greatly stabilized by the inductive influence of the nine chlorines, as well as by rehybridization due to altered bond angles. In fact, we find that acid **2** is smoothly decarboxylated on heating to 120–140° in sulfolane containing a trace of *sym*-collidine and that the decarboxylation product **5**[9] suffers ready reversible base-catalyzed exchange of its single hydrogen with a pseudo-first-order rate constant of 1.1×10^{-4} sec^{-1} in 0.032 *M* sodium methoxide–methanol-O-*d* at 25.0° (one run). Compound **5**, mp 311–314° (sealed tube), $\epsilon_{210}^{\mathrm{cyclohexane}}$ 390, exhibits a single sharp nmr line at τ 5.96 (CDCl$_3$), $J_{\mathrm{C^{13}H}} = 179$ cps,[10] and infrared bands at 3047 (w), 1205 (s), 1160 (s), 1120 (s), 980 (s), 845 (m), 810 (m), 750 (m), and 640 (s) cm^{-1} (C$_2$Cl$_4$, CS$_2$). The bands in the 1250–830 cm^{-1} region, with minor variations in position and structure, are diagnostic of the nonachloropentacyclononyl moiety while the 810 and 750 cm^{-1} bands of **5** are replaced in **5**-*d* by bands at 831 (m), 789 (m), 714 (w), and 697 (w) cm^{-1}. The structure assigned to **5** is confirmed by its dechlorination[11] in low yield to the hydrocarbon homocubane, identical with authentic material.[12] Since the bridgehead proton of **5** undergoes base-catalyzed exchange far more readily than those of tricyclo[4.1.0.0^{2,7}]heptane, despite the latter's greater C^{13}–H coupling constant,[13] we conclude that carbanion stability is much more sensitive to inductive effects than is the coupling constant.[14]

Radical reactivity at C-4 of the chlorinated cage seems low, in agreement with other observations on the stability of bridgehead radicals.[2a,d,15] We have succeeded in preparing perchlorohomocubane **6**[9,16] [mp 327–329° (sealed tube), $\epsilon_{210}^{\mathrm{cyclohexane}}$ 300, $\nu_{\mathrm{max}}^{\mathrm{CS_2}}$ 1217 (s), 1156 (s), 1116 (s), 967 (m), 845 (m), 783 (m), 646 (s), and 631 (s) cm^{-1}] by photochlorination (a solution of **5** and chlorine in carbon tetrachloride or 1,1,3-trichlorotrifluoroethane irradiated through Pyrex with a General Electric sunlamp) but the reaction is very slow and is catalyzed by added water, suggesting that the hydrogen-abstracting species is not a chlorine atom but a hydroxyl radical or kindred species. The bromide **7**, mp 330–332° dec (sealed tube), may be prepared by prolonged refluxing of a mixture of yellow mercuric oxide, excess bromine, and **2** in carbon tetrachloride.[17]

The most promising approach to the C-4 bridgehead carbonium ion appeared to be through the amine **8**, which we first prepared from **2** in about 60% over-all yield *via* its benzylcarbamate, using the sequence worked out earlier for the 9,9-ethylenedioxy analogs.[1b] Amine **8**, mp 260° dec, displays characteristic infrared bands at 3420, 3348, 1603, and 1368 cm^{-1}. Although the acid is unchanged by the usual conditions for the Schmidt reaction, we subsequently found that **8** could be prepared from it in a single step in almost quantitative yield by *cautious* addition of solid sodium azide to a suspension of **2** in 15% fuming sulfuric acid at 60–65°;[18] the free amine precipitates when the reaction mixture is poured on ice. Aside from the anomalous behavior of the amine on diazotization, detailed in the following communication,[19] its most striking property is its great sensitivity to base; it is destroyed almost instantly by 0.01 *N* OH$^-$ in homogeneous solution, and more slowly by 0.5% triethylamine. We have not yet characterized the decomposition products, but presume that the initial reaction is an anionic fragmentation analogous to the far less facile homoketonization of the "birdcage" alcohol[20] and that its ease reflects ring strain in **8** combined with stabilization of a carbanion by chlorine. The surprising base sensitivity of **8** implies that alcohol **9**, which we have so far been unable to prepare, will be much more base labile.[20a]

Acknowledgments. We are indebted to Miss Elaine Holstein for preparative assistance and to Allied Chemical Corporation and Shell Chemical Company for gifts of chemicals.

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[8] M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p 213 ff.

[9] All new compounds gave acceptable elemental analyses.

[10] (a) We thank Professor C. S. Foote for this measurement. (b) Compare the value of 160 ± 5 cps reported for bis(carbomethoxy)cubane: P. E. Eaton and T. W. Cole, Jr., *J. Am. Chem. Soc.*, **86,** 962 (1964).

[11] P. G. Gassman and P. G. Pape, *Tetrahedron Letters*, 9 (1963).

[12] W. G. Dauben and D. L. Whalen, unpublished results; we are greatly indebted to Dr. Whalen for carrying out the dechlorination and making the comparison.

[13] G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **85,** 2022 (1963).

[14] D. M. Grant and W. M. Litchman, *ibid.*, **87,** 3994 (1965).

[15] E. C. Kooyman and G. C. Vegter, *Tetrahedron*, **4,** 382 (1958).

[16] Structure **6** was assigned to a photolysis product of **1** by Griffin and Price (A. K. Price, "Strained Polycyclic Systems," Ph.D. Dissertation, Yale University, 1964; document 65-5261 from University Microfilms, Ann Arbor, Mich.), but the photolysis product and **6** have quite different infrared spectra (Professor G. W. Griffin, private communication).

[17] S. J. Cristol and W. C. Firth, Jr., *J. Org. Chem.*, **26,** 280 (1961).

[18] H. Shechter, 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965, Abstracts, p 4P. We are greatly indebted to Professor Shechter for communicating the details of his procedure.

[19] K. V. Scherer, Jr., and R. S. Lunt, III, *J. Am. Chem. Soc.*, **88,** 2860 (1966).

[20] R. Howe and S. Winstein, *ibid.*, **87,** 915 (1965).

[20a] NOTE ADDED IN PROOF. We have recently obtained **9**, mp 60–65°, $\nu_{\mathrm{OH}}^{\mathrm{CCl_4}}$ 3543 cm^{-1}, by a modified deamination procedure and confirmed its expected instability in basic media. Details will be reported later.

[21] (a) National Institutes of Health Predoctoral Fellow, 1965–1966; (b) National Science Foundation Predoctoral Fellow, 1964–1965; NASA Predoctoral Fellow, 1965–1966.

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Received February 3, 1966

Formation of a Bridgehead Radical by Diazotization of an Aliphatic Amine[1]

Sir:

We have examined the nitrous deamination of the very strained bridgehead amine **1**.[2] Our motives were

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[1] (a) Transformations of Cage Chlorocarbons. III; for paper II see ref 2. (b) Presented in part at the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965. (c) Supported in part by Public Health Service Research Grant No. GM-12731 from the National Institute of General Medical Sciences and by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

[2] K. V. Scherer, Jr., G. A. Ungefug, and R. S. Lunt, III, *J. Am. Chem. Soc.*, **88,** 2859 (1966).