

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, $\nu_{\text{OH}}^{\text{C}^{14}}$ 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 $1.1 \times 10^{-4} \text{ sec}^{-1}$ in 0.032 *M* sodium methoxide-methanol-*O-d* at 25.0° (one run). Compound **5**, mp 311–314° (sealed tube), $\epsilon_{210}^{\text{cyclohexane}}$ 390, exhibits a single sharp nmr line at τ 5.96 (CDCl₃), $J_{\text{C}^{13}\text{H}} = 179$ 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 (C₂Cl₄, CS₂). 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 dechlorination¹¹ 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[4.1.0.0.2⁷]heptane, despite the latter's greater C¹³-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), $\epsilon_{210}^{\text{cyclohexane}}$ 300, $\nu_{\text{max}}^{\text{CS}_2}$ 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

(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).

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" alcohol²⁰ 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.

(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°, $\nu_{\text{OH}}^{\text{C}^{14}}$ 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 Amine¹

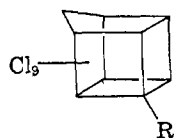
Sir:

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

(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).

in part preparative but, since **1** possesses a combination of electronic and geometric factors which ought to destabilize the derived bridgehead carbonium ion to an unprecedented degree, we also hoped to observe or isolate the elusive aliphatic diazonium salt.^{3,4} Somewhat to our surprise, **1** is deaminated smoothly and rapidly by nitrous acid or nitrosyl chloride near room temperature,⁵ but the products so far characterized are those expected from attack of an intermediate bridgehead *radical* on the solvent or reagent.



1 , R = NH ₂	4 , R = Br	7 , R = <i>o</i> -NO ₂ Ph
2 , R = Cl	5 , R = Ph	8 , R = <i>m</i> -NO ₂ Ph
3 , R = H	6 , R = NO ₂	9 , R = <i>p</i> -NO ₂ Ph

When a dichloromethane solution of **1** was added slowly to a saturated solution of nitrosyl chloride in the same solvent, perchlorohomocubane (**2**)² was formed in 99% isolated yield and 94% purity, but among the contaminants detected by gas-liquid partition chromatography was a trace (~0.6%) of "hydrocarbon" **3**,² most easily rationalized by postulating hydrogen atom abstraction from solvent by an intermediate free radical. Since the main product could have arisen by either the accepted carbonium ion mechanism or by radical attack on the reagent, a good chlorine atom donor, we next combined the reactants in reverse order, introducing the nitrosyl chloride slowly into a dilute dichloromethane solution of **1**; under these conditions **2** and **3** were formed in 30–27% and 17–22% yield, respectively.⁶ By the same procedure, deamination of **1** in bromotrichloromethane led to a mixture of chloride (**2**, 11%) and bromide² (**4**, 61%), while in benzene the bridgehead phenyl derivative **5**⁷ (mp 189.5–191°; $\lambda\lambda_{\text{max}}^{\text{cyclohexane}}$ m μ (ϵ) 223 (12,100), 252 (sh) (510), 259 (450), 262 (460), 266 (440), 273 (340), and 286 (sh) (90); infrared: aromatic absorption at 3050, 1500, 1450 (w), and 745, 692 cm.⁻¹ (s), in addition to bands characteristic of the perchloroalkyl moiety²) was the main product, isolated in 56% yield⁸ (mixed with *ca.* 8% of **2**) by chromatography on alumina.

(3) No diazonium salt with -N₂⁺ bound to sp³-hybridized carbon has been isolated, but several nonbenzenoid, resonance-stabilized aliphatic diazonium salts have been described: K. Bott, *Angew. Chem. Intern. Ed. Engl.*, **3**, 804 (1964), and references therein.

(4) Curtin and co-workers have succeeded in trapping, *via* diazo coupling, 9-triptycyldiazonium salts or closely related species by working at -78°, but were unable to detect the -N₂⁺ function spectrally: (a) D. Y. Curtin, B. H. Klanderma, and D. F. Tavares, *J. Org. Chem.*, **27**, 2709 (1962); (b) D. Y. Curtin and B. H. Klanderma, Abstracts, 145th National Meeting of the American Chemical Society, New York, N. Y., Sept 1963, p 2Q; (c) B. H. Klanderma, Ph.D. Thesis, University of Illinois, 1963 [*Dissertation Abstr.*, **24**, 3984 (1964)].

(5) Using nitrosyl chloride in nonhydroxylic solvents at low temperature, we have been able to isolate coupling products analogous to those obtained by Curtin, *et al.*⁴

(6) Except as indicated, yields were estimated by measuring the areas on glpc traces, relative to internal standards. The identity of products was confirmed by infrared spectra, either of the trapped products or of the mixtures prior to injection. Unidentified involatile by-products account for most of the missing material, but the nitro derivative **6**, mp 338–340° (sealed tube), prepared alternatively by peroxytrifluoroacetic acid oxidation of **1**, was usually present in at least trace amounts.

(7) All new compounds gave acceptable elemental analyses.

(8) Friedman, *et al.*, find that deamination of typical aliphatic amines in benzene or toluene under roughly similar conditions gives up to 2.5% alkylation products, apparently by an ionic mechanism: A. T. Juriewicz, J. H. Bayless, and L. Friedman, *J. Am. Chem. Soc.*, **87**, 5788 (1965).

Even in polar solvents, the identified products are most satisfactorily accounted for by invoking a free-radical intermediate. Thus when **1** was deaminated in 75% formic acid–25% water by addition of a slight excess of sodium nitrite, **3** was formed in 69% yield (corrected for **1** recovered as the N-formyl derivative, mp 260–280° dec) and infrared and glpc examination of the crude reaction mixture indicated that no more than about 3% of the bridgehead formate and a negligible amount of alcohol, neither of which we have yet characterized,^{8a} could be present.

Although we feel that the foregoing data indicate a free radical intermediate, a rather forced *ad hoc* rationalization employing a "hot" carbonium ion may be advanced, particularly since little or no work on aliphatic deamination has been done in several of the solvents we employ. We have accordingly sought to strengthen our case by carrying out the deamination of **1** in nitrobenzene, where the distribution of isomers in the bridgehead nitrophenyl products **7–9** (obtained in up to 67% yield)⁹ permits a clear choice between a cationic and radical intermediate. Analysis of the product mixture by a combination of gas and thin layer chromatography (**7** and **9** were not separated at 250° on a 5 ft × 1/8 in. column packed with 5% SE-30 on Chromosorb W) indicated that **7**, **8**, and **9** were formed in the ratio 29:34:37 (all ±5). Consideration of the steric and polar effects known to operate in homolytic aromatic substitution¹¹ brings these results into accord with expectation for a radical process, whereas electrophilic attack on nitrobenzene typically gives 90% or more *meta* product.¹²

Aryldiazonium salts are known to give rise to aryl radicals under a variety of conditions and by several mechanisms,¹³ but none of the paths identified seems likely under our conditions. We propose tentatively that carbon radicals arise during deamination of **1** *via* fragmentation of a diazonitrite, by analogy with the mechanism for the free-radical decomposition of hypobromous acid identified by Powell and Buchholz.¹⁴ One of several possible routes to the diazonitrite is shown.

(8a) NOTE ADDED IN PROOF. Subsequent preparation of the bridgehead alcohol² has not led us to alter any of the conclusions reported herein.

(9) Gaseous NOCl (Matheson Co.) diluted with nitrogen was introduced slowly into a 0.032 M solution of **1** in redistilled nitrobenzene, until an excess was present. The next morning the solvent was removed under vacuum, then steam distilled, and the crude product, after examination by glpc, was cleaned up by elution with hexane from a short alumina column. The *para* isomer, mp 189.5–191.0°, $\lambda\lambda_{\text{max}}^{\text{cyclohexane}}$ (m μ) 212 (10,000) and 263 (14,000), could be isolated by fractional crystallization, but the *meta*, mp 163.5–164.7°, $\lambda\lambda_{\text{max}}$ (m μ (ϵ)) 217 (24,100) and 253 (8000), and *ortho*, mp 161.7–162.5°, $\lambda\lambda_{\text{max}}$ (m μ (ϵ)) 215 (18,900), 253 (4630), and 290 (sh) (2190), isomers were obtained pure only by thick-layer chromatography. Compound **7** was identified by its symmetrical A₂B₂ nmr spectrum, and **8** and **9** were distinguished by their ultraviolet spectra, by analogy with the isomeric *t*-butylnitrobenzenes.¹⁰

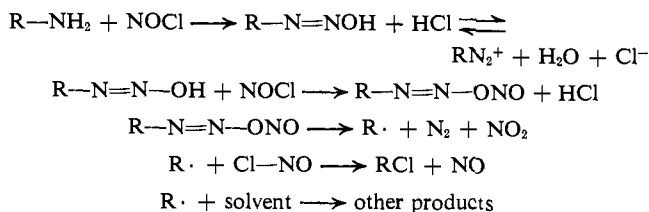
(10) W. G. Brown and H. Reagan, *J. Am. Chem. Soc.*, **69**, 1032 (1947).

(11) (a) G. H. Williams, "Homolytic Aromatic Substitution," Pergamon Press, Oxford, 1960, pp 71, 106 ff; (b) C. Shih, D. H. Hey, and G. H. Williams, *J. Chem. Soc.*, 1885 (1958); (c) B. R. Cowley, R. O. C. Norman, and W. A. Waters, *ibid.*, 1799 (1959).

(12) G. A. Olah, Ed., "Friedel-Crafts and Related Reactions," Vol. III, Interscience Publishers, Inc., New York, N. Y., 1964, pp 1362, 1467, 1548.

(13) (a) H. Zollinger, "Azo and Diazo Chemistry," Interscience Publishers, Inc., New York, N. Y., 1961, p 153 ff; (b) C. Rüchardt and E. Merz, *Tetrahedron Letters*, **36**, 2431 (1964); (c) D. B. Denney, N. E. Gershman, and A. Appelbaum, *J. Am. Chem. Soc.*, **86**, 3180 (1964).

(14) J. R. Buchholz and R. E. Powell, *ibid.*, **87**, 2350 (1965); we are indebted to Professor Powell for stimulating discussions and a copy of this paper in advance of publication.



Decomposition of diazonitrite might be either spontaneous or one step in a chain reaction, again by analogy with proposals of Buchholz and Powell.

Whatever the mechanism, our results demonstrate that a free-radical path for the decomposition of aliphatic diazonium salts (or diazohydroxides) is energetically accessible and may compete with the usual carbonium ion process whenever the latter is relatively unfavorable. The formation of triptycene in the deamination of 9-aminotriptycene with nitrosyl chloride in ether^{4b,c} and the formation of unrearranged chloride in the deamination of 3'-amino-1,2-cyclopropanoaceneaphthene¹⁵ may be examples of such free-radical processes. We are investigating the latter possibility as well as continuing our study of the chemistry of amine 1.

(15) R. Pettit, *J. Am. Chem. Soc.*, **82**, 1972 (1960); see C. H. DePuy, L. G. Schnack, J. W. Hausser, and W. Wiedemann, *ibid.*, **87**, 4006 (1965), for an alternative explanation.

(16) National Science Foundation Predoctoral Fellow, 1964-1965; NASA Predoctoral Fellow, 1965-1966.

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Received February 3, 1966

The Use of Aluminum Chloride-Nitromethane for the Production of Cation Radicals¹

Sir:

Positive ion free radicals have been investigated with esr spectroscopy by Weissman,² Carrington,³ and others, usually by dissolving the appropriate neutral substance in concentrated sulfuric acid. Although

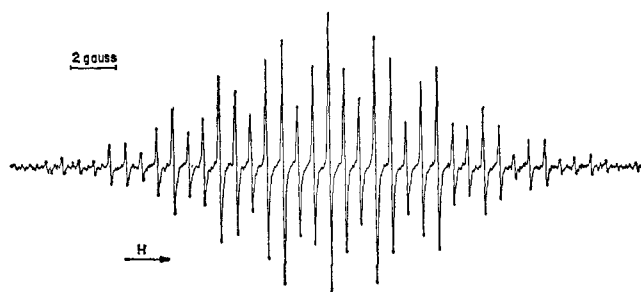


Figure 1. The esr spectrum of dimethoxydurene at -24° in $\text{AlCl}_3\text{-CH}_3\text{NO}_2$.

other chemical methods for producing cation radicals are known (e.g., ref 4), concentrated acid oxidation has become the most frequently used method. The purpose of this communication is to report on the use of aluminum

(1) This research was supported by the National Research Council of Canada.

(2) S. I. Weissman, E. De Boer, and J. J. Conradi, *J. Chem. Phys.*, **26**, 963 (1957).

(3) A. Carrington, F. Dravnieks, and M. C. R. Symons, *J. Chem. Soc.*, 947 (1959).

(4) I. C. Lewis and L. S. Singer, *J. Chem. Phys.*, **43**, 2712 (1965).

chloride-nitromethane ($\text{AlCl}_3\text{-CH}_3\text{NO}_2$), which was found more satisfactory than concentrated sulfuric acid for producing a number of cation radicals. Although $\text{AlCl}_3\text{-CH}_3\text{NO}_2$ is known to produce cation radicals,⁵ except for *p,p'*-dimethoxybiphenyl⁶ the method does not appear to have been used for the investigation of hyperfine structure. Further, we have not been able to find any comparisons of the two systems in the literature.

For a number of radicals, such as the cation radicals of 1,4-dimethoxybenzene and 1,4-diethoxybenzene, the radical concentration obtained with $\text{AlCl}_3\text{-CH}_3\text{NO}_2$ approximates to 100%, whereas the radical concentration obtained in concentrated sulfuric acid was considerably less than 1%.⁷ Sometimes, the low radical concentration obtained in sulfuric acid solution does not permit analysis of the hyperfine structure. This was found to be the case for 1,4-di-*n*-butoxybenzene, where again the $\text{AlCl}_3\text{-CH}_3\text{NO}_2$ system gave a satisfactory spectrum. The increased radical concentration of these compounds permits a spectral analysis to be made in terms of *cis* and *trans* isomerism.⁷ For these and other compounds, $\text{AlCl}_3\text{-CH}_3\text{NO}_2$ was therefore found to be an oxidizing agent superior to sulfuric acid.

Different spectra are sometimes obtained for the two systems as illustrated by the spectrum of dimethoxydurene.⁸ The esr signal in $\text{AlCl}_3\text{-CH}_3\text{NO}_2$ (Figure 1) affords narrow lines (half-width ca. 70 mgauss) and analyses for $a_{\text{CH}_3} = 2.11$ gauss and $a_{\text{OCH}_3} = 2.76$ gauss at $+14^\circ$. Moreover, the dimethoxydurene cation radical showed a marked temperature dependence of the $-\text{OCH}_3$ splitting constant, which is being further investigated. In sulfuric acid solution an esr signal was obtained which was identical with that observed on dissolving duroquinol in sulfuric acid.⁹ Hence in this case only the $\text{AlCl}_3\text{-CH}_3\text{NO}_2$ system gives rise to the appropriate cation radical without further chemical reaction.

Since $\text{AlCl}_3\text{-CH}_3\text{NO}_2$ is less viscous than concentrated sulfuric acid, effects due to the anisotropic dipolar g tensor interaction terms of the line-width equations¹⁰ are of little importance. For example, the duroquinol cation radical can be studied to -95° in the former, whereas in the latter system determinations below 0° are marred by line-width variations. Studies at -95° allow observation of the *cis* and *trans* isomers of the duroquinol cation radical.

Sometimes, $\text{AlCl}_3\text{-CH}_3\text{NO}_2$ permits oxidation beyond the one-electron stage. For example, *p,p'*-biphenol gave a blue paramagnetic solution which analyzed as $a_{4\text{H}} = 1.95$ gauss, $a_{2\text{H}} = 1.64$ gauss, and $a_{4\text{H}} = 0.73$ gauss. Using excess AlCl_3 , the solution became yellow in color and was diamagnetic. This further oxidation was reversed by diluting or by adding more starting material.

Experimentally, the chemicals used were Fisher

(5) H. M. Buck, W. Bloemhoff, and L. J. Oosterhoff, *Tetrahedron Letters*, No. 9, 5 (1960).

(6) D. L. Allara, B. C. Gilbert, and R. O. C. Norman, *Chem. Commun.*, 1, 319 (1965).

(7) W. F. Forbes and P. D. Sullivan, *Can. J. Chem.*, in press, and unpublished information.

(8) We are indebted to Drs. H. G. Cassidy and M. Hashimoto for a sample of this compound.

(9) J. R. Bolton and A. Carrington, *Mol. Phys.*, **5**, 161 (1962).

(10) J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.*, **39**, 326 (1963).