peroxide. After 24 hr, an additional 10 g of hydrogen peroxide was added. Twenty hours later it was treated with platinum black in water. Removal of the solvent gave 11 g (94%) of the *N*-oxide. The latter was heated in a 50-ml flask to 180° (5 mm) and the product was collected in two successive Dry Ice–acetone traps. It was taken up in 150 ml of olefin-free pentane, and the pentane solution was washed with 100 ml of 1 *N* hydrochloric acid, two 50-ml portions of sodium bicarbonate solution, and water. After drying over potassium carbonate, distillation gave 4 g (60%) of 5-methylenebicyclo[2.1.1]hexane, bp 70–72° (100 mm). The nmr spectrum had bands at τ 5.78 (2 H, s), 7.17 (2 H, s), 8.28–9.2 (6 H, m).

Anal. Calcd for C_7H_{10}: C, 89.3; H, 10.7. Found: C, 89.2; H, 10.6.

Oxymercuration–Demercuration of 6-Methylenebicyclo[3.1.1]-heptane.—To a stirred mixture of 9.57 g (0.03 mol) of mercuric acetate, 30 ml of water, and 30 ml of tetrahydrofuran was added 3.24 g (0.03 mol) of 6-methylenebicyclo[3.1.1]heptane. The solution became colorless and clear in 28 sec. After the solution was stirred for an additional 5 min at room temperature, 30 ml of 3 *M* sodium hydroxide was added followed by 30 ml of 3 *M* sodium borohydride in 3 *M* sodium hydroxide. The reduction appeared to be instantaneous. The aqueous layer was saturated with sodium chloride, and the organic layer was separated. The aqueous solution was extracted with ether. The combined organic solution was dried over magnesium sulfate, concentrated using a rotary evaporator, and separated into its components by vpc using a 28 ft × 0.375 in. 20% Carbowax column at 140°. The products were 6-methyl-*endo*-bicyclo[3.2.0]heptan-6-ol (32%, 35 min); 2-methylbicyclo[2.2.1]heptan-2-ol (4%, 40 min); 6-methyl-*endo*-bicyclo[3.1.1]heptan-6-ol (20%, 45 min); 6-methyl-*exo*-bicyclo[3.2.0]heptan-6-ol (35%, 50 min); 6-methyl-*exo*-bicyclo[3.1.1]heptan-6-ol (2%, 58 min); and 2-methylenecycloheptanol (6%, 80 min).

Oxymercuration–Demercuration of 5-Methylenebicyclo[2.1.1]-hexane.—To a mixture of 3.2 g (0.01 mol) of mercuric acetate, 10 ml of water, and 10 ml of tetrahydrofuran was added 0.94 g (0.01 mol) of 5-methylenebicyclo[2.2.1]hexane. The solution became clear and colorless in 32 sec. Reduction with sodium borohydride (10 ml of 0.5 *M*) and subsequent work was effected as described above giving 2-methylenecyclohexanol (44%, 17.7 min, 220-in. TCEP column at 110°), 3-methylenecyclohexanol (28%, 18.7 min), and 3-methyl-Δ^3-cyclohexanol (28%, 21.5 min).

Nmr Study of the Reaction of Mercuric Trifluoroacetate with 5-Methylenebicyclo[2.1.1]hexane in Benzene Solution.—A 2 *M* solution of 5-methylenebicyclo[2.1.1]hexane in benzene (solution A) and a 2 *M* solution of mercuric trifluoroacetate in benzene (solution B) was prepared. Equal volumes of the two solutions were mixed in an nmr tube and spectra were taken 5 min, 20 min, 45 min, 75 min, 24 hr, 40 hr, 60 hr, and 132 hr after mixing. The signal of the original olefinic protons (τ 5.78) had completely disappeared in 5 min and cyclopropyl protons (τ 9–10), new olefinic protons and the proton α to the trifluoroacetyl group (τ 4.5–6) were found. As time went on the cyclopropyl proton bands diminished and were replaced with olefinic protons.

The reaction also was carried out on a preparative scale. To a solution of 0.94 g (0.01 mol) of 5-methylenebicyclo[2.1.1]hexane in 5 ml of benzene was added a solution of 4.35 g (0.01 mol) of mercuric trifluoroacetate in 5 ml of benzene. The reaction was quite exothermic and the temperature increased to 70°. After the solution had cooled to room temperature, a solution of 0.9 g of sodium borohydride in 10 ml of 1:1 benzene-methanol was added. The mixture was filtered, concentrated using a rotary evaporator, and analyzed by vpc using a 220-in. TCEP capillary column at 110°. The products were 2-methylenecyclohexanol (16%), 3-methylenecyclohexanol (70%), and 3-methyl-Δ^3-cyclohexanol (14%). The reaction was repeated with the temperature controlled at 0° throughout. The products were 2-methylenecyclohexanol (71%) and 3-methylenecyclohexanol (29%).

Registry No.—I, 35324-39-1; II, 28366-41-8; 7-formylbicyclo[3.2.1]octan-6-one, 35324-41-5; *N*,*N*-dimethylbicyclo[3.1.1]heptane-6-carboxamide, 35324-42-6; 6-dimethylaminomethylbicyclo[3.1.1]heptane, 35378-27-9; 6-methyl-*endo*-bicyclo[3.1.1]heptan-6-ol, 35378-28-0; 6-methyl-*endo*-bicyclo[3.1.1]heptan-6-ol 3,5-dinitrobenzoate, 35378-29-1; 6,8-epoxybicyclo-[3.1.1]heptene-6, 35323-95-6; 6-methyl-*exo*-bicyclo-[3.1.1]heptan-6-ol, 35323-96-7; 6-methyl-*exo*-bicyclo-[3.1.1]heptan-6-ol 3,5-dinitrobenzoate, 35323-97-8; 6-methyl-*endo*-bicyclo[3.2.0]heptan-6-ol, 13837-37-1; 6-methyl-*endo*-bicyclo[3.2.0]heptan-6-ol 3,5-dinitrobenzoate, 35323-99-0; 6-methyl-*exo*-bicyclo[3.2.0]heptan-6-ol, 35324-00-6; 6-methyl-*exo*-bicyclo[3.2.0]heptan-6-ol 3,5-dinitrobenzoate, 35324-01-7.

Bridged Polycyclic Compounds. LXXIII. Nitrous Acid Deaminations of Some Isomeric Aminodibenzobicyclooctadienes[1]

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Received April 21, 1971

Reaction of 7-aminodibenzobicyclo[2.2.2]octadiene (**1a**) and *exo*- and *endo*-2-aminodibenzobicyclo[3.2.1]octadienes (**2a** and **3a**) with nitrous acid in glacial acetic acid leads primarily to dibenzobicyclo[3.2.1]octadien-*exo*-2-ol (**2c**) and the corresponding acetate (**2d**). Changes in product ratios with solvent composition suggest that the relatively large amount of alcohol product results partly from an intramolecular reaction pathway, involving the diazohydroxide intermediate.

Quantitative differences in product-forming pathways in amine deaminations, compared with halide or sulfonate solvolyses, have been described by many workers.[2] However, the inherent difficulty of using product-distribution studies to determine the roles of diazonium ions and carbonium ions with varying structures and under widely different conditions has led to proposals of a variety of intermediate species in the product-determining steps of the amine–nitrous acid and related reactions. Only recently has a comprehensive theory begun to emerge, which can account for the many "unusual" products in the amine–nitrous acid reaction.[2b–d]

The large body of data concerning solvolytic pathways in the dibenzobicyclooctadienyl system led us to a comparative study of the amine–nitrous acid reaction in this system. Cationic intermediates produced by solvolysis of dibenzobicyclo[2.2.2]octadienyl substrates

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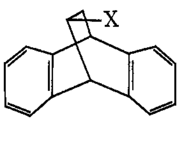
(1) (a) Paper LXXII: S. J. Cristol, A. L. Noreen, and G. W. Nachtigall, *J. Amer. Chem. Soc.*, **94**, 0000 (1972). (b) This work was reported at the 18th National Organic Symposium of the American Chemical Society, Columbus, Ohio, June 1963.

(2) (a) H. Zollinger, "Azo and Diazo Chemistry," Interscience, New York, N. Y., 1961, pp 123–136; (b) R. A. M. O'Ferrall, *Advan. Phys. Org. Chem.*, **5**, 362 (1967); (c) E. H. White and D. J. Woodcock in "The Chemistry of the Amino Group," S. Patai, Ed., Interscience, New York, N. Y., 1968, pp 440–483; (d) L. Friedman in "Carbonium Ions," Vol. II, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1970, pp 655–713.



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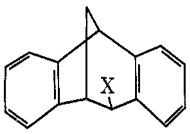

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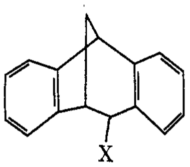

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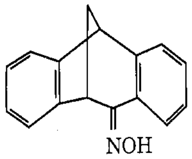
a, $X = NH_2$
b, $X = OTs$
c, $X = OH$

d, $X = OAc$
e, $X = NH_3^+,\ ^-OTs$
f, $X = ONO$

(**1**) almost invariably lead to rearranged [3.2.1] exo C-2 products (**2**) through kinetic control,[3,4] where it has been shown that the usual order of thermodynamic stability is [3.2.1] exo C-2 derivative (**2**) < [3.2.1] endo C-2 derivative (**3**) < [2.2.2] derivative (**1**).[4e] Following the same pattern, reaction of amines **1a**–**3a** and their *p*-toluenesulfonate salts with nitrous acid in acetic acid led completely to dibenzobicyclo[3.2.1]-octadiene products substituted at C-2.

Synthesis of the Amines.—Compound **1a** was prepared by the method of Wawzonek and Hallum.[5] Lithium aluminum hydride reduction of 2-oximinodibenzobicyclo[3.2.1]octadiene (**4**) led primarily to the endo amine **3a**. The exo amine **2a** was obtained in good yield by solvolysis of dibenzobicyclo[2.2.2]octadien-7-yl *p*-toluenesulfonate (**1b**) in liquid ammonia at 100° in a sealed tube. Since the amines **2a** and **3a** proved to be difficult to purify, their *p*-toluenesulfonate salts were isolated, purified, and subsequently used in the deaminations. The *N*-acetyl derivatives of **2a** and **3a** were also prepared and characterized.

Structural assignments of the amines **2a** and **3a** were made on the basis of analogies in their modes of synthesis and reaction. Solvolyses of dibenzobicyclo[2.2.2]-octadien-7-yl derivatives are known to give exclusively or preponderantly dibenzobicyclo[3.2.1]octadien-*exo*-2-yl derivatives.[3,4a,d,f] Therefore the amine produced by ammonolysis of **1b** may confidently be assigned structure **2a**. On the other hand, lithium aluminum hydride reduction of dibenzobicyclo[3.2.1]octadien-2-one (**5**) is known to give predominantly endo 2-alcohol **3c**;[4d] so the endo 2-amine **3a** was anticipated from the corresponding reduction of the oxime **4**. A pmr spectral analysis[6] of amine **1a** was consistent with the structure assignment presented here.



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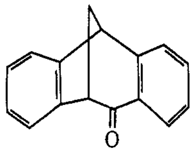

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TABLE I

YIELDS OF DEAMINATION PRODUCTS[a,b]

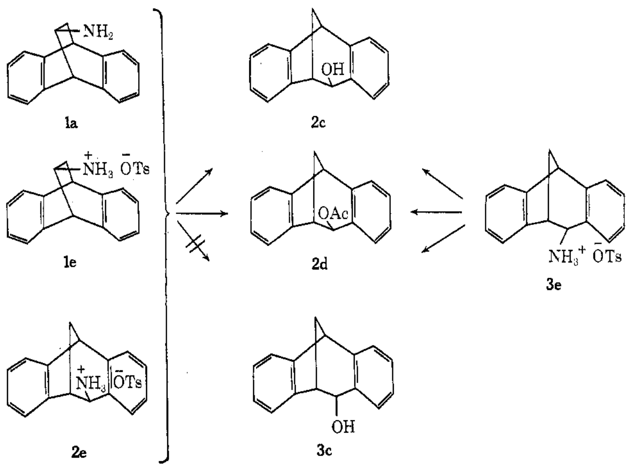
Amine	Exo acetate **2d**, %	Exo ol **2c**, %	Endo ol **3c**, %	Nitrite **2f**, %	Ketone **5**, %
1a[c]	80	19		<1	0.2
1e	76	24			
2e	76	24			
3e	87	9	3	~1	Trace
1a[d]	75	25			

[a] Analysis by quantitative differential infrared method. [b] Using an amine–nitrous acid ratio of 1:7 to 1:10 to ensure complete reaction of the amines. [c] Based upon column chromatographic isolation. [d] Using an amine–nitrous acid ratio of 1:1.

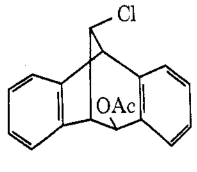
Deamination Results in Glacial Acetic Acid.—Deamination of the amine **1a** and the *p*-toluenesulfonates of amines **1a**–**3a** in glacial acetic acid led to dibenzobicyclo[3.2.1]octadien-*exo*-2-ol (**2c**) and exo 2-acetate **2d** in high yield. The *p*-toluenesulfonate salt of amine **1a** was shown to give a product mixture identical with that produced in the deaminations of the free amine **1a** and its hydrochloride salt. With **3e** a small amount of the endo 2-alcohol **3c** was isolated as well. The exo 2-nitrite **2f** and dibenzobicyclo[3.2.1]octadien-2-one (**5**) formed a small percentage of the products. All alcohol and acetate products were shown to be stable under reaction conditions. No substituted dibenzobicyclo[2.2.2]octadienes or dibenzobicyclo[2.2.2]octatriene was found in the product mixture.

Yields of the various deamination products from reactions in glacial acetic acid are shown in Table I, which is followed by a diagrammatic summary of these reactions (Scheme I).

SCHEME I



Structure Proof of the Deamination Products.—The exo 2-alcohol **2c** and exo 2-acetate **2d** could be interconverted by treatment with an acetic anhydride–pyridine solution and by hydride cleavage. The configuration at C-2 was based upon the known syn–exo acetoxy chloride **6** and syn–endo acetoxy chloride **7**.[4a,b] Reduction of **6** with sodium biphenyl produced the exo alcohol **2c** while the analogous reduction of **7** gave endo alcohol **3c**.[4c] Both alcohols were oxidized to the same ketone **5**. The chemical evidence presented here



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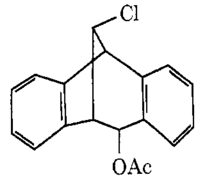

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(3) W. R. Vaughan and A. C. Schoenthaler, *J. Amer. Chem. Soc.*, **80**, 1956 (1958).

(4) (a) S. J. Cristol and R. K. Bly, *ibid.*, **82**, 6155 (1960); (b) S. J. Cristol, R. P. Arganbright, and D. D. Tanner, *J. Org. Chem.*, **28**, 1374 (1963); (c) S. J. Cristol and D. D. Tanner, *J. Amer. Chem. Soc.*, **86**, 3122 (1964); (d) S. J. Cristol, F. P. Parungo, and D. E. Plorde, *ibid.*, **87**, 2870 (1965); (e) S. J. Cristol, F. P. Parungo, D. E. Plorde, and K. Schwarzenbach, *ibid.*, **87**, 2879 (1965); (f) S. J. Cristol, R. Caple, R. M. Sequeira, and L. O. Smith, Jr., *ibid.*, **87**, 5679 (1965).

(5) S. Wawzonek and J. V. Hallum, *J. Org. Chem.*, **18**, 288 (1953).

(6) S. J. Cristol, T. W. Russell, J. R. Mohrig, and D. E. Plorde, *ibid.*, **31**, 581 (1966).

for the structure of the exo alcohol **2c** and exo acetate **2d** has also been substantiated by proton magnetic resonance studies.[7]

Deamination of the Amines in Water–Acetic Acid Mixtures.—The high yields of alcohol from the deamination of amines **1a** and **2a** in acetic acid were reproducible in a number of separate experiments. Although a small amount of water is present when an amine is deaminated in anhydrous acetic acid, due to the production of water in the deamination process itself and to the competitive decomposition of nitrous acid, the water can comprise no more than 4% of the solvent when a tenfold excess of sodium nitrite is used under our reaction conditions.

$$RNH_2 + HNO_2 + CH_3CO_2H \longrightarrow CH_3CO_2R + N_2 + 2H_2O$$

$$3HNO_2 \longrightarrow 2NO + HNO_3 + H_2O$$

In order to test if the high alcohol/acetate ratio was sharply dependent upon the percentage of water in the bulk solvent, the deamination of amine **1a** was effected in four different solvent mixtures (Table II). Proton magnetic resonance spectral analysis showed only a small gradual increase in the mole percentage of exo alcohol **2c** in the product of the nitrous acid deamination of the [2.2.2] amine **1a** when 0, 11, and 25 mol % water were present in the acetic acid solvent. Even deamination of **1a** in the presence of 50 mol % water in the acetic acid solvent increased the proportion of the exo alcohol **2c** to only 50%. Similarly, the product yields were exactly the same for the deamination of endo amine salt **3e** in glacial acetic acid and in the presence of a tenfold mole excess of water in the acetic acid deamination medium. This remarkable lack of solvent sensitivity in the proportion of alcohol in the product leads us to propose that much of the alcohol found in the deamination product results directly from an intramolecular reaction of the diazohydroxide intermediate.

TABLE II

PER CENT ALCOHOL PRODUCTS FROM DEAMINATIONS IN ACETIC ACID–WATER MIXTURES

Amine	Solvent composition,[a] % water	Alcohol products,[b,c] %
1a	0	24
1a	11	29
1a	25	35
1a	50	52
3e	0	12[d,e]
3e	3	12[d,f]

[a] Mole per cent of added water. [b] By pmr integration of C-2 protons. [c] Based on 2-alcohol and 2-acetate comprising 100% of product. [d] By quantitative differential infrared analysis. [e] A mixture of alcohols **2c** and **3c**, see Table I. [f] 10% **2c** and 2% **3c**.

An alternative source for the large amount of alcohol product could have been the nitrite esters sometimes formed in deamination reactions. These esters, if unstable under work-up procedures, could possibly have yielded large amounts of the corresponding alcohols. However, control experiments strongly suggest that this was not the situation here. The exo 2-nitrite **2f** was prepared by the reaction of the exo 2-ol **2c** with nitrosyl chloride in pyridine. The resulting nitrite was subjected to deamination conditions in anhydrous acetic acid. Although indeed 60% of nitrite **2f** was unstable to work-up conditions, the amount of ketone **5**[8] formed in the nitrite decomposition (1.5%) showed that the amount of alcohol formed by this pathway in the deamination could not be more than 14 ± 3%, since only 0.2 ± 0.05% ketone was formed in the amine–nitrous acid reaction. Undoubtedly this 14% represents a maximum percentage of alcohol formed by this route, since the calculation assumes complete destruction of the nitrite under work-up conditions. That the hydrolysis of nitrite esters could not have been an important source of the large amounts of alcohol products in deamination reactions was also demonstrated by the isolation of 25% exo alcohol **2c** in the presence of a limited amount of sodium nitrite (see Table I). No evidence could be found for the presence of any nitrite in this product mixture.

A second alternative is that a small amount of water might be far better able to compete with the bulk acetic acid for combination with the carbonium ion intermediate. This postulate was tested by solvolysis of dibenzobicyclo[2.2.2]octadien-7-yl tosylate in a 3.7 mol % water–96.3 mol % acetic acid mixture. This solvent mixture contained the maximum amount of water that could be produced by the decomposition of nitrous acid (*vide supra*). The product was again composed completely of rearranged [3.2.1] products, with 13% of the exo alcohol and 87% of the exo acetate found. Neither endo acetate nor endo alcohol was formed. This exo alcohol should again represent a maximum amount of alcohol in the deamination product, since the ratio of alcohol to acetate in the product does not change when as little as an equimolar quantity of sodium nitrite was used in the deamination. The decomposition of nitrous acid in this experiment would produce far less than 1 mol % water.

The differences in the products resulting from reaction of exo amine **2a** and endo amine **3a** with sodium nitrite in acetic acid are also consistent with the intervention of an intramolecular pathway leading to much of the alcohol product. Whereas both the [2.2.2] amine and exo [3.2.1] amine gave only exo products, the endo amine produced, in addition to the exo alcohol and acetate, a small amount (3%) of the endo alcohol **3c**. However, no endo acetate was found, although all alcohol and acetate products were shown to be stable under reaction conditions. It does not seem likely that this endo alcohol results from reaction of an intermediate carbonium ion and the bulk solvent, but rather it arises directly from the diazohydroxide intermediate, without intervention of the bulk solvent.

Discussion

The high proportion of exo 2-ol **2c** resulting from nitrous acid deamination of **1a**, **1e**, and **2e** and our stereochemical results can be understood most easily in terms of ion-pair phenomena. This concept of the importance of ion-pair phenomena in the amine–nitrous acid reaction and the closely related nitrosamide decomposition in relatively nonpolar solvents, such as

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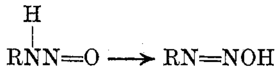
[7] S. J. Cristol, J. R. Mohrig, and D. E. Plorde, *J. Org. Chem.*, **30**, 1956 (1965).

[8] Experiments with 4,4′-dimethoxybenzhydrol suggest that in some cases direct air oxidation of the alcohol may be responsible for the small amounts of ketone formed under deamination conditions.

acetic acid, has been considered by a number of investigators.[2,9–19]

The available evidence suggests that deamination proceeds through an unstable diazohydroxide (**8**),[2,16–18]

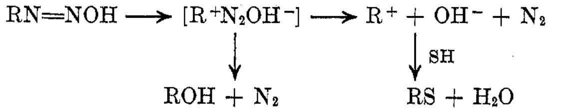


$$R\overset{H}{N}N{=}O \longrightarrow RN{=}NOH$$

8

possibly the syn diazohydroxide. Dissociation would lead to the diazonium cation, which by loss of N_2 would ultimately give stable products.

In our results, it is clear that the diazonium ion loses N_2 before the hydroxide gegenion can diffuse away.[20,21]



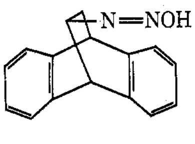
$$\begin{array}{ccccc} RN{=}NOH & \longrightarrow & [R^+N_2OH^-] & \longrightarrow & R^+ + OH^- + N_2 \\ & & \downarrow & & \downarrow{\scriptstyle SH} \\ & & ROH + N_2 & & RS + H_2O \end{array}$$

The timing of C–N *vs.* N–O bond breaking depends upon the nature of the organic group, R. If R is better able to stabilize a positive charge, the C–N bond is more easily cleaved.[22]

Indeed, it has now become quite clear that the importance of ion-pair phenomena as manifested by retention of configuration of substitution products and high amounts of alcohol products in nonpolar solvents in the deamination process is related to the stability of the incipient carbonium ion resulting from loss of molecular nitrogen.[2,9–19] These ion-pair phenomena seem important only with more stable carbonium ion systems in which the alkanediazonium ion is either bypassed as an intermediate species or has an extremely short lifetime. A wide range of "relatively stable" carbonium ions exists, from 4-octyl[10] to 2-phenyl-2-butyl.[9d] Probably, then, ion pairs leading to intramolecular deamination products are but one important part of a total view of amine deamination reactions. White has suggested the importance of vibrationally excited ion pairs in these reactions.[9c]

An SN2 pathway would not be favorable for the diazohydroxide decomposition in the present case[24] because approach of solvent to the back of the developing carbonium ion would be blocked by the bulky carbon skeleton. Also, the ring system does not allow for ready inversion of the attacked carbon atom.

Amines **1a** and **2a** gave identical product distributions, suggesting common intermediates, while **3a** gave a different product distribution, presumably from one or more different intermediates. In the ion-pair representation, we would have (most simply) **11** as the final intermediate from **9** and **10**, leading directly to **2c**. Any acetate from solvolysis would also be exclusively exo (**2d**), as was found to be the case (Table I).



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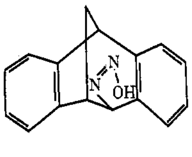

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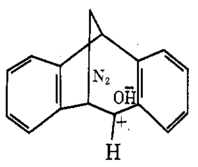

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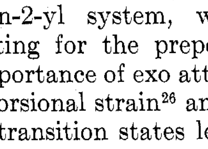
An ion-pair pathway is also consistent with the formation of endo alcohol **3c** with concurrent absence of endo acetate **3d** in the deamination of the *p*-toluenesulfonate salt of endo amine **3e**. The initially formed benzyl cation–hydroxide ion pair **12** from the endo diazohydroxide would have hydroxide ion at a position favorable for attack at the endo side of the carbonium ion, if coordination can occur before hydroxide migrates to the exo position. The predominant formation of exo alcohol and acetate from endo precursor once again demonstrates the marked preference for exo attack on the dibenzobicyclo[3.2.1]octadien-2-yl cation. There is the additional possibility of an SN2 reaction leading to a portion of the exo acetate product. It is difficult to assess the relative important of attack by water in the bulk solvent and an intramolecular inversion pathway[2c] in the formation of exo alcohol from **12**.



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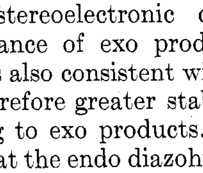

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It has been suggested[4b,e] that the benzyl cation is the most probable product-forming species in the carbonium ion chemistry of the dibenzobicyclo[3.2.1]octadien-2-yl system, with stereoelectronic control accounting for the preponderance of exo products.[25] The importance of exo attack is also consistent with the lower torsional strain[26] and therefore greater stabilities of the transition states leading to exo products. The data also agree with the idea that the endo diazohydroxide leads initially to **12**, while **9** and **10** give the pheno-

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(19) C. W. Shoppee, J. G. Feher, R. M. Hall, R. E. Lack, and L. Tarasoff, Jr., *J. Chem. Soc. C*, 2211 (1968).

(20) Proton transfer from the solvent (SH) could precede the dissociation of cation–hydroxide ion pairs.

(21) Moss has suggested[18a] that in alkaline diazotate hydrolyses the leaving group N=NOH has considerable integrity.

(22) As the stability of the cation R^+ increases, the breaking of the N–O and C–N bonds can become more synchronous.[23] As this occurs, more alcohol product can be directly formed through an intramolecular pathway. This may account for our data on the yields of alcohol from deamination of benzylic amines in glacial acetic acid: $C_6H_5CH_2NH_2$ (1.1% ROH, 1.0% aldehyde, 97.4% ROAc), $(C_6H_5)_2CHNH_2$ (7% ROH, 5% ketone, 88% ROAc), $(p\text{-}CH_3OC_6H_4)_2CHNH_2$ (8% ROH, 92% ROAc), $(C_6H_5)_3CNH_2$ (>95% ROH, <5% ROAc).

(23) For the dependence of concerted two-bond cleavage upon the nature of R, see J. L. Kice, R. A. Bartsch, M. A. Dankleff, and S. L. Schwartz, *J. Amer. Chem. Soc.*, **87**, 1734 (1965).

(24) However, for cases where direct displacement on diazohydroxide or diazonium ion intermediates has been proposed, see (a) J. A. Berson and D. A. Ben-Efraim, *ibid.*, **81**, 4094 (1959); (b) J. A. Berson and A. Remanick, *ibid.*, **86**, 1749 (1964); (c) R. D. Guthrie, *ibid.*, **89**, 6718 (1967); (d) ref 14–16; (e) W. J. Albery, J. E. C. Hutchins, R. M. Hyde, and R. H. Johnson, *J. Chem. Soc. B*, 219 (1968).

(25) However, see (a) H. Tanida, H. Ishitobi, and T. Irie, *J. Amer. Chem. Soc.*, **90**, 2688 (1968); (b) H. C. Brown and G. L. Tritle, *ibid.*, **90**, 2689 (1968); (c) M. C. Kochansky, Ph.D. Thesis, University of Colorado, 1971.

(26) (a) P. v. R. Schleyer, *ibid.*, **89**, 699 (1967); (b) *ibid.*, **89**, 701 (1967).

nium ion–hydroxide ion pair **13**, resulting in exo products.[25c]

Experimental Section

General Deamination Procedure.—The amine or ammonium compound was dissolved in anhydrous acetic acid (Baker and Adamson, distilled from boron triacetate, 0.01% water by Karl Fischer titration) in a round-bottom flask equipped with a condenser, a drying tube, and a magnetic stirring bar. Solid sodium nitrite was added at 18° from an erlenmeyer flask attached to the reaction vessel by means of a rubber sleeve. The solution was then allowed to warm to room temperature and subsequently stirred for 3–4 hr more. Multiple extractions of the reaction mixture with pentane were followed by water and sodium bicarbonate washings of the combined pentane extract. The pentane was removed by rotary evaporation after the solution had been dried ($MgSO_4$). The oily residue was held at 1 Torr until the product had a constant weight. The exo and endo alcohols **2c** and **3c** and acetates **2d** and **3d** were found to be stable to the acetic acid–nitrous acid reaction conditions and isolation procedures, using infrared analysis.

Nitrous Acid Deamination of 7-Aminodibenzobicyclo[2.2.2]-octadiene (1a).—A 3.18-g (46.1 mmol) sample of sodium nitrite was slowly added to a solution of 1.02 g (4.61 mmol) of **1a**[5] in 36 ml of acetic acid over a 2-hr period. The crude oily product weighed 1.10 g.

Conversion of the Deamination Mixture from 1a to Dibenzobicyclo[3.2.1]octadien-*exo*-2-ol (2c).—A 1.25-g sample of the deamination mixture dissolved in anhydrous ether was added dropwise to a vigorously stirred suspension of 220 mg (5.8 mmol) of lithium aluminum hydride in 40 ml of anhydrous ether. Slow addition of water and acidification with 12 *M* hydrochloric acid solution, followed by separation and extraction of the aqueous layer with petroleum ether (bp 60–70°), washing of the ether–petroleum ether solution with 5% sodium bicarbonate solution, drying ($MgSO_4$), and removal of the solvent, gave 1.10 g (100%) of crude **2c**. Crystallization from petroleum ether gave 825 mg (75%), mp 119–119.5°.

Anal.[27] Calcd for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.33; H, 6.12.

Preparation of 2d from 2c.—A 256-mg (1.15 mmol) sample of the exo alcohol **2c**, dissolved in a mixture of 10 ml of acetic anhydride and 2 ml of pyridine, was heated at reflux for 1 hr, cooled, and then poured into 100 ml of water and 100 ml of petroleum ether. The aqueous layer was extracted again with petroleum ether. The two organic extracts were combined, extracted with water, dried, and evaporated under vacuum. The acetate **2d** was crystallized from methanol–water. The first crop, mp 85–85.5° (softening at 83–85°), weighed 242 mg (80%). An infrared spectrum of the crude product was identical with the infrared spectrum of the exo acetate **2d** prepared from the deamination mixture of the amine **1a**. In an analogous experiment, **2d** was crystallized by allowing the crude oil to sit in the refrigerator overnight. Upon recrystallization from methanol–water the acetate **2d**, mp 75–77°, was obtained. The two crystal modifications gave identical infrared spectra in carbon disulfide solution.

Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.55; H, 6.23.

Preparation of Dibenzobicyclo[3.2.1]octadien-2-one (5).—A 193-mg (0.87 mmol) sample of the exo alcohol **2c** was heated at 55–60° for 72 hr with 672 mg (4.25 mmol) of potassium permanganate in a solution made from 13 ml of benzene, 8 g of *tert*-butyl alcohol, and 2 ml of water. After destruction of excess permanganate with ethanol, the manganese dioxide was allowed to coagulate and the mixture was filtered; evaporation of the solvent under vacuum gave the crude ketone. Recrystallization from petroleum ether gave 96 mg (51%) of a white solid, mp 114–114.5°. An infrared spectrum taken in carbon disulfide solution (0.03 *M*) showed the carbonyl absorption at 5.87 μ whereas the carbonyl absorption in a KBr pellet was 5.89 μ.

Anal. Calcd for $C_{16}H_{12}O$: C, 87.24; H, 5.49. Found: C, 87.41; H, 5.72.

Preparation of Dibenzobicyclo[3.2.1]octadien-*exo*-2-ol Nitrite (2f).—Our procedure followed those of Barton and Kornblum.[28] Nitrosyl chloride was passed into a solution of exo alcohol **2c** (1.02 g, 4.6 mmol) in 11 ml of anhydrous pyridine (purged with nitrogen) at −20 to −30° for 20 min. The reaction mixture was poured into 50 ml of water and 50 ml of petroleum ether. After separation, the aqueous layer was further extracted with petroleum ether. The petroleum ether extracts were combined and washed with dilute HCl and then water. The solution of the nitrite **2f** was dried ($MgSO_4$) and evaporated to dryness (reduced pressure). Infrared analysis of the crude oily product (1.16 g, 100% yield) showed the characteristic intense 6.1-μ absorption of a nitrite ester. There was no evidence for an O–H stretching absorption or for carbonyl absorption. The crude nitrite **2f** was not crystallized, since it proved to be extremely soluble in all organic solvents. In methanol–water mixtures the nitrite was converted to the exo alcohol **2c**.

Treatment of Exo Nitrite 2f under Deamination Conditions.—Sodium nitrite (2.80 g) was added to a solution of 1.13 g of the crude exo nitrite in 36 ml of dry acetic acid at 20–22°. After 4.5 hr, the reaction mixture was poured into 200 ml of water, extracted with ether, and then worked up in the usual way. An infrared spectrum of the crude product (1.05 g) showed a very large nitrite absorption at 6.1 μ. A 192-mg sample of the crude product was chromatographed on an alumina column (activity I[29] neutral alumina) using carbon tetrachloride and then chloroform (distilled from phosphorus pentoxide). The recovered material (159 mg) was composed of 36–42% nitrite **2f**, approximately 60% exo alcohol **2c**, and 1.5% ketone **5**. A 857-mg sample of the crude product was hydrolyzed to the exo alcohol **2c** in a mixture of 40 ml of 95% ethanol, 10 ml of water, and 10 ml of a 3% hydrochloric acid solution, at 25° for 30 min. Water was added to the solution, and an ether extraction was performed. The product was worked up in the usual manner, resulting in an oily solid weighing 783 mg (103% yield). A synthetic mixture composed of 1.3 mol % of the ketone **5** and 98.7 mol % of the exo alcohol **2c** in carbon disulfide had the same infrared spectrum as did the product.

Dibenzobicyclo[2.2.2]octadien-7-ol *p*-toluenesulfonate (1b) was prepared from a 998-mg (5.3 mmol) sample of *p*-toluenesulfonyl chloride and 1.05 g (4.75 mmol) of alcohol **1c**[5] in 3.5 ml of pyridine. The usual work-up gave 1.64 g (92%) of crude product, from which 1.00 g of **1b**, mp 105–107° dec, was obtained by recrystallization from petroleum ether.

Anal. Calcd for $C_{23}H_{20}SO_3$: C, 73.38; H, 5.36; S, 8.52. Found: C, 73.10; H, 5.69; S, 8.62.

Preparation of the Hydrochloride of 7-Aminodibenzobicyclo-[2.2.2]octadiene.—Dry hydrogen chloride was bubbled into a solution of 8.06 g of the amine **1a** in 500 ml of petroleum ether. Filtration gave 8.84 g (94%) of amine hydrochloride, mp 264–267° dec, after recrystallization from water.

Anal. Calcd for $C_{16}H_{18}NClO$ (the monohydrate): C, 69.68; H, 6.58; N, 5.08; Cl, 12.86. Found: C, 69.99; H, 6.51; N, 5.13; Cl, 13.09.

Preparation of Dibenzobicyclo[2.2.2]octadien-7-ylammonium *p*-Toluenesulfonate (1e).—A solution of 1.00 g (4.52 mmol) of amine **1a**, 870 mg (4.57 mmol) of *p*-toluenesulfonic acid monohydrate, and 80 ml of distilled water was distilled until crystals began to reappear. Upon addition of water and cooling, 1.36 g (76%) of **1e** resulted. After drying at 110° for 5 hr, **1e** melted at 285–289°. Repeated crystallizations from hot water gave mp 288–290°. A mixture melting point with exo salt **2e**, mp 288–290°, was depressed to 265–270°.

Anal. Calcd for $C_{23}H_{23}NO_3S$: C, 70.20; H, 5.89. Found: 69.65; H, 6.26.

Preparation of Dibenzobicyclo[3.2.1]octadien-*exo*-2-ylammonium *p*-Toluenesulfonate (2e).—*p*-Toluenesulfonate **1b** (1.93 g, 5.13 mmol) was sealed in a Carius tube with 50 ml of anhydrous ammonia and heated at 105–110° for 36 hr. The reaction mixture was cooled and the excess ammonia was evaporated. The residue was dissolved in ether, washed with saturated sodium bicarbonate solution and water, dried ($MgSO_4$), and treated with an excess of dry hydrogen chloride dissolved in dry ether. A white solid, 1.18 g (89%), was collected, mp above 300°. The solid was placed in 5% potassium hydroxide solution and extracted with ether. The combined organic layers were washed

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[27] All analyses were run by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

[28] (a) D. H. R. Barton, J. M. Beaton, L. E. Geller, and M. M. Pechet, *J. Amer. Chem. Soc.*, **82**, 2640 (1960); (b) N. Kornblum and E. P. Oliveto, *ibid.*, **69**, 465 (1947).

[29] H. Brockmann and H. Schodder, *Chem. Ber.*, **74B**, 73 (1941).

with water and dried ($MgSO_4$) and the solvent was removed to give an intractable oil, which could not be crystallized from Skellysolve B or from methanol–water. The oil was reconverted to the amine hydrochloride and purified by means of the *p*-toluenesulfonate salt by crystallization from a water solution containing an equimolar amount of *p*-toluenesulfonic acid monohydrate. After drying at 110° for 2 hr, **2e** melted at 288–290° dec.

Anal. Calcd for $C_{23}H_{23}NO_3S$: C, 70.20; H, 5.89. Found: C, 70.43; H, 5.98.

***N*-Dibenzobicyclo[3.2.1]octadien-*exo*-2-ylacetamide** was prepared from 103 mg (0.40 mmol) of the hydrochloride of **2a** and 3 ml of acetic anhydride in 6 ml of dry pyridine. After 19 hr at room temperature, the solution was poured into 150 ml of water, precipitating 51 mg (49%) of solid. Recrystallization from Skellysolve B–chloroform (95:5) gave white crystals, mp 194–196°.

Anal. Calcd for $C_{18}H_{17}NO$: C, 82.09; H, 6.51. Found: C, 81.93; H, 6.41.

Preparation of 2-Oximinodibenzobicyclo[3.2.1]octadiene (4).—A solution of 1.14 g (5.16 mmol) of the ketone **5**, 2.5 g (36 mmol) of hydroxylamine hydrochloride, 10 g (179 mmol) of potassium hydroxide, and 50 ml of 95% ethanol was heated under reflux for 2 hr and then poured into 650 ml of water. Recrystallization of the air-dried precipitate (900 mg, 74%) from methanol gave **4**, mp 239–240°.

Anal. Calcd for $C_{16}H_{13}NO$: C, 81.68; H, 5.57. Found: C, 81.47; H, 5.58.

Preparation of Dibenzobicyclo[3.2.1]octadien-*endo*-2-ylammonium *p*-Toluenesulfonate (3e).—A solution of 1.90 g (8.06 mmol) of oxime **4** in 150 ml of purified tetrahydrofuran was added dropwise to a stirred mixture of 1.20 g (31.6 mmol) of lithium aluminum hydride in 150 ml of tetrahydrofuran. The solution was heated at reflux for 24 hr. Then 30 ml of ethyl acetate was added (caution!). The mixture was evaporated almost to dryness. Methanol (10 ml) was added, then 200 ml of water. The ether solution obtained from three 100-ml extractions was washed with water, dried ($MgSO_4$), and concentrated to 50 ml. Addition of hydrogen chloride dissolved in dry ether gave 1.77 g (85%) of **3a** hydrochloride. Final purification was done *via* the *p*-toluenesulfonate in the usual way. Recrystallization from water and drying at 94° (1 Torr) for 4.5 hr gave **3e**, mp 232–234°. A mixture melting point with the exo salt **2e**, mp 288–290°, was 222–227°.

Anal. Calcd for $C_{23}H_{23}NO_3S \cdot H_2O$: C, 67.13; H, 6.12. Found: C, 67.33; H, 6.12.

***N*-Dibenzobicyclo[3.2.1]octadien-*endo*-2-ylacetamide** was prepared by the procedure used for the preparation of **2a** acetamide. Recrystallization of the precipitate (330 mg, 79%) gave the endo acetamide, mp 183.5–184.5°.

Anal. Calcd for $C_{18}H_{17}NO$: C, 82.09; H, 6.51. Found: C, 81.97; H, 6.50.

Analytical Infrared Procedure.—A differential technique was used,[30] in which mixtures of unknown composition were compared to synthetic mixtures of known composition at the same concentrations. Purified isooctane and carbon disulfide were suitably transparent solvents (0.1 *M* solutions) for this infrared region. For the dibenzobicyclo[3.2.1]octadiene 2-substituted compounds, characteristic absorption maxima were, for ketone **5**, 14.3 and 14.5 μ; endo alcohol **3c**, 14.1 and 16.2 μ; exo alcohol **2c**, 15.7 μ; and exo acetate **2d**, 19.25 μ. Both exo and endo 2-ols had a common peak at 16.65 μ which was very useful for determining total alcohol concentration in a mixture. The product analysis was accurate to ±2%.

Deamination of 1a. Variation I.—Sodium nitrite (8.66 g, 125 mmol) was added to a stirred solution of amine **1a** (7.3 g, 33 mmol) in 100 ml of anhydrous acetic acid over a 1.5-hr period. The crude product, from the usual work-up procedure, was chromatographed on 65 g of activity I[29] neutral alumina. The 14 collected fractions, eluted with purified CCl_4 and then $CHCl_3$, were evaporated under vacuum and the compounds were identified by infrared spectra run on neat samples. The deamination produced 80 mol % of exo acetate **2d**, 19 mol % of exo alcohol **2c**, and 0.2 ± 0.05 mol % of ketone **5**. The ketone per cent was calculated by a quantitative infrared procedure using the 2.78-μ peak of **2c** and that at 5.87 μ for **5**. The ketone composed 10 ± 2% of one fraction which weighed 160 mg. The total recovered eluted products, when converted to the exo alcohol, weighed 7.18 g (98% yield).

Deamination of 1a. Variation II.—Using the same general procedure as before, a 1.02-g (4.61 mmol) sample of **1a** was dissolved in 36 ml of dry acetic acid. To this stirred solution was added 318 mg (4.61 mmol) of sodium nitrite in portions over a 40-min period. The crude product weighed 442 mg. The aqueous reaction mixture was then made strongly basic with a 6 *M* potassium hydroxide solution and extracted with ether. The ether solution was washed thoroughly with water, dried ($MgSO_4$), and evaporated. By this procedure, 558 mg of the amine **1a**, mp 101.5–104°, was isolated. The differential infrared analysis method (*vide supra*) showed that the deamination product was composed of 25% of **2c** and 75% of **2d**. Absence of any absorption at 6.1 μ showed that no nitrite **2f** was present.

Deamination of 1a. Variation III.—In this series of experiments **1a** was treated with sodium nitrite in acetic acid with varying amounts of water present. The product composition was determined by integration of proton magnetic resonance spectra, using the endo proton on C-2 of the **2c**, **2d**, and **2f** present in the crude product mixture dissolved in $CDCl_3$.[7] A Jeol C60-HL spectrometer was used for the analysis. The doublet present at τ 3.77 was taken as indicating the presence of **2f**. Seven pmr integrations were made on the spectrum of each product mixture. Analytical results recorded in Table II were precise to better than ±1%. The composition of a known mixture of **2c** and **2d** could be determined to within 1% of the actual value. In each product mixture 12 ± 2 mol % **2f** was indicated. Thus, the deamination of **1a** in glacial acetic acid, shown as giving 24% **2c** in Table II, led to 21% alcohol **2c**, 66% acetate **2d**, and 13% nitrite **2f**.

Deamination of 1e.—A solution of **1e** (187 mg, 0.48 mmol), which had been dried for 1 hr at 150°, in 10 ml of dry acetic acid was treated with 320 mg (4.64 mmol) of sodium nitrite over a 10-min period. Differential infrared analysis of the product showed the presence of 24 mol % of **2c** and 70 mol % of **2d**. Comparison of peak height at 6.15 μ with the peak height of a sample of known concentration suggested the presence of about 1% **2f**.

Deamination of 2e.—A solution of 124 mg (0.315 mmol) of this salt (dried for 1 hr at 150°) in 8.0 ml of acetic acid was treated with 200 mg (3.18 mmol) of sodium nitrite under the usual conditions. Work-up gave 67 mg of yellow oil. Differential infrared analysis demonstrated the presence of 24 mol % of [3.2.1] alcohol. Infrared peak positions indicated that the alcohol was exo, and that the rest of the product was exo acetate **2d**. A small amount of nitrite (1–2%) was present.

Deamination of 3e.—The monohydrate of **3e** (241 mg, 0.585 mmol) was converted to **3e** by addition and distillation of benzene (100 ml). Glacial acetic acid (12 ml) was added and the solution was treated as usual with 400 mg (5.80 mmol) of sodium nitrite. The yellow, oily product weighed 151 mg. Differential infrared analysis showed the *total* alcohol content (using only the exo epimer in the synthetic mixture) to be 12 mol %. Chromatography of 126 mg of the deamination product on 5.0 g of activity I alumina[29] in carbon tetrachloride and then chloroform gave 115 mg (88 mol %) of **2d**, containing about 1% of nitrite, and 13.3 mg (12 mol %) of [3.2.1] alcohols. Differential infrared analysis showed the content of this total alcohol portion to be 24% **3c** and 76% **2c**. A duplicate experiment, beginning with 100 mg of **3e**, gave a total [3.2.1] 2-ols content of 12 mol %, which was 21% **3c** and 79% **2c**.

Deamination of 3e in the Presence of Added Water.—A mixture of 100 mg (0.24 mmol) of the monohydrate of **3e**, 47.3 mg (2.63 mmol) of distilled water, and 5.0 ml of glacial acetic acid was treated with 175 mg (2.54 mmol) of sodium nitrite under the usual conditions. Differential infrared analysis of the oily product, 54 mg, gave the total [3.2.1] alcohol content to be 12%. The alcohols were separated from the acetate by chromatography (*vide supra*) and shown by differential analysis to contain 18 ± 6% **3c** and 82 ± 6% **2c**.

Solvolysis of Dibenzobicyclo[2.2.2]octadien-7-ol *p*-Toluenesulfonate (1b) in Acetic Acid.—A solution of **1b** (102 mg, 0.271 mmol) and 26.1 mg (0.318 mmol) of anhydrous sodium acetate in 2.18 ml (38.1 mmol) of dry acetic acid/0.026 ml (1.44 mmol) of distilled water was stirred at room temperature for 359 hr. Ether extraction of a 1.0-ml sample in 20 ml of water and the usual work-up followed. The remaining **reaction** mixture was

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[30] (a) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," 3rd ed, Macmillan, New York, N. Y., 1952, p 632; (b) using a Perkin-Elmer Model 137 infrared spectrophotometer fitted with potassium bromide optics.

stirred at room temperature for a complete reaction time of 432 hr. Normal isolation procedures, using pentane extraction, were used. Product composition of these two solvolysis fractions was determined by differential infrared analysis. The former contained 11 mol % of **2c**, 84.5 mol % of **2d**, and 4.5 mol % of **1b**. Similarly, the product of the solvolysis reaction (after 432 hr) contained 15 mol % of **2c**, 83 mol % of **2d**, and 2 mol % of **1b**.

Registry No.—**1a** HCl, 35079-81-3; **1b**, 2975-83-9; **1e**, 35079-83-5; **2c**, 837-65-0; **2d**, 35079-85-7; **2e**, 35079-86-8; **2f**, 35079-87-9; **3e**, 35079-88-0; **4**, 2969-43-9; **5**, 2198-06-3; *N*-dibenzobicyclo[3.2.1]octadien-*exo*-2-ylacetamide, 35079-91-5; *N*-dibenzobicyclo-[3.2.1]octadien-*endo*-2-ylacetamide, 35079-92-6.

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Synthesis of 1,2-Dialkylcyclopropenes, Methyl Malvalate, and Methyl Sterculate[1a]

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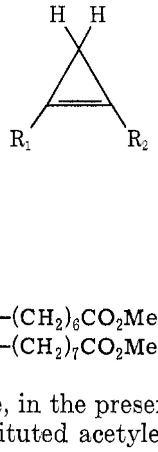
Dipropyl-, dipentyl-, dihexyl-, diheptyl-, and dioctylcyclopropene and methyl malvalate and sterculate have all been synthesized. Ethyl diazoacetate is decomposed in the presence of the appropriate alkyne, followed by hydrolysis to yield a 1,2-disubstituted 3-cyclopropenecarboxylic acid. Exposure to perchloric acid results in decarbonylation to a cyclopropenium ion, which is reduced by sodium borohydride to a 1,2-disubstituted cyclopropene. The absence of any 1,3-disubstituted cyclopropene in the product is consistent with theory. Spectroscopic data is presented. The cyclopropenethiol reaction is discussed.

The 1,2-disubstituted cyclopropene function occurs in the fatty acid chain of lipids from certain plants belonging to the order Malvales, cottonseed oil being the most common. These cyclopropenoid fatty acids have recently been the subject of intense investigation and are held responsible for numerous physiological disorders in farm and laboratory animals.[1]

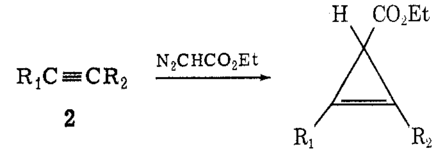
Results

We have developed a synthesis to produce 1,2-disubstituted cyclopropenes (**1**) in quantities for biological testing and feedings. Gensler and coworkers[2] have reported a comparable route to **1f** and **1g**.



1a, $R_1 = R_2 =$ propyl
b, $R_1 = R_2 =$ pentyl
c, $R_1 = R_2 =$ hexyl
d, $R_1 = R_2 =$ heptyl
e, $R_1 = R_2 =$ octyl
f, $R_1 =$ octyl, $R_2 = -(CH_2)_6CO_2Me$ (methyl malvalate)
g, $R_1 =$ octyl, $R_2 = -(CH_2)_7CO_2Me$ (methyl sterculate)

Ethyl diazoacetate, in the presence of a copper catalyst, adds to disubstituted acetylenes (**2**) yielding 1,2-disubstituted cyclopropene-3-carboxylates (**3**).[3] In the present investigation, alkynes are 40–50% converted to the corresponding cyclopropene by an equal molar amount of diazoacetate. About 90–95% of the unreacted acetylenic compound can be recovered, reflecting the rather high selectivity of the carboxylcarbene. Other workers[2] report a 60–70% conversion for this identical reaction.



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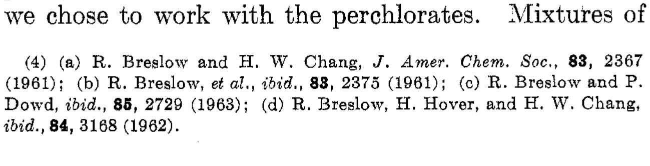
All the resulting 1,2-dialkyl-3-carboxylcyclopropenes can be purified by high vacuum distillation (5×10^{-2} mm), with the exception of one, methyl 9,10-(carboxymethano)-9-octadecenate (**3g**), the precursor for sterculate (**1g**). However, unreacted methyl stearolate (**2g**) can be recovered from this latter product by vacuum distillation without significant decomposition of the desired cyclopropene, thus facilitating purification on a column.

After hydrolysis, treatment of the 1,2-disubstituted cyclopropene-3-carboxylic acid (**4**) with strong mineral acid in acetic anhydride results in decarbonylation[4] to the corresponding cyclopropenium ion (**5**). Cyclopropenium perchlorates are less soluble and easier to purify than the fluoroborates or bromides; therefore, we chose to work with the perchlorates. Mixtures of



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