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AN UNUSUAL REARRANGEMENT OF AN ACYL AZIDE*

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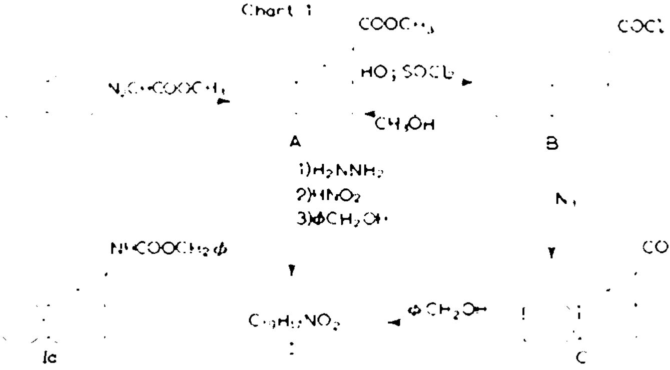
Abstract Benznorcaradienycarbonyl azide (from naphthalene and methyl diazoacetate by known or unexceptional steps) decomposes on heating with benzyl alcohol in benzene to nitrogen and $C_{18}H_{17}NO_2$ (I). It is clear, from the fact that carbon dioxide is not evolved in the hydroxide-catalyzed cleavage to benzyl alcohol and $C_{11}H_{11}NO_2$ (II), that (I) is not a urethane, but a product of unexpected structure. By degradative and analytical methods and by independent synthesis, we have assigned the structure 2-benzyloxy-6:7-benzo-3-aza*bicyclo* [3.2.2] nona-6:8-diene-4-one to (I) (Chart 2). To our knowledge, no similar rearrangement during a Curtius reaction is recorded.

*cyclo*HEPTATRIENYLIUM or tropylium ion, the parent of the seven-membered aromatic series, was discovered in 1954.[1] Subsequently, it was synthesized by Dewar and Pettit[2] from "ethyl norcaradiene carboxylate" by way of the carbonyl azide and Curtius rearrangement to tropylium *iso*cyanate. Benztropylium ion immediately became one of the next members of the series towards which synthetic efforts were directed. Dewar and Pettit‡ at Queen Mary College and Doering and Hoffmann[3] at Yale independently undertook the synthesis by way of the Curtius rearrangement of benznorcaradiene carbonyl azide (Chart 1, C). Both efforts failed and were abandoned on the announcement of a successful synthesis by the group at the E.T.H. in Zürich.[4]

The failure of the Doering–Hoffmann effort (Chart 1) seemed the more unreasonable since the crucial step had apparently proceeded uneventfully. Naphthalene had

Chart 1



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[*] Taken in part from a dissertation submitted by M. J. Goldstein to the Faculty of the Graduate School, Yale University, in candidacy for the degree of Doctor of Philosophy. This work was supported in part by the Office of Ordnance Research, Contract DA-19-059-ORD-1562 with Yale University.

[†] National Science Foundation Predoctoral Fellow, 1954-57.

[1] W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.* **79**, 352 (1957).

[2] M. J. S. Dewar and R. Pettit, *Chem. & Ind.* 199 (1955); *J. Chem. Soc.* 2021, 2026 (1956).

[‡] M. J. S. Dewar and R. Pettit, privately communicated.

[3] W. von E. Doering and A. K. Hoffmann, VIII/'54–V/'55 to remain unpublished except for the relevant experiments reported in the experimental section of this paper. Unless explicitly indicated, the experimental details are those elaborated by the present authors.

[4] H. H. Rennhard, E. Heilbronner and A. Eschenmoser, *Chem. & Ind.* 415 (1955); H. H. Rennhard, G. Di Modica, W. Simon, E. Heilbronner and A. Eschenmoser, *Helv. Chim. Acta* **40**, 957 (1957).

been treated with methyl diazoacetate according to Buchner and Hediger[5] to give methyl benzonorcaradiene carboxylate. By the usual sequence—reacting with hydrazine, nitrous acid and heating with benzyl alcohol in benzene—one had expected to obtain the urethane, (Ia), and, indeed, a crystalline product of this formula, $C_{19}H_{17}NO_2$ (I), had been isolated with no great difficulty. The reduction of (I) with lithium aluminum hydride had been followed by quaternization with methyl iodide, but the resulting quaternary salt failed under a variety of conditions to ionize with valence tautomerism to the desired benztropylium cation.

The possibility that the scheme might have gone amiss prior to the Curtius rearrangement was rejected in the following way. The structure of benznorcaradiene carbonyl chloride (Chart 1, B) was soundly related to that of the original ester (Chart 1, A) by the cyclic interconversion shown in Chart 1. Benznorcaradiene carbonyl azide was then prepared from this acid chloride by treating with sodium azide and rearranged by heating with benzyl alcohol in benzene. The product of this alternate reaction sequence was the same as the compound (I) obtained from the hydrazide.

The possibility was considered that the structure of the starting material had been incorrectly assigned. In the parent series, only ethyl "norcaradiene" carboxylate among the several isomeric *cyclo*heptatriene carboxylic acids (Buchner acids) had been converted successfully to tropylium ion by rearrangement of the corresponding azides.[2] In confirmation of the structural assignment, Buchner and Hediger[5] had degraded benznorcaradiene carboxylic acid to 3-(*o*-carboxyphenyl) *cyclo*propane-1:2-dicarboxylic acid and thence to *transcyclo*propane-1; 2; 3-tricarboxylic acid.* Some measure of further support comes from comparison of the ester with benznorcaradiene itself. Synthesized by the photochemical decomposition of diazomethane in naphthalene and purified by conversion to a crystalline dibromide and regeneration with zinc, benznorcaradiene is oxidized to a dicarboxylic acid, $C_{11}H_{10}O_4$, which resists further oxidation by permanganate-periodate and is consistently formulated as 2-(*o*-carboxyphenyl) *cyclo*propane-1-carboxylic acid. The n.m.r. spectrum of benznorcaradiene shows 3·9 aromatic hydrogen atoms at −12 c.p.s., 2·3 olefinic at 24 c.p.s., and a total of 3·8 aliphatic hydrogen atoms, 2·8 at 205 c.p.s. and 1·0 at 279 c.p.s. The presence of two rather than four olefinic atoms is consistent with the benznorcaradiene structure and inconsistent with the isomeric benz*cyclo*heptatriene structure.† The ultraviolet spectra of benznorcaradiene and methyl benznorcaradiene carboxylate (Chart 1, A; Fig. 1) are almost identical and are closely similar to that of 1:2-dihydronaphthalene.‡ It follows that benznorcaradiene and its derivatives have a double bond conjugated with the benzene ring and that Buchner and Hediger very

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* The stereochemistry of this acid is established.[6]

† In contrast to the tropilidene series where the question of valence tautomerism is difficultly resolvable, in the benztropilidene series, subtle questions of structure are removed by the overwhelmingly dominant influence of the fused benzene ring. Thus, fusion to the $\alpha:\beta$ and $\gamma:\gamma'$ positions (relative to the CH_2 group of *cyclo*heptatriene) must enforce a *cyclo*heptatriene structure on the seven-membered ring, whereas $\beta:\gamma$ fusion demands a norcaradiene structure. Were the ring structures otherwise the benzene ring would become quinonoid.

‡ The spectrum of the last compound has also been compared to that of ethyl benznorcaradiene carboxylate by Badger and coworkers.[8]

[5] E. Buchner and S. Hediger, *Ber. Dtsch. Chem. Ges.* **36**, 3502 (1903).

[6] H. R. Ing and W. H. Perkin, Jr., *J. Chem. Soc.* **125**, 1814 (1924).

[7] E. J. Corey, H. J. Burke and W. A. Remers, *J. Am. Chem. Soc.* **77**, 4941 (1955); W. von E. Doering, G. Laber, R. Vonderwahl, N. F. Chamberlain and R. B. Williams, *J. Am. Chem. Soc.* **78**, 5448 (1956); M. V. Evans and R. C. Lord, *Abstracts of Papers, 130th Meeting, Am. Chem. Soc.* Sept. 16–21, 1956, p. 41 R. Atlantic City, N.J.

[8] M. Badger, B. J. Christie, H. J. Rodda and J. M. Pryke, *J. Chem. Soc.* 1179 (1958).

probably assigned the structure of benznorcaradiene carboxylic acid correctly. It seemed at first implausible that (I) might not have the structure (Ia) and that the Curtius rearrangement itself should be the seat of the trouble, in view of the long history of unchallenged reliability lying behind the Curtius rearrangement.[9] Several properties of (I) are, however, in such complete discord with the structural hypothesis (Ia) that one is forced to suspect the rearrangement step.

The ultraviolet spectrum of (I, Fig. 1) is that of a tetralin and not that of a 1:2-dihydronaphthalene. Consequently (I) cannot contain an olefin grouping conjugated with the aromatic ring. Mild treatment of (I) with alkali causes hydrolysis to benzyl alcohol, (C_7H_8O) and a compound (II), $C_{12}H_{11}NO_2$. The presence in (II) of twelve carbon atoms instead of eleven ($C_{11}H_{11}N$ and CO_2) demanded on hydrolysis of a benzyl carbamate of the empirical formula $C_{19}H_{17}NO_2$ (I) is also inconsistent with

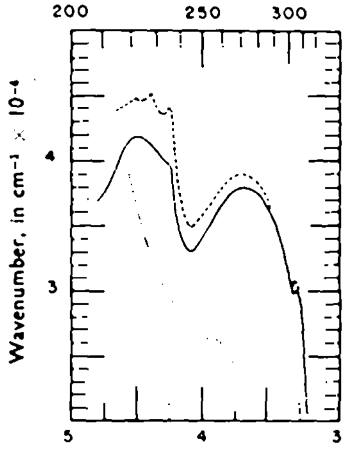

FIG. 1. Ultraviolet spectra of benznorcaradiene (———), methyl benznorcaradiene (- - - - -, Chart 1, A) and compound I (. . . . . . , Chart 2).

the formulation (Ia). The thin reservation that (II) may be a carbamic acid of unusual stability cannot be maintained against the observation that simple heating in benzyl alcohol reconverts (II) to (I).

With the removal of (Ia) as the correct structure, it was clear that the Curtius rearrangement had taken an unexpected turn, the pursuit of which was irresistible. As experimental work progressed, it became increasingly evident that the crucial substance in the structural problem was not (I) but (II), the hydrolysis product; and it was mainly to this substance that our attention was directed.

From an intense band at 5·98 μ (1672 cm^{-1}) in the infrared spectrum (experimental section) the presence of a carbonyl group in (II) can be inferred. Catalytic reduction with the absorption of two atoms of hydrogen indicates the presence of a double bond in (I) and (II). Any question that the unsaturation be of some other type is removed by comparing the n.m.r. spectrum of (I) and its equally accessible dihydro derivative. In dioxane solution (I) shows a peak at 38 c.p.s. which is due to olefinic hydrogen; by contrast dihydro-I has no band in this region.

Consideration of the mechanistically plausible paths of further reaction that might

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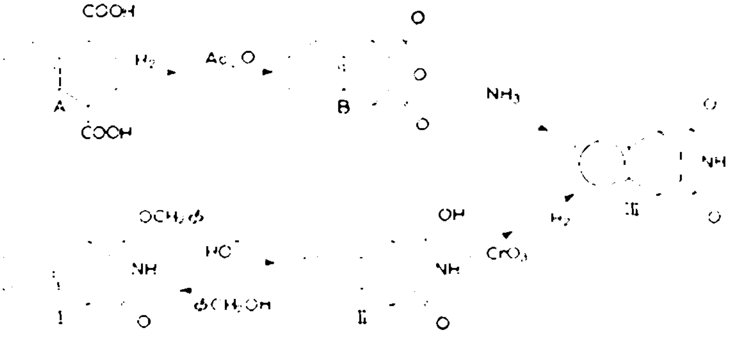
[9] P. A. S. Smith, *Organic Reactions* Vol. III, p. 337. John Wiley and Sons, Inc., New York (1946).

be open to the initially formed *iso*cyanate (Chart 5), coupled with analysis of the facile hydrolysis of (I) to (II) (Chart 3) and the other data above led to a structural hypothesis for (II). The most direct proof of this structure involves a two-step transformation and an independent synthesis.

Oxidation of (II) ($C_{12}H_{11}NO_2$) proceeds smoothly with chromic acid in acetone solution with loss of two hydrogen atoms to $C_{12}H_9NO_2$. This behavior is strongly indicative of the presence of an hydroxyl group in (II). The oxidation product can be hydrogenated catalytically to (III), a dihydro derivative, $C_{12}H_{11}NO_2$, in further confirmation of the presence of an olefinic group in the series. Absorption bands of (III) in the infrared (Experimental Section) at 5·86 (1706) and 5·94 μ (1684 cm $^{-1}$) indicate the presence of two carbonyl groups.

The independent synthesis of (III) is effected from the known 1:4-dihydronaphthalene-1:4-dicarboxylic acid[10] (Chart 2, A). Hydrogenation of the double bond and heating with acetic anhydride produces 1:2:3:4-tetrahydro-1:4-naphthalenedicarboxylic anhydride (Chart 2, B). In a single step the anhydride is opened with ammonia, presumably to the monoamide, and then closed to 1:2:3:4-tetrahydro-1:4-naphthalenedicarboximide (Chart 2, III) by heating to 300°. The synthesis involves reactions of such a transparent nature that the structure assigned to the end-product (III) hardly requires more elaborate justification. This synthetic material is identical in m.p. and infrared spectrum to (III) obtained from (II) by chromic acid oxidation and catalytic hydrogenation. 2-Hydroxy-6:7-benzo-3-aza*bicyclo* [3.2.2] nona-6:8-dien-4-one follows as the structure of (II) (Chart 2, II), once attention is called to the absence of an aldehydic carbonyl group in the infrared spectrum and the structural impossibility of placing the olefinic linkage at any other position in the skeleton.

Chart 2



Assignment of a structure to (I) depends almost solely on rationalizing the facile hydrolysis of (I) by dilute alkali to (II) and the equally facile regeneration of (I) from (II) by heating with benzyl alcohol. The absence of any gross structural change in the interconversion is attested to by the close similarity in the infrared and ultraviolet spectra of (I) and (II) and by the presence in each of an olefinic double bond. The replacement of the benzyloxy group is, furthermore, independent of the presence of the double bond, since dihydro-I can be hydrolyzed to benzyl alcohol under conditions no more drastic than those required to hydrolyze (I). The interconversions therefore

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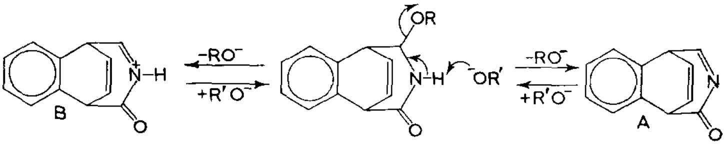
[10] (a) W. Schlenk and E. Bergmann, *Ann.* **463**, 1 (1928); (b) J. F. Walker and N. D. Scott, *J. Am. Chem. Soc.* **60**, 951 (1938).

appear to be simple displacements. Plausible mechanisms involving the adjacent nitrogen atom may be mentioned without laboring the details. In one, a basic catalyst removes the amide hydrogen to form an iminoketone (Chart 3, A perhaps by way of an intermediate amide anion) which then adds the displacing base by steps which are essentially the reverse of the forward ones. In an other, the adjacent nitrogen atom facilitates a first-order ionization, perhaps with acid-catalysis, to an iminonium ion (Chart 3, B) which then adds water or the new alcohol in a reversal of the first step. Facile displacements of this type are recorded in the literature.[11,12] Although iminoketones of the sort considered as intermediate have been claimed,[13] no case has been adequately substantiated. One example which might have lead to a system of this type in fact furnished a tautomer.[14]

Chart 3



Compound (I) and presumably (II) also undergoes an interesting transformation to an isomer of (II), $C_{12}H_{11}NO_2$ (IV) on more drastic treatment with alkali. Examination of the ultraviolet spectrum discloses no similarity to those of (I) and (II) but quite close correspondence to that of an α-substituted naphthalene. The infrared spectrum likewise shows marked and significant changes. Whereas (I) and (II) show amide absorption at 5·98 μ (1672 cm^{-1}) amide (I) band and no absorption of the amide (II) type (generally lacking in cyclic lactams), (IV) shows amide (II) absorption at 6·19 μ (1616 cm^{-1}) in addition to the amide (I) type at 5·95 μ (1681 cm^{-1}).[15] Consequently compound (IV) almost certainly contains a primary amide grouping. Oxidation of (IV) with permanganate affords benzene-1:2:3:4-tetracarboxylic acid* and naphthalene-1:4-dicarboxylic acid depending on the conditions. Finally (IV) can be converted to an O-acetate, indicative of the presence of an hydroxyl group.

The structural hypothesis indicated for (IV) in Chart 4 was constructed largely on mechanistic grounds and was proved by independent synthesis. Starting with naphthalene-1:4-dicarboxylic acid (obtained from the dihydro acid, Chart 2, A), the half methyl ester was prepared by partial saponification of the dimethyl ester and converted to the acid chloride (Chart 4, A). Reduction of the acid chloride to the hydroxymethyl compound (Chart 4, B) and conversion of the carbomethoxy grouping to carboxamide by heating with ammonia led to 1-hydroxymethylnaphthalene-4-carboxamide, identical in all respects to (IV), the product of hydrolysis and rearrangement of (I).

A mechanistic rationalization of the formation of (IV) involves the assumption that (I) is first hydrolyzed to (II), as it is on milder treatment with alkali (refer to

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* We are most grateful to Dr. F. González-Sánchez, Instituto del Combustible, Zaragoza, Spain, for sending us infrared spectra of the acid and its tetramethyl ester as well as a sample of the pure acid.

[11] A. Dunet and A. Willemart, *Bull. Soc. Chim. Fr.* 887 (1945).

[12] P. C. Jocelyn and A. Owen, *J. Chem. Soc.* 4437 (1957).

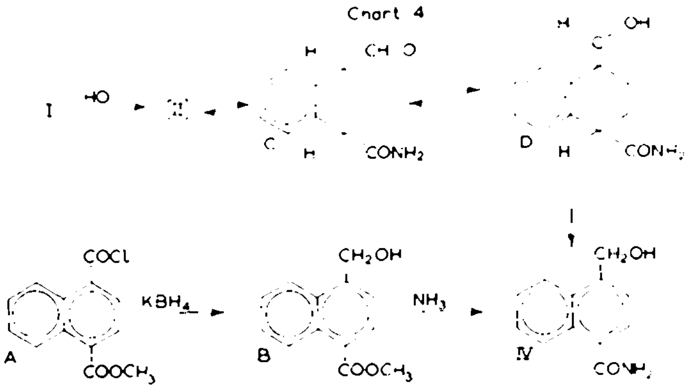
[13] A. Hantzsch, *Ber. Dtsch. Chem. Ges.* **27**, 1248 (1894); F. Feist, *Ibid.* **45**, 945 (1912); A. W. Titherley and M. E. Marples, *J. Chem. Soc.* **93**, 1933 (1908); K. C. Pandya and T. S. Sodhi, *Proc. Indian Acad. Sci.* **7**, 361 (1938).

[14] E. Tagman, E. Surz and K. Hoffmann, *Helv. Chim. Acta* **37**, 185 (1954).

[15] L. J. Bellamy, *The Infrared Spectra of Complex Molecules* pp. 175–189. Methuen, London (1954).

Chart 2), and that (II) is in equilibrium with its open tautomer, the aldehyde amide (Chart 4, C). A series of prototropic rearrangements, perhaps passing over the related enol (Chart 4, D), leads to (IV) in a straightforward way. The rearrangement is an internal oxidation-reduction reaction whose driving force comes, to a first approximation, from the resonance energy of the new benzene ring.

Chart 4



What there is to say at present about the mechanism of formation of (I) is based on the assumption that the rearrangement of the azide proceeds normally to the *iso*cyanate (Chart 5, A), which then undergoes the unusual transformation to (I). This assumption is supported by the fact that the product of rearranging the carbonyl azide (Chart 1, C) in benzene, in the absence of benzyl alcohol, shows absorption in the infrared at 4·43 μ (2259 cm^{-1}).* The assumption is consistent with the fact that *cyclo*propane carboxylic acid undergoes a normal Hofmann[17] and Schmidt[18] reaction while 2-phenyl*cyclo*propropane carbonyl azide and 2-(3′:4′-dimethoxyphenyl) *cyclo*propane carbonyl azide rearrange normally.[19]

A grossly reasonable mechanism for the rearrangement of the *iso*cyanate can be proposed independent of the stereochemistry. Breaking of the *cyclo*propane bond to the β-carbon atom of the naphthalene ring system leads to the redistribution of the pair of electrons of that bond between two portions (Chart 5, B). In the one portion the unbonded orbital is α to the *iso*cyanate grouping and is itself in resonance with the form in which the carbonyl group of the *iso*cyanate bears the unbonded orbital. This type of resonance, the energetic value of which is not possible to guess either in theory or by analogy with pertinent experimental observations, presumably prevails no matter how the pair of electrons is distributed. In the other portion, the unbonded orbital is involved much as it is in α-substitution reactions of naphthalene. In principle rebonding can now occur between the carbon atom of the *iso*cyanate grouping and the 4-position of the naphthalene ring or the 2-position.

If the *iso*cyanate be *trans* (Chart 5, A_{trans}) as indeed it appears from the isolation by Buchner and Hediger[5] of *trans-cyclo*propane tricarboxylic acid and the established stereochemistry of the Curtius rearrangement, extensive rotation of the *iso*cyanate group is required to rebond at either the 2- or 4-position and the non-bonded system

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* 4·40–4·45 μ is reported for the *iso*cyanate grouping.[16]

[16] H. Hoyer, *Chem. Ber.* **89**, 2677 (1956).

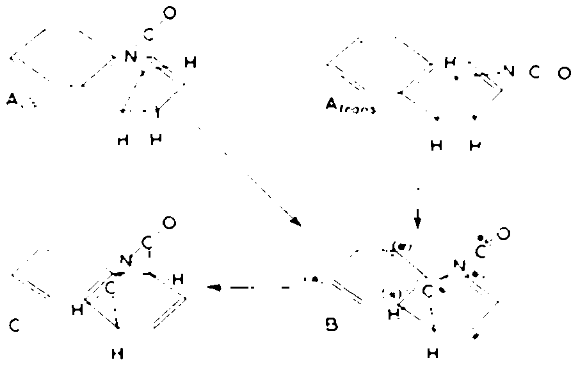
[17] P. Lipp, J. Buchkremer and H. Seeles, *Ann.* **499**, 1 (1932).

[18] M. J. Slatter, *J. Am. Chem. Soc.* **63**, 1733 (1941).

[19] A. Burger and W. L. Jost, *J. Am. Chem. Soc.* **70**, 2198 (1948); A. Burger and G. T. Fitchett, *Ibid.* **74**, 3415 (1952).

must be considered to be an intermediate in which the two portions function relatively independently of each other. If contrary to the literature the *iso*cyanate be *cis* (Chart 5, A_{cis}), rearrangement may occur with a remarkably small readjustment of bond

Chart 5



angles and distance through a transition state in which the new bond may be formed simultaneously with the breaking of the old and in which the two portions need never be free (Chart 5, B).*

Overlap simultaneously between C_2 and $C\alpha$ to $N=C=O$ and between C_4 and carbonyl C of $N=C=O$ (even though unequal in contribution) in the product-determining transition state may account for the overwhelming predominance of bonding at C_2 (Chart 5, C). In this analysis the rearrangement would be encouraged more by a *cis*-configuration of the starting *iso*cyanate than by the *trans* indicated in the literature. The question of stereochemical assignment is under investigation.

In completing a hypothetical mechanism for the formation of (I), the entirely reasonable reaction of the imino ketone (Chart 5, C) with benzyl alcohol must occur. Mechanisms for this reaction have already been considered above and are outlined in Chart 3.

EXPERIMENTAL†

Methyl 1-Benznorcaradienecarboxylate from Naphthalene and Methyl Diazoacetate[3]

Following the procedure for the reaction of naphthalene and ethyl diazoacetate,[5] 2800 g (22·5 moles) naphthalene was heated to 150° in a 5-l., three-necked flask fitted with therm, stirrer, water-cooled addition funnel, and two Vigreux columns in series. Over an 8 hr period, 450 g (4·50 moles) methyl diazoacetate was added dropwise during stirring. After being heated an additional 2 hr, the crude product was distilled

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* We wish to thank Prof. R. B. Woodward, Harvard University, for emphasising the importance of continuous overlapping of the two positions during the rearrangement.[10]

† All boiling and melting points are uncorrected. The latter were taken on a Kofler micro hot stage. Analyses were performed by Scwarzkopf Microanalytical Laboratories, 56–19 37th Avenue, Woodside 77, New York. Infrared spectra were taken on a Perkin Elmer Model 21 recording spectrophotometer using sodium chloride optics and were calibrated against the spectrum of atmospheric water. Ultraviolet spectra were taken on a Cary Model 11S recording spectrophotometer.

The n.m.r. spectra were determined using a Varian Associates Model 4300 V High Resolution spectrometer with super-stabilizer and spinning sample. Peak positions are reported in cps at 40 mc relative to benzene.

[10] R. B. Woodward and T. J. Katz, *Tetrahedron* 5, 70 (1959).

through a 2 × 30-cm Vigreux column collecting the first fraction, largely naphthalene, at 130–140°/45 mm in an externally cooled, three-necked flask to prevent clogging. The second fraction, 203 g (45%), b.p. 150–152°/6 mm was collected in a water-cooled condenser and receiving flask.

Purified material was obtained by redistillation through a 0·5 × 50-cm, glass-spiral column; b.p. 109°/0·6 mm; n_D^{25} 1·5882. The ultraviolet spectrum (acetonitrile), shown in Fig. 1, had λ_{max} at 222, 228, 235, 271, and 304 mμ (log ϵ 4·47, 4·52, 4·40, 3·90, and 3·08, respectively).

2-*Benzyloxy-6:7-benzo-3-azabi*cyclo [3.2.2] *nona-6:8-dien-4-one* (I)

(1) *By way of* 1-*benznorcaradienecarbonyl hydrazide* (*Hoffman*[3])

A mixture of 55 g methyl 1-benznorcaradienecarboxylate and 150 ml 85% hydrazine hydrate in 300 ml methanol was refluxed for 36 hr. The product, obtained by diluting the cooled solution with water, was recrystallized from ethyl acetate: m.p. 211·0–211·5° (Found: C, 72·2; H, 6·1; N, 14·3. $C_{12}H_{12}N_2O$ requires C, 72·0; H, 6·0; N, 14·0%). A solution of 12 g (0·17 mole) sodium nitrite in the minimum amount of water was added slowly during stirring to a cooled (0°) solution of 30 g (0·15 mole) hydrazide in 400 ml acetic acid containing 100 ml each of benzene and water. The solution was then poured into 1 l. water separating a benzene layer which was washed with water and aqueous sodium bicarbonate and dried over anhydrous sodium sulfate.

The dried solution of azide was diluted to 1 l. with benzene, treated with 40 g (0·37 mole) benzyl alcohol, and refluxed for 7 hr. Removal of the benzene by distillation and trituration of the residue with ether yielded 27 g (61%) of compound (I), m.p. 180–184° after recrystallization from acetone (Found: C, 78·5; H, 5·7; N, 5·0. $C_{19}H_{17}NO_2$ requires C, 78·3; H, 6·0; N, 4·8%).

(2) *By way of* 1-*benznorcaradienecarbonyl chloride*

(a) *Hydrolysis of methyl ester.* A solution of 100 g (0·5 mole) methyl benznorcaradienecarboxylate and 56·1 g (1·00 mole) KOH in 500 ml 40% aqueous ethanol, was refluxed for 3 hr in a nitrogen atmosphere. After being cooled and poured into 1500 ml ice-water, the reaction mixture deposited naphthalene which was filtered. The aqueous filtrate was covered with 1 l. ether and acidified with conc HCl during vigorous stirring. The etheral solution was washed twice with 250-ml portions water, dried over anhydrous sodium sulfate, and concentrated to 81·7 g (88%) of crude 1-benznorcaradienecarboxylic acid, m.p. 168·0–168·2° after recrystallization from ethanol (reported[5] m.p. 165–166°).

To avoid the isolation of ester, the following procedure proved expedient. Most of the excess naphthalene, boiling at 110–120°/38 mm, was distilled from the completed reaction of 2 moles of crude methyl diazoacetate and 10 moles of naphthalene. A solution of 112·2 g (2 moles) KOH in 1500 ml of 50% aqueous methanol was added to the residue and stirred vigorously for 8 hr at reflux. The cooled reaction mixture was poured into 1 l. water and filtered to remove naphthalene. The clear filtrate was acidified during cooling and scratching. After several hours at 5°, the oily acid had become sufficiently crystalline to be filtered, washed, and dried. The yield was 49% of theory based on glycine hydrochloride methyl ester.

(b) 1-*Benznorcaradienecarbonyl chloride.* A solution of 50 g (0·269 mole) 1-benznorcaradienecarboxylic acid and 51·2 g (0·429 mole) thionyl chloride (purified according to Vogel [21]) in 3 l. of anhydrous benzene was refluxed 16 hr. Freed of solvent and excess thionyl chloride *in vacuo*, the product was distilled at 98–100°/0·05 mm as a yellow oil, crystallizing in the receiver; 46·5 g (85%). Recrystallization from pentane at 5° afforded colorless crystals, m.p. 70·0–70·5° (Found: C, 70·4; H, 4·6; Cl, 17·1 $C_{12}H_9ClO$ requires C, 70·4; H, 4·4; Cl, 17·3%).

After having been refluxed for 12 hr, a solution of 15·0 g (0·0732 mole) of the acid chloride in 25 ml methanol was concentrated and fractionally distilled through a 1·5 × 30-cm glass-helix packed column yielding methyl 1-benznorcaradienecarboxylate: n_D^{25} 1·5892; and having an infrared spectrum superimposable on that of a sample prepared directly from naphthalene (*vide supra*).

(c) *Preparation and decomposition of* 1-*benznorcaradienecarbonyl azide.* To a magnetically stirred solution of 31·1 g (0·152 mole) acid chloride in 120 ml acetone cooled in ice, 13·4 g (0·204 mole) sodium azide in 40 ml water was added during 45 min, maintaining the temp below 20°. The precipitated NaCl was filtered and washed with 75 ml benzene. The filtrate and benzene liquid were poured into 750 ml benzene and extracted with 250 ml saturated aqueous sodium bicarbonate, three 250-ml portions water, and 250 ml saturated aqueous sodium chloride. The benzene solution was dried over anhydrous sodium sulfate at 5° prior to decomposition.

To 750 ml of this solution, theoretically containing 0·152 mole of azide, 25·7 ml (0·378 mole) of freshly distilled benzyl alcohol was added. Refluxing for 24 hr afforded 84% of the theoretical amount of nitrogen. Removal of the solvent and most of the benzyl alcohol *in vacuo* left a yellow oil which crystallized upon trituration with ether; 30·17 g (69%). An oil, obtained by evaporation of the ether washings, contained none of the product, as determined by infrared spectrum and was not further investigated.

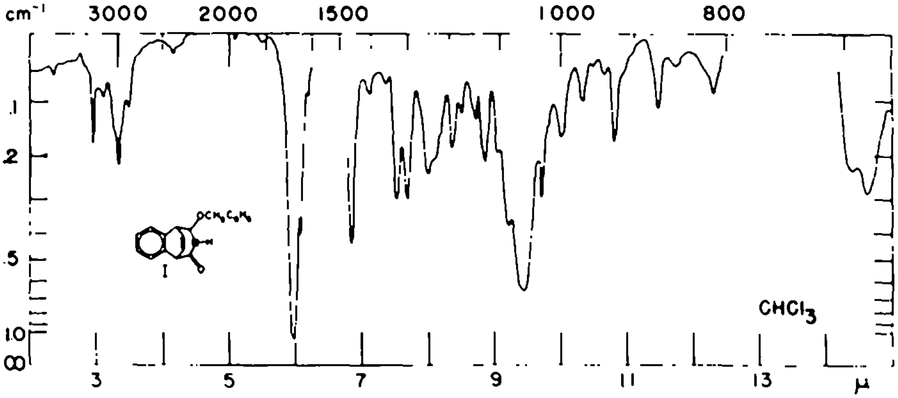

FIG. 2.

(I) is insoluble in ether, benzene, hexane, and carbon tetrachloride, soluble in ethyl acetate, methylene chloride, dioxane, and dimethyl formamide, and slightly soluble in chloroform, acetonitrile and acetone. The crude product may be recrystallized from acetonitrile or acetone. Six recrystallizations from acetone furnished

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[21] A. I. Vogel, *A Textbook of Practical Organic Chemistry* p.185. Longmans, Green and Co., New York (1951).

colorless crystals, m.p. 183 187° (Found: C, 78·4; H, 5·7; N, 4·8. $C_{19}H_{17}NO_2$ requires C, 78·3; H, 6·0; N, 4·8%). A mixture with the sample, m.p. 180-184°, prepared above, melted at 182–186°.

When the decomposition was carried out in the absence of benzyl alcohol, the benzene solution yielded oily crystals, decomposing slowly at room temp. The infrared spectrum of this material, taken in chloroform, disclosed typical *iso*cyanate absorption at 4·43 and 5·92 μ.* All attempts to recrystallize led to decomposition and disappearance of these bands.

(I) is unsaturated to permanganate, gives a negative Tollens test, and is insoluble in neutral, acidic, or alkaline water. The ultraviolet spectrum in acetonitrile, shown in Fig. 1, has λ_{max} 258 and 270 mμ (log ϵ 2·63 and 2·35, respectively). In the infrared, NH and carbonyl absorption occur at 2·97, 3·14, and 6·00 μ in chloroform, 2·95, 3·13, and 6·01 μ in potassium bromide, and 2·85, 3·08, and 5·98 μ in dioxane.

Lithium aluminum hydride reduction of (I)[3]

A solution of 800 mg (2·75 mmoles) of (I) in 20 ml tetrahydrofuran, freshly distilled from butyl magnesium bromide, was added to a stirred slurry of 155 mg (4·14 mmoles) lithium aluminum hydride in 20 ml of the same solvent in a nitrogen atmosphere. After being stirred 24 hr, the reaction mixture was refluxed 1 hr, cooled in ice, diluted with 2 ml water in 10 ml tetrahydrofuran and centrifuged. The supernatant liquid was decanted into water and extracted with chloroform. The chloroform extracts were washed with water and extracted with 3 M HCl. The acid extracts were neutralized and re-extracted with chloroform. Finally the chloroform solution was dried over anhydrous potassium carbonate and evaporated *in vacuo* to a residue which yielded on evaporative distillation 158·5 mg (34%) amine as a pink oil.

The N-*phenylthiourea* was prepared by Hoffmann[3] from the amine and phenyl *iso*thiocyanate and recrystallized from ethanol-water (Found: C, 74·7; H, 5·6; N, 8·9; S, 10·5. $C_{19}H_{18}N_2S$ requires C, 74·5; H, 5·9; N, 9·1; S, 10·5%).

The N, N-*dimethyl ammonium iodide* was prepared (Hoffmann), by treating 1 g (5·86 mmoles) of the amine above with 1 g (7·25 mmoles) potassium carbonate and 1 g (7·06 mmoles) methyl iodide in 7 ml chloroform. After the exothermic reaction had subsided, the solution was kept for 24 hr. Washing the crude product with chloroform afforded 1·3 g of colourless crystals which upon recrystallization from chloroform, m.p. 200-201° with dec. (Found: C, 51·1; H, 5·7; I, 38·8; N, 4·0. $C_{14}H_{18}IN$ requires C, 52·6; H, 5·5; I, 38·8; N, 4·3%).

A slurry of 130 mg (0·41 mmole) of the ammonium salt and 100 mg (2·5 mmoles) sodium hydroxide in 800 mg ethylene glycol was refluxed for 1 min and cooled. Extraction with pentane and concentration of the pentane left 70 mg of an oil which was treated with methyl iodide as above to give 100 mg of quaternary ammonium salt, m.p. 201–202° with dec; mixed m.p. with starting material of m.p. 200·2–200·8° was 194·0 200°.

Benznorcaradiene

(a) *The reaction of naphthalene with diazomethane.*[3] A solution of 2·38 kg (18·5 moles) naphthalene in 6·84 l. benzene was prepared in two 5-l. flasks lacking ground glass surfaces and equipped with motor-driven, glass stirrers. A total of 495 ml

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* 4·40 4·45 μ is reported for the *iso*cyanate grouping.[14]

(3·54 moles) 40% aqueous KOH was added to both flasks which were then cooled to −5° by ice and salt. Over the course of 2·5 hr, 291 g (2·82 moles) N-nitroso-N-methylurea[22] was added in small portions, maintaining the temperature below 0° during vigorous stirring. The contents of the flasks were allowed to warm to 15° and the organic layers were decanted onto KOH pellets and dried for 4 hr while cooled in ice. The benzene solution was then transferred to two similar 5-l. flasks, fitted with drying tubes containing KOH and cooled by an external stream of water. Irradiation, by six Westinghouse, type RS sunlamps, was continued until nitrogen evolution ceased. This required 18 to 36 hr depending on the age of the bulbs.

Attempts to separate benznorcaradiene from naphthalene by careful fractional distillation were frustrated by the solidification of naphthalene. Benzene was distilled from the combined solutions through a 2 × 95-cm Stedman column until the volume of material in the pot had been halved. Naphthalene crystallized on cooling and was filtered and washed with pentane. The combined washings and filtrate were reconcentrated. This process of concentration, cooling, filtration of the naphthalene, and reconcentration of the filtrate was repeated four or five times until no more naphthalene would precipitate from the concentrate at 0°.

The final, dark, oily concentrate was steam-distilled to give a condensate of naphthalene crystals and liquid benznorcaradiene from which the naphthalene was removed by filtering. A pentane extract of the filtrate was dried over anhydrous sodium sulfate and concentrated to crude benznorcaradiene.

(b) *Benznorcaradiene dibromide.*[3] To a solution of 35 g of crude benznorcaradiene in 300 ml carbon tetrachloride, cooled to −25°, 40 g bromine in 300 ml of the same solvent was added over a 1-hr period, maintaining a reaction temperature of −25 to −20° during stirring. Evaporation of the solvent and excess bromine at room temp, *in vacuo*, afforded a viscous oil which was extracted with 900 ml hexane in several portions. On concentrating the washings to 120 ml at room temp and cooling to 0°, the dibromide crystallized. The first two crops of colorless crystals weighed 17·27 g (1·7%, based on nitrosomethylurea; in several experiments, the yield varied from 1·5–2·5%); m.p. 85·8–86·8° with dec. This material can be kept indefinitely at −78° but decomposes slowly at room temp making it impossible to obtain satisfactory analyses (Found: C, 41·7; H, 3·8; Br, 42·1. $C_{11}H_{10}Br_2$ requires C, 43·7; H, 3·3; Br, 52·9%).

(c) *Debromination of benznorcaradiene dibromide.*[3] A 150-ml portion ether, freshly distilled from *n*-butyl magnesium bromide, and 8·45 g (0·130 g-atom) zinc dust were placed in a 500-ml, three-necked flask equipped with a pressure compensating addition funnel, stirrer, and reflux condenser protected from atmospheric moisture. A few ml of a solution of 16·9 g (0·0562 mole) recrystallized dibromide in 150 ml ether, freshly distilled as above, were added during vigorous stirring. Heat was carefully applied to initiate the exothermic reaction and then removed. The dibromide solution was added at such a rate that the ether was maintained at gentle reflux. After the addition, the solution was stirred for an additional 12 hr, and filtered to remove unreacted zinc. The filtrate was washed with 50 ml 3 M HCl, three 50-ml portions water, 50 ml saturated aqueous sodium chloride, and dried over anhydrous sodium sulfate. Evaporation of solvent, followed by distillation through a 0·5 × 50-cm, glass-spiral

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[22] C. R. Noller and S. Lieberman, *Organic Syntheses*, Coll. Vol. II, p. 461. John Wiley and Sons, Inc., New York.

column, afforded 6·11 g (75%) of *benznorcaradiene*, collected at 96–97°/6·5 mm. A center cut, b.p. 96·5°/6·5 mm, had n_D^{25} 1·6056 (Found: C, 93·1; H, 7·4; C-methyl "very small, could be 0". $C_{11}H_{10}$ requires C, 92·9; H, 7·1; C-methyl, 0%).

Benznorcaradiene exhibits λ_{max} at 222, 274, and 306 mμ (log ϵ 4·19, 3·82, and 3·02, respectively) in hexane, shown in Fig. 1, and 221, 274, and 306 mμ (log ϵ 4·32, 3·81, and 3·02, respectively) in 95% ethanol.

2-(o-*Carboxyphenyl*)-cyclo*propanecarboxylic acid*

The oxidative procedure employed is based on that of Lemieux and von Rudloff.[23] A solution of 50 mg (0·352 mmole) benznorcaradiene in 20 ml dioxane, distilled from permanganate and dried over potassium hydroxide, was diluted to 70 ml with water and treated with 35 mg (0·25 mmole) potassium carbonate, 634 mg (2·76 mmoles) potassium metaperiodate, and 7·5 mg (0·047 mmole) potassium permanganate. Within 4 hr at room temp with magnetic stirring, the permanganate had been reduced and a few more crystals were added. After an additional 24 hr, the manganese dioxide was filtered. The clear filtrate was acidified with 2 ml of 3 M HCl and extracted continuously with ether. Drying of the extract over anhydrous sodium sulfate and and evaporation of the solvent gave material which was sublimed at 120°/0·003 mm yielding 20·7 mg (29%) of colorless crystals, m.p. 192–200°. Material recovered from the titration was sublimed at 120°/0·005 mm and recrystallized (Found: C, 63·9; H, 4·8; neut. equiv. 106·9. $C_{11}H_{10}O_4$ requires C, 64·1; H, 4·9%; neut. equiv. 103·1).

2-*Hydroxy*-6:7-*benzo*-3-*azabi*cyclo [3.2.2] *nona*-6:8-*dien*-4-*one* (II)

Two grams (6·88 mmoles) of (I) were added to a solution of 1·6 g (28·6 mmoles) potassium hydroxide in 25 ml ethanol and the slurry was stirred magnetically for 12 hr in a nitrogen atmosphere. Unreacted (I) was recovered by filtering: 870 mg (40%). The recovery of starting material and yield of product was sensitive to the presence of impurities in the former and to the presence of air, both factors tending to decrease both the recovery and the yield but resulting in an increase in the percent conversion.

The ethanolic filtrate was poured into 75 ml saturated aqueous sodium chloride and continuously extracted with ether. Removal of the ether and its dissolved ethyl and benzyl alcohols, finally *in vacuo*, furnished a viscous residue which was extracted with 25 ml boiling toluene. Concentration of the toluene solution yielded 701·1 mg (90% based on unrecovered I) of (II) which was recrystallized from toluene: m.p. 183–191·5° with dec. (Found: C, 71·9; H, 5·5; N, 7·0 $C_{12}H_{11}NO_2$ requires C, 71·6; H, 5·5; N, 7·0%): ultraviolet spectrum in acetonitrile: λ_{max} 262 and 271 mμ (log ϵ 2·28 and 2·16, respectively); infrared spectrum in potassium bromide: 3·14, 3·27, and 6·00 μ; in dioxane: 2·84, 3·04, and 5·98 μ.

(II) could not be converted to an acetate or α-naphthyl urethane; it did give positive permanganate and Tollens tests.

Reconversion of (II) *to* (I). A solution of 100 mg of (II) and 10 ml freshly distilled benzyl alcohol in 40 ml anhydrous benzene was refluxed in a Dean Stark water-separation apparatus in a nitrogen atmosphere. After 12 hr, benzene and excess benzyl alcohol were removed *in vacuo* leaving an oil which was triturated with ether (86·5 mg; 60%). One recrystallization from acetone gave (I), m.p. 178–187° alone

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[23] R. U. Lemieux and E. von Rudloff, *Canad. J. Chem.* 33, 1701, 1710, 1714 (1955).

and 175·5–181·5° in admixture with a sample of (I), m.p. 180–184°. Infrared spectra of the two samples were superimposable.

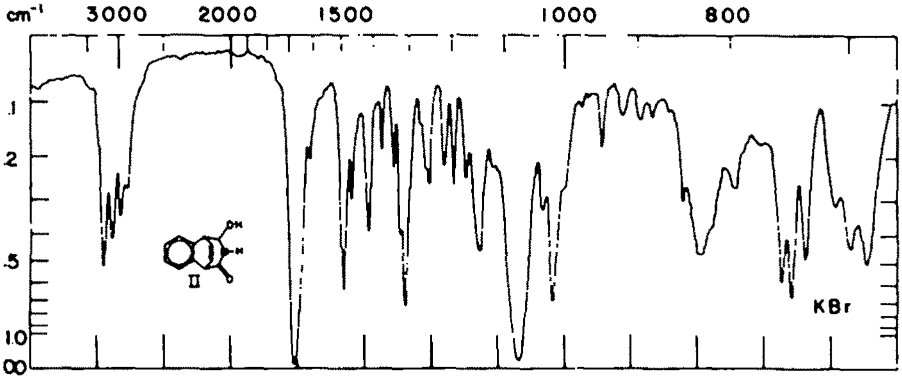

FIG. 3.

Hydrogenation of (II). Catalytic hydrogenation at atmospheric pressure of 201 mg of (II) in 35 ml ethyl acetate with 90 mg 5% palladium-on-charcoal, proceeded with the rapid uptake of 1·01 equivalents of hydrogen. Filtration and concentration afforded 199 mg of colorless crystals which could be recrystallized (but ineffectively purified) from *cyclo*hexane; m.p. 129·0–133·0° (Found: C, 71·9; 71·8; H, 7·0; 7·1; N, 6·7; 6·5. $C_{12}H_{13}NO_2$ requires C, 70·9; H, 6·5; N, 6·9%).

*Hydrogenation of 2-benzyloxy-6:7-benzo-3-azabi*cyclo-[3.2.2]*nona-6;8-dien-4-one* (I)[3]

A solution of 900 mg of (I) in 70 ml ethyl acetate was hydrogenated at atmospheric pressure using 450 mg 5% palladium-on-charcoal as catalyst. Within 16 min, 0·94 equivalents hydrogen were consumed. Removal of the catalyst and evaporation of the solvent left a colorless oil. Trituration with pentane furnished 704·5 mg (78%) of colorless crystals of *2-benzyloxy-6:7-benzo-3-azabi*cyclo [3.3.2] *nona-6-en-4-one*. This material no longer decolorized permanganate and was soluble in carbon tetrachloride and benzene but not in hexane. Recrystallization from *cyclo*hexane gave material; m.p. 145–146·5° (Found: C, 78·0; H, 6·8; N, 4·6. $C_{19}H_{19}NO_2$ requires C, 77·8; H, 6·5; N, 4·8%).

Ultraviolet spectrum in acetonitrile λ_{max} 247, 251, 253, and 259 mμ: (log ϵ 2·67, 2·65, 2·65, and 2·45, respectively); the infrared spectrum showed NH and carbonyl absorption at 2·97, 3·14, and 6·00 μ in chloroform and 2·93, 3·08, and 5·99 μ in dioxane.

When the hydrogenation was repeated in acetic acid as solvent, 2·1 equivalents of hydrogen was absorbed, the first half far more rapidly than the second. However, only amorphous material could be isolated. The hydrolysis of dihydro-I was attempted both at reflux and at room temp using a solution of 300 mg and 252 mg KOH in 3·6 ml ethanol. All efforts to isolate a crystalline product failed. In one experiment, performed at reflux, benzyl alcohol could be detected as one of the components of the crude reaction product by infrared spectroscopy.

Chromic acid oxidation of (II): 1:4-*dihydro*-1:4-*naphthalenedicarboximide*

The procedure employed is a modification of that used by Henbest, et al.[24] To a solution of 1·0 g of (II) in 200 ml acetone, 1 ml 2·67 M chromic acid was added dropwise during magnetic stirring. The oxidant was prepared by dissolving 6·67 g chromium trioxide in the minimal amount of water, adding 5·3 ml conc H_2SO_4 and diluting the solution to 25 ml with water. After 5 min stirring, excess chromic acid was destroyed by a few ml of a saturated solution of sulfur dioxide in acetone. The reduced solution, containing a colloidal dispersion of chromic salts, was filtered from the precipitated salts, treated with an equal volume of ethyl acetate, extracted with three 50-ml portions saturated aqueous potassium carbonate and 25 ml saturated aqueous sodium chloride, dried over anhydrous magnesium sulfate and concentrated to yield 701 mg (71 %) of crude imide. *cis*-1:4-Dihydro-naphthalenedicarboximide was insoluble in benzene and could be recrystallized from toluene; m.p. 240·0–240·5° (in a sealed capillary; otherwise sublimation begins about 200°) (Found: C, 72·5; H, 4·7; N, 7·3. $C_{12}H_9NO_2$ requires C, 72·6; H, 4·6; N, 7·0%); infrared spectrum disclosed significant peaks at 3·13, 5·85, and 5·93 μ in potassium bromide and 3·22 and 5·84 μ in dioxane.

1:2:3:4-*Tetrahydro*-1:4-*naphthalenedicarboximide* (III)

Catalytic hydrogenation of 701 mg of the unsaturated imide above in 95 ml ethyl acetate at atmospheric pressure using 500 mg 5% palladium-on-charcoal, proceeded with the consumption of 0·908 molar equivalents of hydrogen. The addition of filter-aid was followed by filtration and evaporation of solvent. Recrystallization from benzene furnished crystals, m.p. 206·5–207·0° in a sealed capillary (Found: C, 71·9; H, 5·7; N, 7·0. $C_{12}H_{11}NO_2$ requires C, 71·6; H, 5·5; N, 7·0%); infrared spectrum in potassium bromide: 3·16, 5·86, and 5·94 μ.

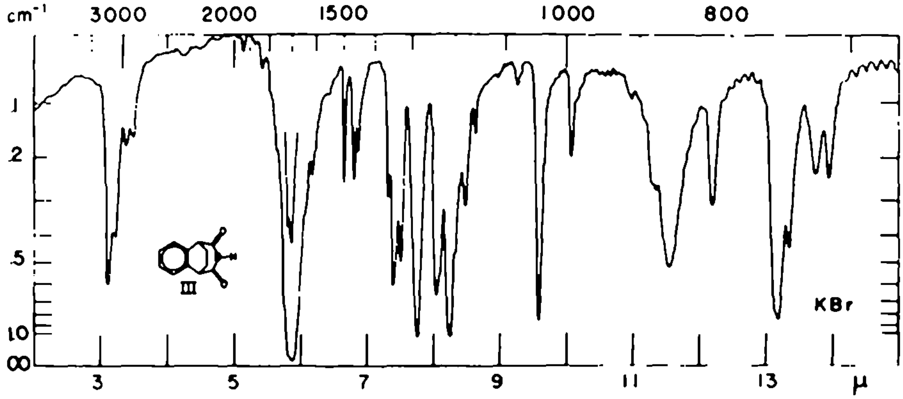

FIG. 4.

Synthesis of authentic 1:2:3:4-*tetrahydro*-1:4-*naphthalenedicarboximide* (III)

(a) 1:2:3:4-*Tetrahydro*-1:4-*naphthalenedicarboxylic anhydride*. A solution of 10 g 1:4-dihydro-1:4-naphthalenedicarboxylic acid,[10(b)] m.p. 200–210°, in 300 ml acetic acid

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[24] P. Bladen, J. M. Fabian, H. B. Nenbest, H. P. Koch and G. W. Wood, *J. Chem. Soc.* 2407 (1951).

was hydrogenated at 40 p.s.i. using 50 mg platinum oxide as catalyst. Filtration of the catalyst, followed by evaporation of the solvent *in vacuo*, afforded 8·60 g 1:2:3:4-tetrahydro-1:4-naphthalenedicarboxylic acid, of which the ultraviolet spectrum in acetonitrile (λ_{max} 263 mμ, log ϵ 2·71) was quite similar to that of starting material: (λ_{max} 262 mμ, log ϵ 2·02).

A solution of 2·0 g of this diacid in 6·0 ml acetic anhydride was heated for 1 hr at 100° and concentrated *in vacuo* at room temp to a viscous oil. Sublimation at 130°/0·05 mm afforded 1·18 g (65%) of the anhydride as colorless crystals exhibiting characteristic infrared absorption at 5·60 and 5·70 μ in potassium bromide; m.p. 107·5–112°, solidifying and remelting at 154·5–162·5° (Found: C, 71·5; H, 5·1. $C_{12}H_{10}O_3$ requires C, 71·3; H, 5·0%).

(b) 1:2:3:4-*Tetrahydro*-1:4-*naphthalenedicarboximide*. Five hundred milligrams of the anhydride was cautiously dissolved in 20 ml concentrated aqueous ammonia in a 50-ml round-bottomed flask. A 2 × 15-cm Vigreux column was attached as an air condenser and the flask was heated in a Wood's metal bath. After boiling away the ammonia and water, the temp was slowly raised to 300° and maintained there for 1 hr. The cooled reaction product was extracted with 25 ml of refluxing benzene to yield, on concentration, 460 mg (94%) of crude (III). Insoluble in *cyclo*hexane and carbon tetrachloride, this material could be recrystallized from either ethyl acetate or benzene, the latter solvent furnishing colorless crystals of m.p. 205·5–206·0° in a sealed capillary; mixed m.p. with the sample above, 206·5°; infrared spectra of the two samples were superimposable (Found: C, 71·9; H, 5·6; N, 6·9. $C_{12}H_{11}NO_2$ requires C, 71·6; H, 5·5; N, 7·0%).

Hydrolysis of (I) *to 4-hydroxymethyl-1-naphthamide*

A solution of 20·0 g of (I) and 16 g KOH in 250 ml ethanol was refluxed 1 hr in a stream of dry nitrogen and then poured into 1·5 l. saturated aqueous sodium chloride. Continuous extraction by ether followed by concentration, ultimately at 0·005 mm for 8 hr furnished a viscous residue. One recrystallization from acetone gave 9·62 g (70%) of 4-hydroxymethyl-l-naphthamide. In another experiment, the alcoholic reaction mixture was diluted with water and extracted with ether. The dried extract was concentrated and evaporatively distilled at 85° and 45 mm to give benzyl alcohol in 56% of theory, identified by infrared spectrum. The hydroxyamide is insoluble in benzene or chloroform and slightly soluble in ether, water, acetonitrile and acetone. Three recrystallizations from acetone, followed by sublimation at 120° and 0·02 mm, afforded 4-hydroxymethyl-1-naphthamide with the following melting characteristics. Sublimed material always melts at 152–153·5°. Recrystallized material shows a phase transition beginning at 143·5° from prism to needles which under the polarizing microscopic appears as a change from colorless prism (presumably anistropic) to colored, highly refractive needles. The needles then melt at 152–153·5°. The substance gives negative permanganate and Tollens tests and cannot be hydrogenated at an appreciable rate in ethyl acetate with 5% palladium-on-carbon; λ_{max} 226 and 285 mμ (log ϵ 4·78 and 3·88 respectively); NH and carbonyl absorption in the infrared: 3·00, 3·17, 6·08 and 6·20 μ in potassium bromide and 2·93, 5·95 and 6·19 μ in dioxane (Found: C, 71·9; H, 5·8; N, 7·3. $C_{12}H_{11}NO_2$ requires C, 71·6; H, 5·5; N, 7·0%).

The *acetate* could be prepared by dissolving 200 mg of the hydroxyamide in 2 ml pyridine and 0·8 ml acetic anhydride during cooling. After 24 hr at room temp, the crystalline product was filtered, washed with water, dried, and recrystallized from ethyl acetate; m.p. 198·5–200·0° (Found: C, 69·1; H, 5·6; N, 6·1 $C_{14}H_{13}O_3N$ requires C, 69·1; H, 5·4; N, 5·8%). Its infrared spectrum in dioxane solution showed the expected absorption in the 6 μ region; *viz.* 5·74, 5·94, and 6·20 μ corresponding to acetate carbonyl and amide (I) and (II), respectively; as well as the expected shift of C–O frequency from 9·30 to 8·04 μ (in potassium bromide).

Permanganate-oxidation of 4-hydroxymethyl-1-naphthamide

(a) 1:2:3:4-*benzenetetracarboxylic acid.* The procedure employed is a modification of that described for the oxidation of 1:4-naphthalenedicarboxylic acid.[25] To a stirred slurry of 150 mg (0·748 mmole) 4-hydroxymethyl-l-naphthamide and 21 mg (0·374 mmole) KOH in 10 ml water, 1·18 g (7·48 mmoles) potassium permanganate was added *slowly.* The contents were stirred for one hour at room temp and then for two at 90°.

After the destruction of excess permanganate with methanol, the manganese dioxide was filtered and washed with 20 ml hot water. Treatment of the filtrate with 307 mg (1·5 mmoles) barium chloride dihydrate gave a precipitate which was digested for 2 hr on the steam bath. Upon filtering the barium salt, 159 mg (1·5 mmoles) sodium carbonate was added to the filtrate, precipitating barium carbonate which was digested, filtered, and combined with the barium salt.

The combined precipitate was then treated with 1 ml of 1·47 M H_2SO_4 at 70° for 12 hr. After removing the barium sulfate and washing with water, the filtrate and washings were concentrated to 0·1 ml when crystals began appearing. The solution was cleared when two drops 1 M HCl were added and was kept at 5° for 12 hr, giving 7·4 mg crude 1:2:3:4-benzenetetracarboxylic acid of m.p. 224·5–237° (dec.); reported,[25] m.p. 236–238°. Concentration of the mother liquors afforded an additional 2 mg bringing the total yield to 5·0% of theory.

Because of the report that the m.p. of this acid is a poor criterion of purity,[26] the *tetramethyl ester* was prepared by treating the crude acid, in methanol, with ethereal diazomethane. Filtration, evaporation of the filtrate, and two recrystallizations afforded ester, m.p. 131·0–133·0°; m.p. 131·5–132·0° in admixture with an authentic sample of tetramethyl 1:2:3:4-benzenetetracarboxylate of m.p. 132·5–133·5°; infrared spectra of the two esters were superimposable.

(b) 1:4-*Naphthalenedicarboxylic acid.* A slurry of 1·50 g (7·48 mmoles) 4-hydroxymethyl-1-naphthamide in 100 ml water containing 3·55 g (22·5 mmoles) potassium permanganate was stirred at room temp for 1 hr and then at 80° for two. Manganese dioxide was filtered with the aid of Super-cel and washed with 100 ml hot water. The alkaline filtrate and washings were concentrated to 25 ml on the steam bath and, after the addition of 3 ml 2·5 M NaOH, refluxed for 48 hr. Acidification afforded 934 mg (58%) of dicarboxylic acid as finely divided white crystals. Sublimation at 150° and 0·005 mm followed by crystallization from acetic acid gave material of m.p. 309·0–327·5° in a sealed capillary; reported m.p. 325°.[27]

The *dimethyl ester* was prepared by treating a slurry of the di-acid, in methanol,

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[25] L. I. Smith and E. J. Carlson, *J. Am. Chem. Soc.* **60**, 290 (1939).

[26] F. González-Sánchez, *Tetrahedron* **1**, 231 (1957).

[27] G. Lock and R. Schneider, *Chem. Ber.* **84**, 639 (1951).

with excess ethereal diazomethane. Filtration, evaporation of solvent, and recrystallization from pentane afforded crystals of m.p. 67·5–68·0°; m.p. 67·5–68·0° in admixture with an authentic sample (*vide infra*) of m.p. 68·0–68·5°. Infrared spectra of the two esters were superimposable.

Synthesis of authentic 4-hydroxymethyl-1-naphthamide

1:4-Naphthalenedicarboxylic acid (3·0 g), prepared according to the procedure of Walker and Scott[10(b)] from dihydro acid (*vide supra*), was treated with excess ethereal diazomethane. Filtration and evaporation yielded the crystalline dimethyl ester which was dissolved in methanol (25 ml) for the next step, but which, in a separate experiment was isolated and recrystallized from pentane; m.p. 60–67·5° (90%) after one recrystallization; m.p. 68·0–68·5° (reported[28] 66·5°) after the third recrystallization. Addition of potassium hydroxide (900 mg) in methanol (3 ml) to the methanolic solution of dimethyl ester followed by refluxing for 1 hr, gave a solution which was poured into ice-water (30 ml) and extracted with three 20-ml portions ether. The combined ethereal extracts were washed with three 20-ml portions water and saturated aqueous sodium chloride (20 ml). Evaporation of the ether afforded 812·6 mg (24% recovery) dimethyl ester. The ether-extracted, aqueous, alkaline solution was heated to remove last traces of ether and acidified to furnish 2·03 g of crystalline *methyl hydrogen* 1:4-*naphthalenedicarboxylate* (64% of theory based on starting 1:4-napthalenedicarboxylic acid). The infrared spectrum of this material, in potassium bromide, exhibited carbonyl absorption at 5·78 and 5·90 μ (ester and acid, respectively).

Monomethyl ester (1·0 g) was added cautiously to 10 ml of purified[29] thionyl chloride and refluxed 1 hr. Excess thionyl chloride was removed *in vacuo* leaving crude *methyl* 4-*chlorocarbonyl*-1-*naphthoate*, which was dissolved in purified dioxane[30] (10 ml) and treated with potassium borohydride (700 mg). This slurry was refluxed, stirring magnetically, for 3 hr while protected by a calcium chloride-filled drying tube. Water (20 ml) was added, cautiously at first, during stirring. The last traces of borohydride were finally decomposed by the addition of 3 M HCl in an amount insufficient to neutralize the alkaline solution. The aqueous solution was diluted further with water (10 ml) and extracted with three 10-ml portions methylene chloride. The combined extracts were washed with three 20-ml portions water and dried over anhydrous magnesium sulfate. Evaporation afforded 759 mg methyl 4-hydroxymethyl-1-naphthoate as an oil which crystallized on cooling and scratching; yield, 81% based on methyl 1:4-naphthalenedicarboxylate or 71% based on 1:4-naphthalenedicarboxylic acid.

A solution of methyl 4-hydroxymethyl-1-naphthoate (354·3 mg) in methanol (25 ml) was saturated with anhydrous ammonia at 0°, sealed in a Carius tube and heated at 131° for 24 hr. Methanol and excess ammonia were evaporated, finally *in vacuo*, furnishing a brown oily mixture of product and starting material. The former could be separated by crystallization from chloroform-acetone. Charcoal decolorization, followed by recrystallization from acetone afforded 4-hydroxymethyl-1-naphthamide; m.p. 151·5–152·0°, exhibiting the characteristic phase transition at 143·5° (*vide supra*); mixed m.p. with the sample described above was 150·0–151·5°.

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[28] E. F. Bradbook and R. P. Linstead, *J. Chem. Soc.* 1739 (1936).

[29] D. L. Cottle, *J. Am. Chem. Soc.* **68**, 1380 (1946).

[30] K. Hess and H. Frahm, *Ber. Dtsch. Chem. Ges.* **71**, 2627 (1938).