it is not necessary to suffer the loss on recrystallization since the crude oil is sufficiently pure for use as an aminating agent.

***t*-Butyl Hydrazine-1,1-dicarboxylate.**—The sodium salt of *t*-butyl iminodicarboxylate was obtained as described above from 4.94 g. of the ester, 0.55 g. of dry sodium hydride, and 25 ml. of dimethylformamide by warming for 12 hr. in a water bath at 55–60°. The mixture was treated with 3.58 g. of mesitoxyamine in 5 ml. of dimethylformamide, heated for 6 hr. to 55–60°, diluted to 350 ml. with water, treated with decolorizing carbon, and filtered. The filtrate was extracted with about 12–15 12-ml. portions of ether. Evaporation of the combined ether extracts gave 2.7 g. of white solid, m.p. 74–92°. Two recrystallizations from ligroin (b.p. 60–70°) gave 1.2 g. (26%) of the pure N-amino compound as white needles, m.p. 104–106°. Better yields (35–40%) were obtainable by using an excess of mesitoxyamine (2 moles per mole of imide).

Anal. Calcd. for $C_{10}H_{20}N_2O_4$: C, 51.71; H, 8.68; N, 12.06. Found: C, 51.94; H, 8.69; N, 12.15.

The **benzal derivative**, obtained in the usual manner with a trace of acetic acid as catalyst, was recrystallized from ligroin (b.p. 60–70°) as white block-like crystals, m.p. 73–75°. There was no depression of the melting point on admixture with a sample prepared by acylation of the hydride-derived sodium salt of *t*-butyl 2-benzalcarbazate by means of *t*-butyl azidoformate.

Anal. Calcd. for $C_{17}H_{24}N_2O_4$: C, 63.73; H, 7.55; N, 8.74. Found: C, 63.83; H, 7.70; N, 8.73.

2-[Bis(*t*-butyloxycarbonyl)]amino-2,3-dihydro-1H-benzo[*de*]isoquinoline.—A solution of 1.02 g. of 1,8-bis(bromomethyl)naphthalene[23] and 0.75 g. of *t*-butyl hydrazine-1,1-dicarboxylate in 10 ml. of dimethylformamide was warmed to 55–60° and 0.95 ml. of triethylamine added. The mixture was stored at room temperature for 36 hr. and diluted with 100 ml. of water. Cooling and scratching caused deposition of 0.65 g. (52%) of cream-colored solid, m.p. 150–157°. Recrystallization from ethanol–nitromethane (3:1) gave 0.55 g. (44%) of the carbazate as flat white needles, m.p. 159–161°.

Anal. Calcd. for $C_{22}H_{28}N_2O_4$: C, 68.73; H, 7.34; N, 7.29. Found: C, 68.60; H, 7.25; N, 7.41.

Cleavage of 2-[Bis(*t*-butyloxycarbonyl)]amino-2,3-dihydro-1H-benzo[*de*]isoquinoline.—A stream of gaseous hydrogen chloride was passed into a solution of 0.06 g. of XII in 5 ml. of nitromethane for 2–3 min. After standing for 5–10 min., filtration gave 0.02 g. (58%) of snow-white crystalline solid, m.p. 236.5–238.5° dec. (darkening at 230°), lit.[14] m.p. 233–237° dec. The infrared spectrum was identical with that of an authentic sample[14] of the hydrochloride of 2-amino-2,3-dihydro-1H-benz[*de*]isoquinoline.

(23) L. A. Carpino, *J. Am. Chem. Soc.*, **85**, 2144 (1963).

Alkaline Degradation of 1,1-Disubstituted Sulfonhydrazides. Synthesis of a Pair of Cyclic, Benzylic Hydrazines Derived from Acenaphthene and Acenaphthylene[1]

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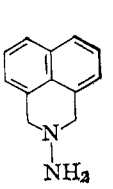
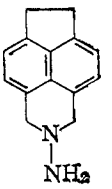
In order to test some hypotheses relating to the oxidation and sulfonhydrazide degradation of 1,1-disubstituted hydrazines two appropriate model hydrazines have been prepared for further study, namely 2-amino-2,3-dihydro-1H-indeno[1,6,7-*def*]isoquinoline (III) and 2-amino-2,3,6,7-tetrahydro-1H-indeno[1,6,7-*def*]isoquinoline (II). Treatment of acenaphthene-5,6-dicarboxylic acid anhydride with hydrazine hydrate gave the corresponding cyclic hydrazide (XI) which was reduced by means of sodium borohydride and lithium bromide to II. An alternate route to II involved lithium aluminum hydride reduction of dimethyl acenaphthene-5,6-dicarboxylate (XII) to the diol (XIII). Treatment of the diol with hydrobromic acid gave the dibromide (XIV) which upon treatment with *t*-butyl carbazate and triethylamine in dimethylformamide solution gave the carbo-*t*-butoxy derivative (XVI) which was converted to II by cleavage with hydrogen chloride. The most direct route to the corresponding unsaturated hydrazine (III) involved treatment of 5,6-bis(bromomethyl)acenaphthene with N-bromosuccinimide to give the corresponding tribromide XXII. Treatment of XXII with *t*-butyl carbazate and triethylamine in dimethylformamide was accompanied by dehydrobromination to give the protected unsaturated hydrazine derivative XXIII which on removal of the carbo-*t*-butoxy group gave the unsaturated hydrazine III. An alternate route to III involved bromination of the saturated diester XII with N-bromosuccinimide followed by dehydrobromination with lithium bromide in dimethylformamide to the unsaturated diester XVIII, reduction of which by means of lithium aluminum hydride gave the unsaturated diol XX. The diol (XX) was converted to the dichloride XXI by reaction with thionyl chloride in benzene and the dichloride was cyclized to the protected unsaturated hydrazine (XXIII) by reaction with *t*-butyl carbazate and triethylamine in dimethylformamide. The ultraviolet and n.m.r. spectra of the substituted acenaphthene and acenaphthylene derivatives obtained during the course of this work were examined and correlated with the spectra of the parent hydrocarbons.

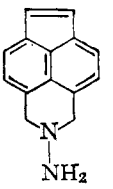
Based on studies of the oxidation and sulfonhydrazide degradation of benzylic hydrazines such as 1,1-dibenzylhydrazine,[2,3] N-aminodihydroisoindole,[4] and the corresponding dibenzazepine[3a] it was expected that similar treatment of 2-amino-2,3-dihydro-1H-benz[*de*]-isoquinoline (I) would yield acenaphthene. However this proved not to be the case.[5] Instead, mercuric oxide oxidation of I yielded a small amount of the tetrazene, considered to be the "normal" oxidation product of nonbenzylic 1,1-disubstituted hydrazines. Treatment



I



II



III

of the *p*-toluenesulfonyl derivative of I with aqueous alkali gave a high-melting isomer of the tetrazene, the structure of which is currently under study. In order to explain this unusual result it was postulated that the differences between the dihydroisoindoles and dibenzazepines on the one hand and compound I on the other might be ascribed to the opportunity for a low-energy

(1) Supported by a grant (NSF G-19506) from the National Science Foundation.

(2) M. Busch and B. Weiss, *Ber.*, **33**, 2701 (1900).

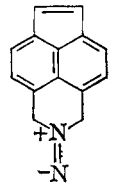
(3) (a) L. A. Carpino, *J. Am. Chem. Soc.*, **79**, 4427 (1957); (b) C. G. Overberger, *Record Chem. Progr.*, **21**, 21 (1960).

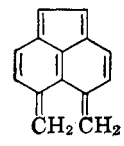
(4) L. A. Carpino, *ibid.*, **84**, 2196 (1962).

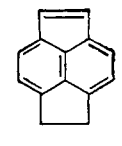
(5) L. A. Carpino, *ibid.*, **85**, 2144 (1963).

fragmentation in the former two cases to yield *o*-quinodimethane intermediates which could subsequently cyclize or dimerize to the observed products. It was also considered that lack of conversion of I to acenaphthene might simply reflect the stability of systems formed by fusion of three-atom bridges across the *peri* positions of the naphthalene nucleus relative to the strained acenaphthene system.

Having excluded the possibility that an α-naphthylmethyl substituent might not provide stabilization of the transition state for conversion to hydrocarbon coupling products equal to that provided by a simple benzyl group by a study of 1,1-bis-α-menaphthylhydrazine,[6] studies were initiated in order to shed further light on the nature of the intermediates in these reactions. It was considered of interest to prepare the two benzylic hydrazines II and III since in both cases the stereochemical arrangement around the nitrogen function is essentially the same. If concerted fragmentation of an azamine intermediate is necessary for the success of the reaction in the case of these cyclic systems the saturated derivative II should be no more reactive than the parent compound I. On the other hand the unsaturated analog might undergo concerted fragmentation of the azamine (IV) to the 1,8-quinodimethane (V)

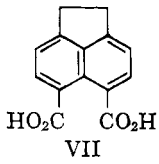

IV

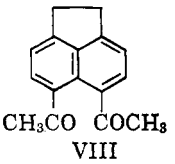

V

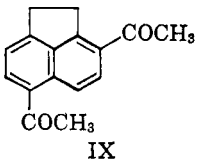

VI

yielding eventually the tetracyclic hydrocarbon, 1,2-dihydropyracylene (VI).[7] It is interesting in this connection that Lemal[8] has recently observed a related fragmentation during the alkaline degradation of the *p*-toluenesulfonyl derivative of N-aminopyrrolidine.

In the present paper we report the synthetic methods used to obtain the two model hydrazines II and III. Acenaphthene-5,6-dicarboxylic acid (VII) was used as the starting point in the synthesis of both compounds. The diacetyl derivative obtained by treatment of acenaphthene with acetyl chloride in the presence of aluminum chloride was considered by Dziewonski and Spirer[9] to be the 5,6-derivative (VIII). More recently

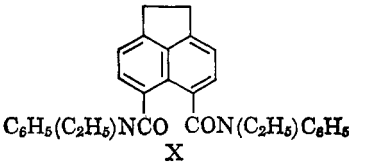

VII

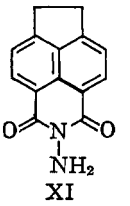

VIII


IX

Anderson and Anderson[10] improved the yield of the diacetyl derivative, m.p. 149°, obtained in this reaction and converted it by hypohalite oxidation to a dicarboxylic acid, m.p. 290–296°. This agreed with the reported melting point (293–294° dec.) of the 5,6-diacid (VII) obtained by Freund and Fleischer[11] by another route. Subsequently Richter and Stocker[12] reported that the same diacetylation product (m.p. 148–149°) of acenaphthene gave on hypohalite oxidation a diacid which did not melt up to 340°. By application of the Beckmann rearrangement to the dioxime it was shown that the acetyl groups had entered the 3,6- rather than the 5,6-positions. In the present study repetition of the improved procedure of Anderson and Anderson for diacetylation gave a 29% yield of a diacetyl derivative (m.p. 145–147°) which with potassium hypochlorite gave in 90% yield a diacid which, in agreement with the work of Richter and Stocker, did not begin to decompose until about 350°. In addition, in agreement with the 3,6-arrangement of the two carboxyl groups attempts to convert the compound to a cyclic anhydride or a cyclic hydrazide were unsuccessful. As noted below an authentic sample of the 5,6-diacid readily yields such a cyclic hydrazide.

A report in the patent literature[13] indicates that acenaphthene undergoes Friedel–Craft's acylation by means of N-ethyl-N-phenyl carbamoyl chloride in the presence of aluminum chloride to give the 5,6-dicarboxamide (X). Hydrolysis of X by means of dilute sulfuric acid was reported[13] to yield acenaphthene-5,6-


X


XI

dicarboxylic acid anhydride. Repetiton of the procedure described gave the 5,6-anhydride in 35–40% yield, m.p. 288–291° dec. (lit[13] m.p. 294° dec.). The structure of this anhydride has been established beyond any doubt by conversion (see below) to two compounds of known structure, 5,6-dimethylacenaphthene[14] and pyracene (XV).[15] The reason for the 3,6-orientation in the case of diacetylation (and dibenzoylation[12]) and 5,6-orientation in the case of carbamoylation is not clear. Treatment of the crude anhydride with hydrazine hydrate in dimethylformamide gave 95% of the cyclic hydrazide, N-amino-5,6-acenaphthalimide (XI). Reduction of XI by means of sodium borohydride–lithium bromide in diglyme gave the desired saturated hydrazine (II) in 25–30% yield. A similar method had been used earlier[16] in the synthesis of I.

An alternate route to II was also developed which involved reduction of the dimethyl ester (XII) of the 5,6-diacid to the diol (XIII) in 88% yield. The most convenient method for conversion of the diol (XIII) to

(6) In unpublished studies it has been shown that 1,1-bis(α-menaphthyl)-2-*p*-toluenesulfonhydrazide on treatment with ethanolic sodium methoxide gives 1,2-di-α-naphthylethane in a yield of 87%.

(7) A. G. Anderson, Jr., and R. G. Anderson, *J. Org. Chem.*, **23**, 517 (1958).

(8) D. M. Lemal, T. W. Rave, and S. D. McGregor, *J. Am. Chem. Soc.*, **85**, 1944 (1963).

(9) K. Dziewonski and J. Spirer, *Bull. intern. acad. polon sci.*, **A**, 232 (1931); *Chem. Abstr.*, **26**, 2191 (1932.

(10) A. G. Anderson, Jr., and R. G. Anderson, *J. Org. Chem.*, **22**, 1197 (1957).

(11) M. Freund and K. Fleischer, *Ann.*, **399**, 182 (1913).

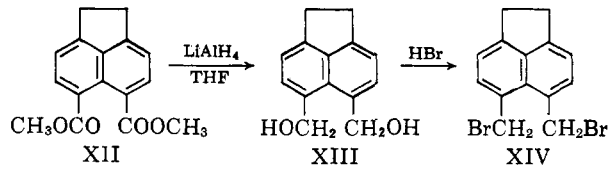
(12) H. J. Richter and F. B. Stocker, *J. Org. Chem.*, **24**, 214 (1959).

(13) M. Wyler and A. Kershaw, U. S. Patent 2,072,237 (March 2, 1937); *Chem. Abstr.*, **31**, 2615 (1937).

(14) G. Wittig, H. G. Reppe, and T. Eicher, *Ann.*, **643**, 47 (1961). Professor Wittig kindly provided an infrared spectrum of his original sample of 5,6-dimethylacenaphthene. This spectrum matched that of our sample obtained by reduction of 5,6-bis(bromomethyl)acenaphthene.

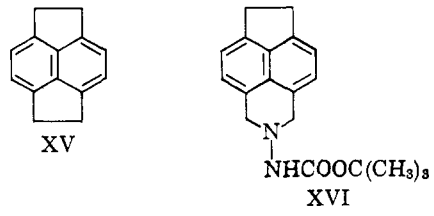
(15) A. G. Anderson, Jr., and R. H. Wade, *J. Am. Chem. Soc.*, **74**, 2274 (1952).

(16) L. A. Carpino, A. A. Santilli, and R. W. Murray, *ibid.*, **82**, 2728 (1960).



XII XIII XIV

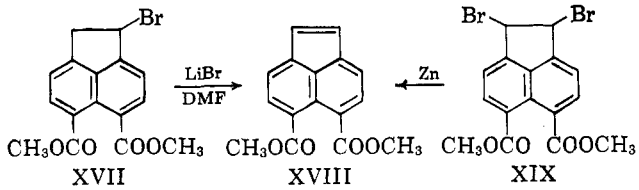
the dibromide (XIV) involved treatment with aqueous hydrobromic acid in dioxane. Reduction of the dibromide (XIV) by means of sodium borohydride in the presence of aqueous alkali[17] gave the known 5,6-dimethylacenaphthene,[14] whereas reaction with phenyllithium gave, as expected, the known hydrocarbon pyracene (XV).[15,18] Reaction of the dibromide (XIV)



XV XVI

with *t*-butyl carbazate in the presence of triethylamine in dimethylformamide gave, in 61% yield, the protected hydrazine (XVI) which upon cleavage with hydrogen chloride in methylene dichloride gave the hydrochloride of the desired hydrazine (II) in quantitative yield.

Attention was next turned to the development of a synthetic route to the unsaturated hydrazine III. Although acenaphthene and various halogenated derivatives are attacked by lead tetraacetate with introduction of an acetoxy group at the 1-position,[14,19] the dimethyl ester XII proved to be completely inert to lead tetraacetate under the same conditions. On the other hand treatment with N-bromosuccinimide gave the 1-bromo derivative XVII which could be dehydrohalogenated to the unsaturated ester (XVIII) by treat-

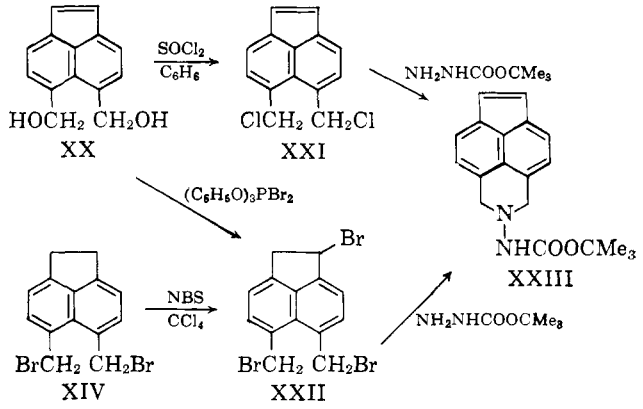


XVII XVIII XIX

ment with lithium bromide in dimethylformamide.[20] Classical methods of dehydrohalogenation involving the use of pyridine or quinoline were unsatisfactory for this conversion. The unsaturated ester was also obtained by treatment of XII with 2 moles of N-bromosuccinimide followed by zinc dehalogenation of the resultant dibromo derivative XIX. The route through the monobromo compound was preferred since the dibromide could be obtained only in an impure state. In order to establish that no skeletal changes had accompanied bromination and dehydrobromination, the unsaturated diester (XVIII) was hydrogenated over a palladium catalyst. One mole of hydrogen was taken up and the saturated ester XII was isolated in quantitative yield.

(17) H. C. Brown and H. M. Bell, *J. Org. Chem.*, **27**, 1928 (1962).
(18) This route to pyracene was first suggested by Anderson and Anderson.[19]
(19) L. F. Fieser and J. Cason, *J. Am. Chem. Soc.*, **62**, 432 (1940).
(20) R. P. Holysz, *ibid.*, **75**, 4432 (1953).

Reduction of the unsaturated diester by means of lithium aluminum hydride in benzene–ether under carefully controlled conditions gave the unsaturated diol XX in 43% yield. Conversion of compound XX to the corresponding unsaturated dibromide was fraught with considerable difficulty presumably because of accompanying addition of hydrogen halide or other halogen-containing species to the reactive double bond. For example it was not possible to obtain the pure unsaturated dibromide XXI (Br instead of Cl)



XX XXI XXIII XIV XXII

by treatment of XX with hydrobromic acid or phosphorus tribromide in dioxane or methylene dichloride. In an attempt to improve the reaction, the diol was treated with triphenyl phosphite dibromide.[21] Strangely enough the only compound isolated (31%) in this reaction was the tribromide XXII, the structure of which was established by its formation from the saturated dibromide XIV and N-bromosuccinimide and by its ready dehydrohalogenation across the 1,2-positions. The accidentally formed tribromide (XXII) proved to be a valuable intermediate in completing the synthesis of the unsaturated hydrazine III. Since the yield of tribromide by the N-bromosuccinimide route was high (86%) it was possible to utilize the readily available saturated dibromide XIV in further synthetic work and dispense with the more devious route through the unsaturated diol. It was found possible to combine dehydrohalogenation and ring closure of the tribromide XXII by treatment with *t*-butyl carbazate and triethylamine in dimethylformamide solution. This gave in 52% yield the desired unsaturated protected hydrazine derivative XXIII, the structure of which was established by comparison of its ultraviolet spectrum with that of acenaphthylene (see below) and its catalytic hydrogenation to the saturated derivative XVI by the uptake of 1 mole of hydrogen. Subsequently it was shown that 5,6-bis(chloromethyl)acenaphthylene (XXI) could be obtained without undue difficulty by treatment of the unsaturated diol XX with thionyl chloride in benzene solution. Treatment of XXI with *t*-butyl carbazate and triethylamine in dimethylformamide gave the unsaturated protected hydrazine XXIII in 65% yield.

Cleavage of the carbo-*t*-butoxy group of XXIII by means of hydrogen chloride in warm methanol gave a hydrochloride which was converted to the free hydrazine III without purification by treatment with sodium bicarbonate in aqueous solution.

(21) D. G. Coe, S. R. Landauer, and H. N. Rydon, *J. Chem. Soc.*, 2281 (1954).

Examination of the ultraviolet spectra between 250–350 mμ of the series of acenaphthene and acenaphthylene derivatives obtained in the course of this investigation provided additional evidence for the structural assignments. In the case of acenaphthene[15] itself a series of bands appears in the 250–300-mμ region with the strongest absorption at 288 mμ (log ε 3.75), whereas with acenaphthylene[22] the corresponding absorption is shifted to the 280–340-mμ region with the strongest absorption at 321 mμ (log ε 3.96). Acenaphthene and acenaphthylene derivatives having only alkyl substitution in the 5,6-positions show a similar series of bands shifted slightly to longer wave lengths. The main absorption maximum in the case of the 5,6-dialkyl acenaphthenes appears near 297, whereas with acenaphthylenes it is found at about 325 mμ. The ultraviolet curve of the saturated hydrazine (II) matched that of acenaphthene except for expected bathochromic shift. Maxima appeared at 285 mμ (log ε 3.96), 294 (4.04), 297 (4.05), 306 (3.91), 312 (3.86), and 326 (3.60). Similarly the spectrum of III matched that of acenaphthylene, showing maxima at 268 mμ (log ε 3.52), 279 (3.52), 323 (4.00), 332.5 (3.91), and 348 (3.74).

Further confirmation of the structural assignments came from an examination of the n.m.r. spectra of II and III in deuteriochloroform. The saturated hydrazine II exhibited four singlets at δ 3.27 (2H, NH_2), 3.37 (4H, CH_2), 4.15 (4 H, CH_2N), and 7.15 (4H, aromatic protons). The values for the amino and methylene protons correspond to those previously determined for 2-amino-2,3-dihydro-1H-benz[*de*]isoquinoline (I) and acenaphthene (methylene protons at δ 3.40). The unsaturated hydrazine III exhibited three singlets at δ 3.42 (2H, NH_2), 4.12 (4H, CH_2N), and 6.99 (2H, vinyl protons) in addition to the AB system of aromatic protons at 7.19 and 7.56 (4H, J = 7.0 c.p.s.). The vinyl protons of acenaphthylene itself appeared as a sharp singlet at δ 6.98.

Studies on the oxidation and sulfonhydrazide degradation of II and III will be reported separately.

Experimental[23–25]

N-Ethyl-N-phenylcarbamoyl Chloride.[26]—A suspension of 606 g. of N-ethylaniline and 278 g. of powdered calcium hydroxide in 2.5 l. of water was stirred at 0–5° and a rapid stream of phosgene was led into the mixture until it tested weakly acidic (3–4 hr.). After an additional 30 min. of stirring the acid chloride was filtered and washed with ice-cold water and then recrystallized as rapidly as possible from 1.1 l. of warm (35–40°) methanol with the addition of 8 g. of decolorizing charcoal. After cooling to −20° for several hours, 829 g. (90%) of the chloride separated as snow white crystals, m.p. 44–47°. A sample, recrystallized from ligroin (b.p. 50–60°), had m.p. 46–57° (lit.[27] m.p. 52°).

Acenaphthene-5,6-dicarboxylic Anhydride.—Acenaphthene-5,6-dicarboxylic acid di-N-ethylanilide (X) was prepared according to a method described in the patent literature[13] on a scale of not greater than 0.75 mole per run. The diamide was purified by extracting tarry impurities from the reaction product by means of hot methanol. After hydrolysis with 60% sulfuric acid solution in 2 *N* sodium hydroxide solution (charcoal), precipitation with dilute sulfuric acid, and 30-min. refluxing with 60% sulfuric acid, the anhydride was obtained in 35–40% yield as a nearly white powder, m.p. 288–291° dec. (lit.[11] m.p. 294°). The crude anhydride was pure enough for further use.

N-Amino-5,6-acenaphthalimide (XI).—A mixture of 33.6 g. of acenaphthene-5,6-dicarboxylic acid acid anhydride in 300 ml. of dimethylformamide was warmed to 100–110° to dissolve most of the solid and treated with 9 g. of 64% hydrazine solution. The yellow imide which separated at once was filtered after cooling to room temperature and washed well with dimethylformamide and water to give 34 g. (95%) of the imide. An analytical sample was obtained by recrystallization from acetic acid and nitromethane, m.p. 250° dec. (darkening at 240°).

Anal. Calcd. for $C_{14}H_{10}N_2O_2$: C, 70.58; H, 4.23. Found: C, 70.33; H, 4.25.

The **benzal derivative** was obtained in the form of white flakes, m.p. 263° dec. (sintering from about 255°).

Anal. Calcd. for $C_{21}H_{14}N_2O_2$: C, 77.29; H, 4.32; N, 8.58. Found: C, 77.33; H, 4.63; N, 8.37.

2-Amino-2,3,6,7-tetrahydro-1H-indeno[1,6,7-*def*]isoquinoline Hydrochloride (II HCl).—To a suspension of 9.5 g. of sodium borohydride and 21.8 g. of lithium bromide in 200 ml. of diglyme at room temperature there was added 23.8 g. of N-amino-5,6-acenaphthalimide (XI). After stirring for 6 hr., 200 ml. of water was added and the precipitated white addition product decomposed with a hot mixture of 3 *N* hydrochloric acid–methanol (1:1). On cooling 6.35 g. (26%) of the hydrochloride separated in the form of long, white needles. No sharp melting point was observed; rather blackening and decomposition began above about 210–220°. An analytical sample was obtained by recrystallization from dilute hydrochloric acid–methanol.

Anal. Calcd. for $C_{14}H_{15}ClN_2$: C, 68.15; H, 6.13; Cl, 14.37. Found: C, 68.57; H, 6.06; Cl, 14.19.

2-Amino-2,3,6,7-tetrahydro-1H-indeno[1,6,7-*def*]isoquinoline (II).—A solution of 2.47 g. of the hydrochloride in 150 ml. of hot water was cooled and treated with 1 *N* sodium carbonate solution until weakly alkaline to precipitate 2 g. (95%) of the free hydrazine, m.p. 186–188° dec. The analytical sample was obtained from methanol.

Anal. Calcd. for $C_{14}H_{14}N_2$: C, 79.97; H, 6.71; N, 13.32. Found: C, 79.72; H, 6.81; N, 13.28.

The **benzal derivative** was obtained from ethanol and benzene–ligroin (b.p. 50–60°) in the form of white, felt-like needles, m.p. 158–161° dec.

Anal. Calcd. for $C_{21}H_{18}N_2$: C, 84.53; H, 6.08; N, 9.38. Found: C, 85.00; H, 6.12; N, 8.82.

The *p*-**toluenesulfonyl** derivative obtained in the usual manner[38] was recrystallized from benzene as white, felt-like needles, m.p. 167–168° dec. (sintering at 165°).

Anal. Calcd. for $C_{21}H_{20}N_2O_2S$: C, 69.20; H, 5.53; N, 7.69. Found: C, 69.10; H, 5.23; N, 7.94.

Dimethyl Acenaphthene-5,6-dicarboxylate (XII).—Acenaphthene-5,6-dicarboxylic acid (VII) was prepared by dissolving the crude anhydride in hot, 2 *N* sodium hydroxide solution, treating with charcoal, and acidifying. A mixture of 194 g. of this crude acid and 127 g. of sodium carbonate was dissolved in 1.5 l. of warm water (40°) and treated with 202 g. (152 ml.) of dimethyl sulfate. After stirring for 45 min. at 40–50°, another 152-ml. portion of dimethyl sulfate and 85 g. of sodium carbonate were added. At the end of a second 45-min. period of stirring, an additional 76 ml. of dimethyl sulfate and 42.5 g. of sodium carbonate were added. After stirring for a final 45-min. period, the very tacky diester was filtered and recrystallized from 800 ml. of dioxane which gave 172 g. (80%) of the crude diester. Recrystallization from 500 ml. of dioxane (charcoal) gave 154 g. (71%) of white solid, m.p. 171–177°. Methylation of a suspension of the acid in methylene dichloride by means of diazomethane gave the same ester, m.p. 169–174°.

An analytical sample was obtained from a portion of the acid prepared from a carefully purified sample of the diamide and anhydride. A sample recrystallized from methanol, acetic acid, dioxane, and benzene had m.p. 176–178°, $\lambda_{max}^{C_2H_5OH}$ 315 mμ (log ε 3.88).

Anal. Calcd. for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22. Found: C, 70.83; H, 5.24.

(22) L. C. Craig, W. A. Jacobs, and G. I. Lavin, *J. Biol. Chem.*, **139**, 277 (1941).

(23) All melting points and boiling points are uncorrected. In the case of compounds showing decomposition points the substance was placed in the heating bath at temperatures 20–30° lower than the decomposition point and the temperature of the bath was raised at the rate of 5°/min.

(24) Elemental analyses are by Weiler and Strauss, Oxford, England, Galbraith Laboratories, Knoxville, Tenn., and Alfred Bernhardt, Mülheim (Ruhr), Germany.

(25) Ultraviolet spectra were measured in 95% ethanol on a Cary Model 14 recording spectrophotometer and n.m.r. spectra in deuteriochloroform on a Varian A-60 spectrometer using tetramethylsilane as internal standard.

(26) British Dyestuffs Corp., Ltd., R. W. Everatt and E. H. Rodd, German Patent 468,304 (May 3, 1927); *Chem. Abstr.*, **23**, 605 (1929).

(27) W. Michler, *Ber.*, **9**, 399 (1876).

5,6-Bis(hydroxymethyl)acenaphthene (XIII).—With stirring there was added slowly 29.8 g. of dimethyl acenaphthene-5,6-dicarboxylate (m.p. 171–177°) to a solution of 8.35 g. of lithium aluminum hydride in 800 ml. of dry tetrahydrofuran. By occasional cooling the temperature was maintained between 30–35°. The mixture was stirred for 1 hr. at room temperature and 2 hr. at 50° and finally the complex was destroyed by careful addition of tetrahydrofuran–water (2:1). After filtration the white solid was stirred vigorously in dilute sulfuric acid (1:10) at 0° for 30 min. and finally filtered and washed well with water to give 20.8 g. (88%), m.p. 205–206° (sintering began at 202°). Evaporation of the tetrahydrofuran filtrate gave an additional 1.8 g. (7.5%) of less pure diol, m.p. 200–202°. Recrystallization from dioxane did not raise the melting point. The analytical sample showed $\lambda_{max}^{C_2H_5OH}$ 299 mμ (log ε 4.07).

Anal. Calcd. for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.49; H, 6.46.

5,6-Bis(bromomethyl)acenaphthene (XIV).—With stirring there was added at room temperature 21.4 g. of 5,6-bis(hydroxymethyl)acenaphthene (XIII) to a mixture of 200 ml. of dioxane and 100 ml. of 48% aqueous hydrobromic acid. The diol slowly dissolved over the course of 1 hr. and the dibromide began to separate. After stirring for an additional 2 hr. the dibromide was precipitated completely by the addition of 200 ml. of water. There was obtained 32 g. (94%) of a slightly yellow, crystalline mass. On recrystallization from benzene or benzene–ligroin 27.9 g. (82%) of the dibromide was obtained in the form of beautiful white needles, m.p. 157–159° dec., sintering from about 145°. On storage at room temperature the dibromide showed signs of decomposition after a few weeks. This may account for the unsatisfactory bromine analyses obtained. In a refrigerator it could be stored indefinitely without change. The same compound was obtained utilizing phosphorus tribromide (86%), triphenyl phosphite dibromide (79%), and triphenyl phosphite–benzyl bromide[28] (50%).

Anal. Calcd. for $C_{14}H_{12}Br_2$: C, 49.45; H, 3.56; Br, 47.00. Found: C, 49.74; H, 3.68; Br, 46.10.

2-*t*-Butyloxycarbonylamino-2,3,6,7-tetrahydro-1*H*-indeno[1,6,7-*def*]isoquinoline (XVI).—To a stirred suspension of 2.9 g. of *t*-butyl carbazate[29–32] and 6.8 g. of 5,6-bis(bromomethyl)acenaphthene (XIV) in 40 ml. of dimethylformamide there was added 4.45 g. of triethylamine. With considerable spontaneous warming the dibromide dissolved and triethylamine hydrobromide began to separate. The reaction mixture was warmed to 50–60° for 30 min. and then let stand at room temperature overnight. Dilution with 120 ml. of water gave 4.45 g. (72%) of almost white crystals which were filtered and washed well with methanol. Recrystallization from nitromethane gave 3.75 g. (60.5%) of white flakes, m.p. 212–215° dec. (sintering from about 200°). Several recrystallizations from benzene and dioxane gave an analytical sample, m.p. 214–215° dec. (sintering from 202°).

Anal. Calcd. for $C_{19}H_{22}N_2O_2$: C, 73.52; H, 7.14; N, 9.03. Found: C, 73.62; H, 6.80; N, 9.04.

Cleavage of 2-*t*-Butyloxycarbonylamino-2,3,6,7-tetrahydro-1*H*-indeno[1,6,7-*def*]isoquinoline (XVI).—A solution of 6.2 g. of the protected hydrazine XVI in 25 ml. of 2 *N* methanolic hydrogen chloride deposited the hydrochloride of II on standing for a short time. Cooling to 0° and filtering gave a quantitative yield of the hydrochloride. Conversion to the free base was carried out as before using sodium carbonate solution. The free hydrazine had m.p. 186–188° and showed no depression of the melting point on mixing with a sample prepared by reduction of N-amino-5,6-acenaphthalimide.

5,6-Dimethylacenaphthene.—To a well-stirred solution of 7.56 g. of sodium borohydride in 30 ml. of diglyme was added a solution of 2 g. of sodium hydroxide dissolved in 15 ml. of water and 3.4 g. of 5,6-bis(bromomethyl)acenaphthene (XIV). After stirring for 1.5 hr. at 50° there was obtained 1.8 g. (quantitative yield) of small, pure white needles, m.p. 164–168° (sintering from 145°). After recrystallization from ligroin, benzene, and ethanol the hydrocarbon had m.p. 167.5–170°, with slight previous sintering (lit.[14] m.p. 167–169°). The ultraviolet spectrum was similar to that of acenaphthene: $\lambda_{max}^{C_2H_5OH}$ 297 mμ (log ε 3.89), 308 (3.73), 316 (3.66), 323 (3.29), and 331 (3.63).

Pyracene.—A solution of phenyl lithium prepare under nitrogen from 4.08 g. of bromobenzene and 0.40 g. of lithium turnings in 50 ml. of dry ether was filtered and added dropwise over the course of 45 min. to a well-stirred solution of 6.8 g. of 5,6-bis(bromomethyl)acenaphthene (XIV) in 100 ml. of dry benzene at −10°. The mixture was allowed to stir for 1 hr. at room temperature and then refluxed for a second hour and finally shaken twice with 100-ml. portions of water. Removal of the ether–benzene solvent yielded 3.4 g. (95%) of rather impure pyracene. Recrystallization from 55 ml. of benzene gave 2.1 g. (58%) of white crystals, m.p. 210–215° (sintering from 200°). After sublimation at 150–160° (0.2 mm.) followed by recrystallization from *n*-butanol, dioxane, and benzene the pyracene still melted over a range at 214–217°, sintering from 208–209° (lit.[15] m.p. 214.5–217.5°). The 1,3,5-trinitrobenzene adduct had m.p. 205–209° dec. (lit.[15] m.p. 206–207°).

Dimethyl 1-Bromoacenaphthene-5,6-dicarboxylate (XVII).—A suspension of 81 g. of dimethyl acenaphthene-5,6-dicarboxylate (XII) in 1600 ml. of carbon tetrachloride was boiled in order to dissolve as much of the ester as possible and then 56 g. of N-bromosuccinimide and 0.75 g. of benzoyl peroxide were added. The mixture was heated cautiously which caused a strongly exothermic reaction. After a total reflux period of 35 min. the mixture was filtered while hot to remove the succinimide. The filtrate on cooling for many hours at −20° deposited 83.6 g. (80%) of the bromo compound as a faintly yellow solid which was washed well with methanol to remove any remaining succinimide. By recrystallization as rapidly as possible from 200 ml. of dioxane there was obtained 70.7 g. (68%) of pure white crystals of the bromide, m.p. 162–165.5° dec. (becoming brown in spots from 155°). An analytical sample recrystallized from carbon tetrachloride and ethanol had m.p. 164.5–166° dec. (previous development of yellow color).

Anal. Calcd. for $C_{16}H_{13}BrO_4$: C, 55.03; H, 3.75; Br, 22.89. Found: C, 54.91; H, 3.88; Br, 22.86.

Dimethyl Acenaphthylene-5,6-dicarboxylate (XVIII).—A solution of 69.8 g. of dimethyl 1-bromo-5,6-acenaphthenedicarboxylate (XVII) and 52.2 g. of lithium bromide in 600 ml. of dimethylformamide was heated for 3 hr. with stirring at 110–115°. After cooling and dilution with 600 ml. of water, 37.9 g. (70.5%) of the crude unsaturated diester was precipitated. Two recrystallizations from considerable methanol (charcoal) gave 20.9 g. (39%) of material, m.p. 131–135°, pure enough for further use. Cooling of the filtrates from the recrystallizations to −20° gave 6.5 g. (12%) of less pure diester, m.p. 127–132°.

The same substance was obtained by dehydrobromination with quinoline in ethylene glycol although in only 16% yield. Several recrystallizations from ether and methanol gave tiny yellow needles, m.p. 134–136°, $\lambda_{max}^{C_2H_5OH}$ 335 mμ (log ε 4.07).

Anal. Calcd. for $C_{16}H_{12}O_4$: C, 71.63; H, 4.51. Found: C, 71.30; H, 4.16.

Hydrogenation of Dimethyl Acenaphthylene-5,6-dicarboxylate (XVIII).—A suspension of 4.02 g. of the unsaturated diester (XVIII) in 75 ml. of dioxane was treated with hydrogen at atmospheric pressure in the presence of 250 mg. of palladium on charcoal (10%). Within 50 min. the theoretical amount of hydrogen had been absorbed. The mixture which had become colorless during the reduction was warmed to dissolve any saturated diester which had precipitated. Removal of catalyst and concentration of the dioxane solution followed by recrystallization of the crude product from 15 ml. of dioxane gave 3.8 g. (94%) of nearly white crystals, m.p. 175–178°. The melting point was not depressed on admixture with an authentic sample of dimethyl acenaphthene-5,6-dicarboxylate (XII) prepared as described above.

Dimethyl 1,2-Dibromoacenaphthene-5,6-dicarboxylate (XIX).—A mixture of 2.7 g. of dimethyl acenaphthene-5,6-dicarboxylate (XII), 3.6 g. of N-bromosuccinimide, 50 ml. of carbon tetrachloride, and 25 mg. of benzoyl peroxide was refluxed for 20 min. After filtration of the succinimide formed, the red filtrate was evaporated under reduced pressure and the residue recrystallized from 100 ml. of ethanol which gave 2.8 g. (85%) of reddish-colored crystals, m.p. 147–157° dec. A second recrystal-

(28) S. R. Landauer and H. N. Rydon, *J. Chem. Soc.*, 2224 (1953).

(29) *t*-Butyl carbazate was prepared from *t*-butyl S-ethylthiolcarbonate by a method similar to that described[30] for the corresponding methyl ester except that during the 24-hr. heating period (bath temperature 120°) ethyl mercaptan (b.p. 37°) was continuously removed through an efficient fractionating column. The yield was 80%. The *t*-butyl S-ethylthiolcarbonate was prepared from ethyl chlorothiolformate in a manner analogous to that reported[31] for the methyl derivative except that methylene dichloride was substituted for chloroform as solvent. The yield was 73% of a colorless liquid, b.p. 57–59° at 10 mm. (lit.[32] b.p. 166°). Use of the ethyl ester offered no advantage over use of the corresponding methyl derivative.

(30) L. A. Carpino, *J. Am. Chem. Soc.*, **82**, 2725 (1960).

(31) L. A. Carpino, *J. Org. Chem.*, **28**, 1909 (1963).

(32) G. W. Driver and M. F. C. Paige, British Patent 789,985 (Jan. 29, 1958); *Chem. Abstr.*, **52**, 13,804g (1958).

lization from ethanol gave 1.75 g. (41%) of the diester, m.p. 160–163° dec. (sintering from 157°).

An analytical sample was obtained from methanol as well-formed white rhombic crystals decomposing sharply at 162–164°. All samples submitted for analysis showed low values for bromine suggesting loss of bromine or hydrogen bromide from the 1,2-positions during or after recrystallization.

Anal. Calcd. for $C_{16}H_{12}Br_2O_4$: C, 44.89; H, 2.83; Br, 37.34. Found: C, 44.89; H, 2.85; Br, 36.47.

Debromination by solution of 1 g. of the dibromide (XIX) in 25 ml. of dioxane and refluxing for 1 hr. with 6 g. of zinc dust gave on filtration, precipitation with water, and recrystallization from methanol 63% of dimethyl acenaphthylene-5,6-dicarboxylate (XVIII), m.p. 132–135°. There was no depression of the melting point on admixture with a sample prepared by dehydrobromination of the monobromide.

5,6-Bis(hydroxymethyl)acenaphthylene (XX).—A solution of 20.8 g. of dimethyl acenaphthylene-5,6-dicarboxylate (XVIII) in 400 ml. of dry benzene was added dropwise at 0° with stirring to a solution prepared from 5.9 g. of lithium aluminum hydride in 600 ml. of dry ether. The mixture was allowed to stir for 2 hr. at 0° and then was decomposed by the cautious addition of 50 ml. of water. The filtered product was suspended in 250 ml. of water at 0° and stirred vigorously for 15 min. after the addition of 500 ml. of ice-cold dilute hydrochloric acid (1:3). The diol was filtered and washed well with water; the crude material (12.8 g., 78%) was recrystallized from 65 ml. of dioxane (charcoal) which gave 6.95 g. (42.5%) of small yellow needles, m.p. 162–166°, pure enough for further use. An analytical sample, m.p. 163–165°, was obtained by recrystallization from dioxane.

Anal. Calcd. for $C_{14}H_{12}O_2$: C, 79.23; H, 5.70. Found: C, 79.11; H, 5.84.

Reduction in ether alone gave poorer yields of the diol. In tetrahydrofuran an unidentified high-melting substance was obtained.

1-Bromo-5,6-bis(bromomethyl)acenaphthene (XXII) from 5,6-Bis(hydroxymethyl)acenaphthylene (XX).—To a suspension of triphenyl phosphite dibromide[21] prepared from 29.8 g. of triphenyl phosphite in 40 ml. of dry benzene and 14.1 g. of bromine in 60 ml. of dry benzene there was added with stirring at 0° in small portions 8.5 g. of 5,6-bis(hydroxymethyl)acenaphthylene. The resulting clear red solution was allowed to stir for 1 hr. at room temperature and after evaporation of the benzene *in vacuo* treated with 40 ml. of methanol. The residue was filtered and washed well with methanol which gave 9.85 g. (59%) of yellow powder, m.p. 149–155° dec. (sintering from 130–135°). Two recrystallizations from carbon tetrachloride gave 5.1 g. (30%) of the tribromide, m.p. 161–162° dec. (browning from 150°). Further recrystallization from carbon tetrachloride raised the decomposition point to 163° (browning from 150°).

Anal.[33] Calcd. for $C_{14}H_{11}Br_3$: C, 40.13; H, 2.65; Br, 57.22. Found: C, 39.37; H, 2.31; Br, 57.85.

1-Bromo-5,6-bis(bromomethyl)acenaphthene (XXII) from 5,6-Bis(bromomethyl)acenaphthene (XIV).—A solution of 25.5 g. of 5,6-bis(bromomethyl)acenaphthene (XIV) in 200 ml. of boiling carbon tetrachloride was treated with 14.1 g. of N-bromosuccinimide and 250 mg. of benzoyl peroxide. The vigorous reaction which set in at once was controlled by occasional cooling without allowing the mixture to cease boiling. After an additional 15 min. of refluxing the mixture was filtered while hot to remove the succinimide. The filtrate on standing for several hours at −20° deposited 26.9 g. (85.5%) of the tribromide, m.p. 159–160° dec. (browning from 150–155°), which was washed well with methanol to remove any residual succinimide. The purest samples had m.p. 161–162° dec. (sintering from 155°). There was no depression of the decomposition point on admixture with a sample of the tribromide prepared from 5,6-bis(hydroxymethyl)acenaphthylene.

(33) Although this compound could not be obtained in analytically pure form, possibly because of some addition of bromine as well as hydrogen bromide to the double bond, there is little doubt as to its constitution from the alternate mode of synthesis from 5,6-bis(bromomethyl)acenaphthene and its further reactivity. Indeed several of the bromoalkyl derivatives prepared during the course of this work appeared to be unstable and gave rather poor results on elemental analysis. This was true for XIV and XIX as well as XXII.

5,6-Bis(chloromethyl)acenaphthylene (XXI).—To a solution of 15.7 g. (9.6 ml.) of thionyl chloride (distilled from linseed oil, b.p. 76–77°) in 240 ml. of benzene at room temperature there was added with stirring over 8–10 min. 7 g. of 5,6-bis(hydroxymethyl)-acenaphthylene (XX). The solid slowly dissolved in 20–25 min. and after stirring at room temperature for an additional 3 hr., the solution was evaporated to dryness from a water bath at 45–50° with the aid of a water aspirator. The residual solid was washed out with ethanol–water (1:2), dried in air, and recrystallized from carbon tetrachloride. Storage at −20° gave 4.5 g. (55%) of bright yellow crystals, m.p. 143–147° (softening at 138°). Recrystallization of an analytical sample from benzene–ligroin, ethanol–nitromethane, and finally ethanol–dimethylformamide gave orange-yellow flakes, m.p. 154–156° (softening at 148°).

Anal. Calcd. for $C_{14}H_{10}Cl_2$: C, 67.49; H, 4.05; Cl, 28.46. Found: C, 67.81; H, 4.37; Cl, 28.85.

2-*t*-Butyloxycarbonylamino-2,3-dihydro-1H-indeno[1,6,7-*def*]-isoquinoline (XXIII).—A suspension of 26.9 g. of 1-bromo-5,6-bis(bromomethyl)acenaphthene (XXII), prepared by N-bromosuccinimide bromination of 5,6-bis(bromomethyl)acenaphthene (XIV), in a solution of 10.3 g. of *t*-butyl carbazate in 125 ml. of dimethylformamide was treated with 60 ml. of triethylamine with stirring. Considerable spontaneous warming occurred and the tribromide dissolved. At the beginning the temperature was kept at 55–60° by occasional cooling and finally the mixture was heated to this temperature for 1 hr. with stirring. The solid, precipitated by dilution with 250 ml. of water, was filtered and was washed well with water and methanol. There was obtained 10.3 g. (52%) of a yellow powder. Two recrystallizations from dioxane gave 6.3 g. (32%) of beautiful, bright yellow needles. In a melting point capillary the compound began to darken at about 225–230° and became darker and darker up to about 239–245° when the material underwent a slight expansion without melting. No further change occurred up to 260–270°.

An analytical sample was obtained from nitromethane as bright yellow flakes which decomposed without melting at 237–240° after prior darkening which began at 220–225°. If dropped into a bath held at 245° it decomposed suddenly with apparent gas evolution. The same compound was obtained (65%) by treatment of 5,6-bis(chloromethyl)acenaphthylene (XXI) with *t*-butyl carbazate and triethylamine in dimethylformamide. Identity was established by comparison of infrared spectra.

Anal. Calcd. for $C_{19}H_{20}N_2O_2$: C, 74.00; H, 6.54; N, 9.09. Found: C, 73.91; H, 6.41; N, 9.22.

Hydrogenation of 2-*t*-Butyloxycarbonylamino-2,3-dihydro-1H-indeno[1,6,7-*def*]isoquinoline (XXIII).—A suspension of 394 mg. of XXIII and 150 mg. of palladium on carbon (10%) in dioxane was hydrogenated at room temperature and atmospheric pressure. The substance dissolved rapidly and the yellow color disappeared within 15 min. when the theoretical quantity of hydrogen had been absorbed. Evaporation of the solvent *in vacuo* after removal of catalyst gave a gray solid which on recrystallization from 10 ml. of benzene gave 300 mg. (75.5%) of dark crystals. Two additional recrystallizations from benzene (charcoal) gave the hydrogenated material as nearly white crystals, m.p. 210–213° dec. (darkening from about 200–205°). There was no depression of the decomposition point on admixture with an authentic sample of 2-*t*-butyloxycarbonylamino-2,3,6,7-tetradihydro-1H-indeno[1,6,7-*def*]isoquinoline (XVI).

2-Amino-2,3-dihydro-1H-indeno[1,6,7-*def*]isoquinoline (III).—There was added 3.08 g. of the protected hydrazine XXIII with stirring to 75 ml. of 2 *N* methanolic hydrogen chloride. Solution occurred followed by precipitation of the hydrochloride of the protected derivative. The mixture was warmed to 55°, whereupon the yellow solid dissolved. On the following day the mixture was treated with decolorizing carbon at 50° and the dark yellow solution was evaporated to dryness *in vacuo*. There was obtained 2.45 g. (100%) of a dark yellow substance which was recrystallized from 25 ml. of a mixture of concentrated hydrochloric acid, water, and methanol (1:4:5). The hydrochloride separated as small golden yellow flakes. In a melting point capillary the compound began to darken at about 195–200° and got darker and darker but showed no visible decomposition up to 300°. However if a sample was added to a bath held at a temperature above 255–260° sudden darkening and visible decomposition ("puffing up") occurred.

The crude hydrochloride was converted to the free base in 40–45% yield by solution in water, neutralization with sodium bicarbonate, extraction with ether, evaporation, and recrystalliza-

tion of the brown residue from ligroin (b.p. 88–98°). The hydrazine separated in the form of small yellow-orange needles, m.p. 145–150° dec. (darkening from about 130°).

Anal. Calcd. for $C_{14}H_{12}N_2$: C, 80.74; H, 5.81; N, 13.45. Found: C, 81.08; H, 5.95; N, 13.14.

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Rearrangements of Norbornene Oxide

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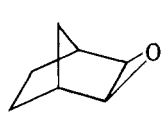
The acid-catalyzed hydration of norbornene oxide has been reinvestigated. Isomerization of the oxide under acidic conditions produces 3-cyclohexene-1-carboxaldehyde, norcamphor, and nortricyclanol. Rearrangement under strongly basic conditions gives nortricyclanol exclusively.

During the course of an investigation on the bicyclo[2.2.1]heptane-2,5-diols,[2] a brief examination of the related 2,7-diols was undertaken. The present report is an account of the resulting studies.

The product obtained either by acid-catalyzed hydration of *exo*-2,3-epoxybicyclo[2.2.1]heptane (I, norbornene oxide) or by peracid hydroxylation of norbornene has been the subject of several publications. The structure II was suggested[3] for this material at an early data on the expectation of a normal *trans* addition of water to the epoxide ring. Independent studies by two groups[4,5] resulted in the revision of this assignment to bicyclo[2.2.1]heptane-*exo*-2-*syn*-7-diol (III). The diol gave a negative vicinal diol test, had a strong intramolecular hydrogen



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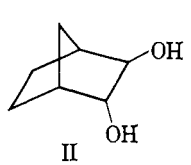

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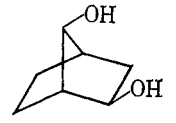

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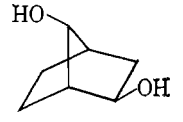
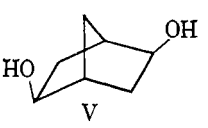


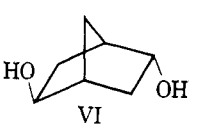
IV

bond in its infrared spectrum, and formed a cyclic acetal with *p*-nitrobenzaldehyde in good yield. Later work by Krieger,[6] however, resulted in the separation of this material into a low melting diol (181°) and a higher melting product (200°). The properties of the former were uniquely accommodated by III, while the higher melting product was assigned formula IV, mainly on the basis of mechanistic considerations.

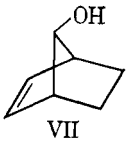
In the present work the two products were examined by gas–liquid chromatography (g.l.c.) of the derived acetates. Although the 181° diol was homogeneous, the 200° material was found to be a mixture which consisted of *ca.* 80% of a major component plus *ca.* 20% of three other diols. The minor components were identified as III, V,[2] and VI[2] on the basis of g.l.c. retention times. Column chromatography provided a homogeneous sample of the major component, m.p. 204.5–206°. This diol was shown to possess structure IV by comparison with an authentic sample.



V



VI



VII

The authentic sample was prepared by subjecting the tetrahydropyranyl ether of *anti*-7-hydroxybicyclo[2.2.1]hept-2-ene[7] (VII) to the hydroboration–oxidation procedure[8] of Brown. Utilization of bicyclo[2.2.1]heptenes in this reaction has been shown to give *exo* alcohols without the occurrence of skeletal rearrangements.[9] This determines IV as the structure of the synthetic product and this material is identical in every respect with the diol obtained above.

A more quantitative estimate of the diol mixture was obtained by treating I with aqueous perchloric acid[5] and examining the total crude product by g.l.c. In this manner the mixture was found to consist of 74% III, 22% IV, and 4% total of V and VI. The observed major and minor products formed by the hydration of norbornene oxide can now be rationally interpreted as resulting from various combinations of the usual Wagner–Meerwein rearrangements and 1,3-hydride shifts.[10] Chart I shows such a scheme.

During the course of the above work an attempt was made to purify a sample of I by preparative g.l.c. However, when I was passed through a column of Carbowax 20M on Chromosorb P at 120°, three new compounds were eluted from the column while the epoxide was completely consumed.[11] This unexpected

(1) (a) National Institutes of Health Predoctoral Fellow, 1960–1963. (b) Correspondence should be addressed to the Department of Chemistry, Indiana University, Bloomington, Ind. 47405.

(2) J. Meinwald, J. K. Crandall, and P. G. Gassman, *Tetrahedron*, **18**, 815 (1962).

(3) S. F. Birch, W. S. Oldham, and E. A. Johnson, *J. Chem. Soc.*, 818 (1947).

(4) H. M. Walborsky and D. F. Loncrini, *J. Am. Chem. Soc.*, **76**, 5396 (1954).

(5) H. Kwart and W. G. Vosburgh, *ibid.*, **76**, 5400 (1954).

(6) H. Krieger, *Suomen Kemi.*, **B31**, 340 (1958).

(7) P. R. Story, *J. Org. Chem.*, **26**, 287 (1961).

(8) For a detailed discussion of this synthetic method and related ones, see H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962.

(9) See ref. 8, p. 126.

(10) J. A. Berson, "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience Publishers, New York, N. Y., 1963, p. 111. This reference provides an excellent review of these interesting topics.

(11) K. Watanabe, C. N. Pillar, and H. Pines, *J. Am. Chem. Soc.*, **84**, 3934 (1962). These workers have also observed that I gives three peaks upon g.l.c. on a Carbowax column. However, they tentatively suggested that the standard epoxidation procedure had produced a mixture of isomeric oxides.