and δ-substituent effects of the tertiary amine group. Although the mechanism of these metalations has not yet been established, the transition state presumably involves coördination of the free pair of electrons of the amine with lithium.

Experimental[8]

Starting Amines.—Benzyldimethylamine (I, b.p. 178–179°) was obtained commercially.

Dibenzylmethylamine (IV) was prepared from 130 g. (1.03 moles) of benzyl chloride and 78 g. (2.6 moles) of methylamine in 600 ml. of methanol (refluxed overnight). The methanol was removed, and the residue was dissolved in 2 *N* hydrochloric acid. This solution was washed twice with ether and made basic with solid sodium hydroxide. The liberated amine mixture was extracted with ether. The extract was dried over magnesium sulfate and fractionated to give 44 g. (35%) of benzylmethylamine, b.p. 68–69° at 12 mm., reported b.p. 180–181° at 765 mm.,[9] and 47 g. (43%) of IV, b.p. 96–97° at 0.45 mm., reported b.p. 178–180° at 32 mm.[10]

2-Methylbenzyldimethylamine (IVa, b.p. 78–79° at 13 mm.) and 2,3-dimethylbenzyldimethylamine (VIb, b.p. 98–99° at 13 mm.) were synthesized by the ortho substitution–rearrangements of benzyltrimethylammonium iodide and 2-methylbenzyltrimethylammonium iodide, respectively.[11] The reported boiling points are 80–80.2° at 14 mm. and 99–101° at 14 mm., respectively.[11]

N,N-Dimethyl-3-phenylpropylamine (VIII) was prepared from 153 g. (0.77 mole) of 3-phenyl-1-propyl bromide (b.p. 107–108° at 9 mm.) and 140 g. (3.1 moles) of dimethylamine in 500 ml. of absolute ethanol (warmed at 55° for 2 hr. and left to stand overnight). The reaction mixture was worked up essentially as described above for isolation of amine IV to give 72 g. (58%) of amine X, b.p. 95–96° at 7.3 mm. The picrate melted at 98.5–99.5°, reported m.p. 99°.[12]

N,N-Dimethyl-2-phenylethylamine (X) was prepared from 120 g. (2.7 moles) of dimethylamine and 172 g. (0.94 mole) of 2-phenylethyl bromide essentially as described above for preparation of amine X. Fractionation gave 93 g. (66%) of amine XII in two fractions, b.p. 82–84° at 8 mm. (21 g.) and b.p. 84–85° at 8 mm. (72 g.), reported b.p. 205°.[13]

Metalations and Deuterations (Table I).—In a 50- or 125-ml. erlenmeyer flask were combined 0.03–0.08 mole of starting amine and 0.06–0.16 mole of ethereal *n*-butyllithium, prepared and analyzed as described.[2] The flask was filled with anhydrous ether, tightly stoppered, and allowed to stand for 3–48 hr. at room temperature. The resulting solution was poured in a stream of nitrogen into a 500-ml. erlenmeyer flask containing a stirred mixture of 5–8 ml. of deuterium oxide (99.8% deuterium) and 50–75 ml. of anhydrous benzene. The benzene was used to absorb some of the heat of reaction. The resulting mixture was stirred for 1 hr. The organic layer was filtered free of the damp solid which had separated, dried over magnesium sulfate, and the solvent was distilled. In all cases except that of amine X, the recovery of undistilled deuterated amines was nearly quantitative. The crude amines were fractionated through a 15-cm. Vigreux column, a mid-cut being collected for deuterium analysis (see Table I).

Metalation of amine VIII and the attempted metalation of amine X were effected by refluxing the amine with 2 molecular equivalents of *n*-butyllithium in ether under nitrogen for 24 hr. in a 300-ml. three-neck flask. Deuterium oxide was slowly added to the resulting mixture, and the reaction mixture was worked up as described for the other deuterations.

Oxidation of Amine IIa.—A sample of amine IIa containing 0.92 D atom/molecule was oxidized with alkaline potassium permanganate by the procedure described[14] for a related oxidation to give benzoic acid-2*d* (III), m.p. 121.5–122°, containing 0.93 D atom/molecule.

(8) Melting points and boiling points are uncorrected. N.m.r. spectra were determined by Mr. John Baxter and Mr. James Randall using a Varian HR-60 device and by the Varian A-60 Applications Laboratory, Palo Alto, Calif. Deuterium analysis (combustion–falling drop) was performed by Josef Nemeth, Urbana, Ill.

(9) H. Emde, *Arch. Pharm.*, **247**, 251 (1909).

(10) G. M. Coppinger, *J. Am. Chem. Soc.*, **76**, 1372 (1954).

(11) S. W. Kantor and C. R. Hauser, *ibid.*, **73**, 4122 (1951).

(12) L. Senfter and J. Tafel, *Ber.*, **27**, 2309 (1894).

(13) J. v. Braun, *ibid.*, **43**, 2309 (1910).

(14) F. N. Jones and C. R. Hauser, *J. Org. Chem.*, **26**, 2979 (1961).

Bicyclic Bases. V. Epoxidation of 7-Diphenylmethylenenorbornenes[1]

GEORGE I. POOS AND JANET D. ROSENAU

McNeil Laboratories, Inc., Fort Washington, Pennsylvania

Received May 23, 1962

The *endo*-diphenylfulvene-*N*-methylmaleimide adduct I is shown to epoxidize preferentially at the diphenylmethylene double bond with perbenzoic acid. The structure and stereochemistry of the resulting monoepoxide II is proved. Epoxidation of the *exo*-imide IX is shown to give only the ring monoepoxide X. However, the *endo*-benzamide XIV epoxidizes to give a mixture of monoepoxides. These differences are attributed to the operation of a field effect in the case of the imides.

In part IV of this series,[2] we described the preparation of a series of aryl-substituted bridged hydroisoindolines by lithium aluminum hydride reduction of the corresponding diarylfulvene-maleimide adducts. In the course of this work, it became of interest to investigate the epoxidation of the *endo* doubly unsaturated imide I. Alder and co-workers had reported[3] on the oxidation of the *endo*-maleic anhydride–diphenylfulvene adduct with excess peracetic acid at 80–90°. Their product, obtained after mild saponification, was an oxido lactone hydroxy carboxylic acid resulting from oxidation of both double bonds and interaction of the ring epoxide with a carboxy function. In the case of the *exo*-maleic anhydride–diphenylfulvene adduct, the German workers[3] obtained a rearranged hydroxy lactone carboxylic acid resulting from oxidation of only the ring double bond. It was also reported[3] that the dihydronorbornane-*exo*-adduct failed to react with peracetic acid under the same conditions.

With our *endo*-imide I, we hoped to epoxidize preferentially the ring double bond in order to obtain ring substituted analogs of pharmacologically interesting hydroisoindolines.[2] The known reactivity of the norbornene double bond[4] and possible steric hindrance of the tetrasubstituted exocyclic double bond of I led us to predict the desired selective oxidation.

When imide I was treated with an equivalent amount of perbenzoic acid in chloroform solution at room temperature, a single monoepoxide was obtained in 84%

(1) Presented in part at the Fourth Delaware Valley Regional American Chemical Society Meeting, Philadelphia, Pa., January 26, 1962.

(2) G. I. Poos, M. M. Lehman, E. B. Landis, and J. D. Rosenau, *J. Med. Pharm. Chem.*, **5**, 883 (1962).

(3) K. Alder, F. W. Chambers, and W. Trimborn, *Ann.*, **566**, 27 (1950).

(4) H. Kwart and L. J. Miller, *J. Am. Chem. Soc.*, **83**, 4552 (1961).

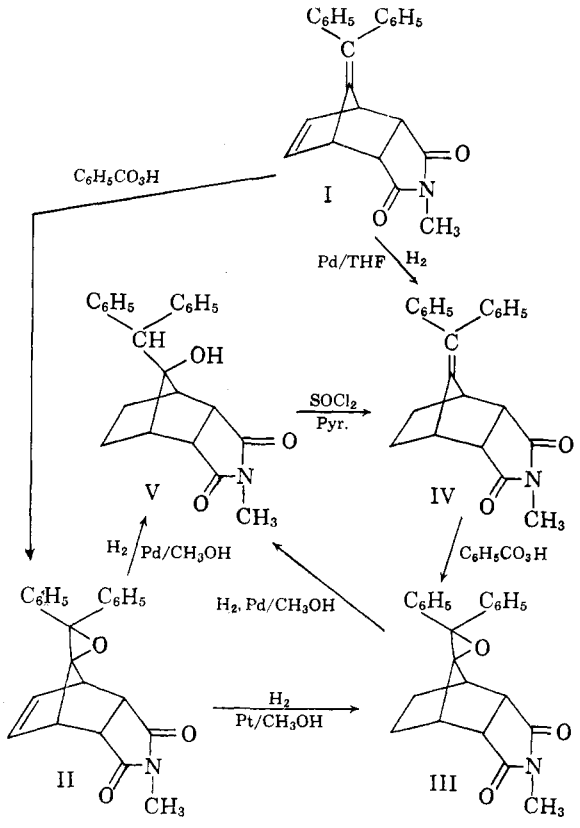
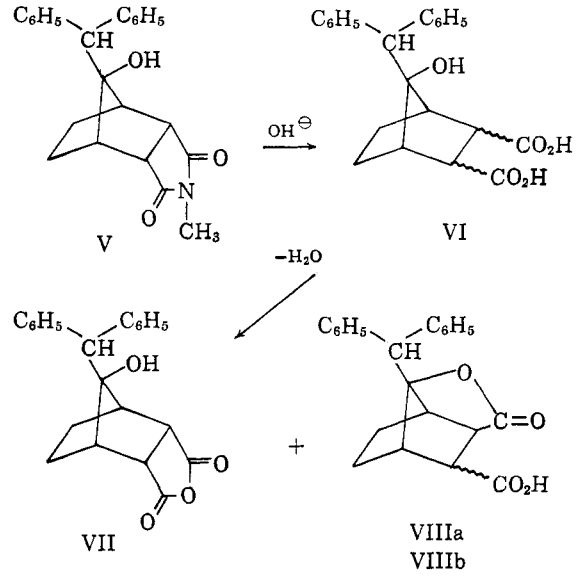


CHART I

yield. This product lacked the characteristic diphenylmethylene chromophore at 245 mμ which suggested the epoxidation had occurred selectively at the exocyclic double bond contrary to our expectations. Proof for the location of the epoxide function and lack of skeletal rearrangement in this product (II) is shown in Chart I. Selective hydrogenation of II over platinum led to dihydroepoxide III which was also prepared by epoxidation of the dihydroimide IV.[2] More vigorous hydrogenation of II or III gave a hydroxy imide (V). Dehydration of the hydroxy imide with thionyl chloride in pyridine led back to compound IV, proving that no rearrangement had taken place.[5]

We next sought evidence for the proof of the stereochemistry of epoxide II as well as the position of the hydroxyl group in the hydroxy imide. Hydrogenolytic cleavage of the epoxide function would be expected to proceed by cleavage of the benzhydryl carbon–oxygen bond to give the bridge alcohol (V). This expectation was confirmed by the n.m.r. spectrum of the hydroxy imide in deuteriochloroform which showed an unsplit resonance peak at 4.43 p.p.m. in the range for a benzhydryl proton.[6] In order to prove the stereochemistry and provide further evidence for the position of the hydroxyl group, it was reasoned that if the hydroxy imide were converted to a compound with an *exo*-carboxyl group, the *syn* stereoisomer would readily dehydrate to a γ- or δ-lactone while the *anti* isomer could not lactonize.



Vigorous saponification of the hydroxy imide (V) produced a good yield of the stereoisomeric mixture of diacids (VI). Attempts to separate this mixture were fruitless. By the dehydration of hydroxy diacid mixture with acetyl chloride, a neutral and an acidic fraction were obtained. From the neutral part, a small amount of a single hydroxy anhydride was isolated to which we have tentatively assigned *endo* structure VII.[7] The acid fraction yielded a sharply melting compound in moderate yield which was assigned carboxy-γ-lactone structure VIIIa (λ $CHCl_3$ 5.62μ). Thus structure V is proved for the hydroxy imide. Several attempts to convert acid mixture VI to the single *trans* stereoisomer were unsuccessful. Diacid VI was converted to the oily diester with diazomethane which was then treated with ethanolic sodium ethoxide followed by water according to the isomerization procedure of Meinwald and Gassman.[8] The acid recovered from this process (53% yield over-all) was very similar in properties to the starting mixture. From one attempt, a small amount of a high-melting, apparently homogeneous hydroxy diacid was isolated. Dehydration of this material with acetyl chloride gave an excellent yield of an isomeric high-melting carboxy-γ-lactone VIIIb.[9]

Returning to the epoxidation of I, further studies showed that only II was obtained even when I was treated with a 100% excess of perbenzoic acid. Monoepoxide II was recovered unchanged when treated with excess perbenzoic acid in chloroform. Several reasons could be offered to explain the selectivity of this epoxidation. The *endo*-dicarboximide group of I could sterically block approach of the peracid to the *endo* side of the norbornene double bond while the bridge diphenylmethylene group could shield the top side of the norbornene double bond of I. If this were the case, the *exo* isomer of I should epoxidize at the ring double

(5) Perbenzoic acid is reported to epoxidize norbornene without rearrangement; S. B. Soloway and S. J. Cristol, *J. Org. Chem.*, **25**, 327 (1960).

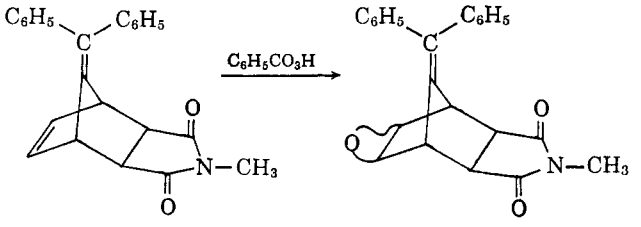
(6) G. Van Dyke Tiers, "Characteristic Nuclear Magnetic Resonance (*N.m.r.*) *'Shielding Values' (Spectral Positions) for Hydrogen* in Organic Structures," Minnesota Mining and Manufacturing Company, St. Paul, Minn., 1958, p. 12.

(7) This assignment is based on our supposition that the *exo*-anhydride is very much less likely due to the expected facile intramolecular reaction of the hydroxyl and anhydride functions to give the *exo*-carboxy-γ-lactone VIII.

(8) J. Meinwald and P. G. Gassman, *J. Am. Chem. Soc.*, **82**, 5449 (1960).

(9) There were insufficient data to permit assignment of *endo* and *exo* configurations to carboxy-γ-lactones VIIIa and VIIIb. Examination of the near infrared spectra of VIIIa and VIIIb was inconclusive, due in part to the low solubility of VIIIb. We are indebted to Dr. W. C. Wildman for this study.

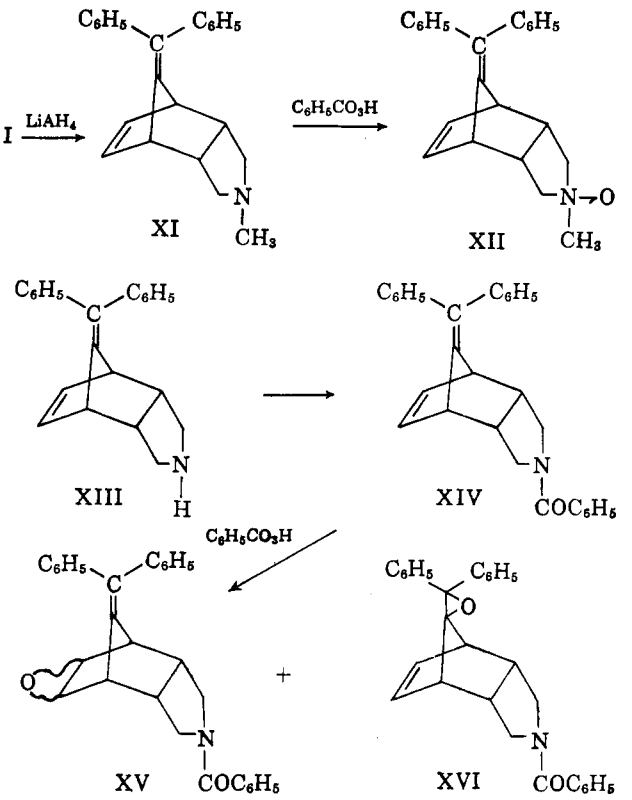
bond. When the isomeric *exo*-imide IX[2] was treated with an equivalent amount of perbenzoic acid in chloroform, an excellent yield of the ring monoepoxide X was obtained. Analysis and spectra supported the structure; an assignment of stereochemistry for the epoxide function of X was not possible from the evidence available.



IX X

An alternate explanation for the selectivity of these epoxidations would be the existence of a field effect.[10] Thus, in the case of I, an interaction of the ring double bond and imide carbonyl groups through space would be expected to reduce the susceptibility of the double bond to electrophilic attack by perbenzoic acid. Support for this interpretation is found in some recent work of Kwart and Miller[4] who reported that the *endo*-cyclopentadiene–maleic anhydride adduct adds 2,4-dinitrobenzenesulfenyl chloride at a rate less than one fiftieth that of the *exo* isomer. Although the geometry is less favorable in the case of *exo*-imide IX, the selective epoxidation of the ring double bond of IX could be explained by assuming an interaction of the imide carbonyl groups with the diphenylmethylene double bond.

In order to decide whether steric or field effects were responsible for the selectivity observed in the epoxidation of imides I and IX, the behavior toward epoxidation of a compound having methylene groups in place of the imide carbonyl groups of I was investigated. The *endo* bridged hydroisoindoline XI, available from I by lithium aluminum hydride reduction,[2] when treated with excess perbenzoic acid in chloroform gave a 60% yield of a basic product. This base was isolated as the maleate salt and showed one more oxygen atom than the starting base by analysis. It retained the diphenylmethylene chromophore in the ultraviolet and was initially thought to be an epoxide.[1] However, the n.m.r. spectra of this compound showed two vinyl protons and hence the *N*-oxide structure XII is assigned.[11] To get around the problem of oxidation of the amine function, secondary amine XIII[2] was converted to the benzoyl derivative XIV. The latter was epoxidized in several experiments with varying proportions of perbenzoic acid. In all cases, inseparable mixtures of oxidation products were obtained. The mixture obtained from XIV and one equivalent of perbenzoic acid was chromatographed over alumina. Early and late fractions from this chromatogram were recrystallized and examined. Combustion analyses on these fractions were consistent with monoepoxide structures XV and XVI. Both the ultraviolet and n.m.r. spectra agreed with the interpretation that a mixture of monoepoxides XV and XVI was obtained.



XI XII XIII XIV XV XVI

From these results it can be concluded that the presence of the imide carbonyl groups in compound I is important for its selective epoxidation, most probably through the operation of a field effect.

Experimental[12]

endo-N-**Methyl-3′,3′-diphenylspiro[5-norbornene-*syn*-7,2′-oxirane]2,3-dicarboximide** (II).—To a solution of 12.35 g. (0.0362 mole) of *endo*-7-diphenylmethylene-*N*-methyl-5-norbornene-2,3-dicarboximide (I)[2] in 100 ml. of chloroform, cooled in an ice–water–salt bath, was added a solution of 5 g. (0.0362 mole) of perbenzoic acid[13] in chloroform. The solution was allowed to stand at room temperature for 36 hr. The chloroform solution was washed three times with 5% sodium carbonate and once with water. The solution was dried over magnesium sulfate, filtered, and concentrated to dryness *in vacuo*. The product crystallized from ether, giving 10.8 g. (84%) of II, m.p. 181.5–182.5°; λ_{max}^{KBr} 2.90, 3.30, 5.61, 5.86, 6.22, 6.69, sh 6.90, 6.98, 7.24 μ; the ultraviolet spectrum showed only phenyl and end absorption. A recrystallized sample, m.p. 181.5–182.5°, was analyzed.[14]

Anal. Calcd. for $C_{23}H_{19}NO_3$: C, 77.29; H, 5.36; N, 3.92. Found: C, 77.14; H, 5.43; N, 3.86.

endo-N-**Methyl-3′,3′-diphenylspiro[norbornane-*syn*-7,2′-oxirane]2,3-dicarboximide** (III).—A. To 2 g. (0.0058 mole) of *endo*-7-diphenylmethylene-*N*-methyl-2,3-norbornanedicarboximide (IV)[2] in 20 ml. of chloroform at 0° was added 0.80 g. (0.0058 mole) of perbenzoic acid in chloroform. The solution, after standing for 2 days at room temperature, was washed three times with 5% sodium bicarbonate solution, once with water, dried over magnesium sulfate, filtered, and concentrated to dryness *in vacuo*. The oil was dissolved in methylene chloride and crystallized by adding ether and boiling off the methylene chloride. Thus, 1.3 g. of product was obtained (62.5%) m.p. (100°) 149–150.5°; λ_{max}^{KBr} 2.85 (w), 3.35, 5.61, 5.86, 6.21 (w), 6.74 (w),

(10) J. D. Roberts and W. T. Moreland, *J. Am. Chem. Soc.*, **75**, 2167 (1953).

(11) We are indebted to a referee for pointing out this possibility.

(12) Melting points are corrected and were determined on a Kofler block. Ultraviolet spectra were determined in methanol with a Cary Model 14 spectrometer, infrared spectra were obtained on a Perkin–Elmer Model 21 or 37 spectrometer and n.m.r. spectra were determined with a Varian A-60 spectrometer.

(13) Prepared by the method of W. J. Bailey and C. E. Knox, *J. Org. Chem.*, **25**, 511, (1960).

(14) Thin-layer chromatography of this sample in several different systems showed only one spot.

6.96, 7.23 μ; the ultraviolet spectrum showed only benzene ring and end absorption. A 0.085-g. sample was recrystallized from methylene chloride–ether, affording 0.075 g., melts and resolidifies at 145–152°, m.p. 177.5–180°.[14]

Anal. Calcd. for $C_{23}H_{21}NO_3$: C, 76.86; H, 5.89; N, 3.90. Found: C, 77.02; H, 6.16; N, 4.18.

B. A 0.5-g. sample (0.0014 mole) of *endo*-*N*-methyl-3′,3′-diphenylspiro[5-norbornene-syn-7,2′-oxirane]2,3-dicarboximide (II) was hydrogenated over 0.05 g. of platinum dioxide in 50 ml. of methanol at atmospheric pressure. After a rapid uptake of slightly more than one molar equivalent of hydrogen, the reaction leveled off and was stopped. The solution was filtered and concentrated to dryness *in vacuo*. The product, which was crystallized from methylene chloride–ether, was obtained in 100% yield, m.p. 135–145°. After a recrystallization from methylene chloride–ether, the compound melted at (90°) 148–150°. The infrared spectrum was identical with that of the sample described in section A above. A small sample, after recrystallization from ethanol, exhibited the double melting point, 144–153°, 176–178°.

***endo*-[*anti*-7-Diphenylmethyl-*syn*-7-hydroxy-*N*-methyl]-2,3-norbornanedicarboximide (V).**—A. A 2-g. sample of *endo*-*N*-methyl-3′,3′-diphenylspiro[5-norbornene-*syn*-7,2′-oxirane]2,3-dicarboximide (II) was hydrogenated over 0.5 g. of 10% palladium on carbon in 100 ml. of methanol on a Paar shaker. After 6 hr., the reaction was stopped and the mixture was filtered. The catalyst was washed well with methylene chloride and the filtrate was concentrated to low volume on the water pump. The product crystallized from methanol and was filtered and dried, giving 1.63 g. (81.5%) of V, m.p. (268°) 274–278°; λ_{max}^{KBr} 2.88, 3.35, 5.66, 5.90, 6.24, sh. 6.67, 6.71, 6.87, 6.96, 7.24 μ; the ultraviolet spectrum showed only benzene ring and end absorption. Recrystallization of a small sample from methylene chloride–ether afforded an analytical sample, m.p 276–280°.[14]

Anal. Calcd. for $C_{23}H_{23}NO_3$: C, 76.43; H, 6.41; N, 3.88. Found: C, 76.74; H, 6.17; N, 3.72.

The n.m.r. spectrum[15] of V in deuteriochloroform showed the following values in p.p.m.: 7.30 (aromatic protons), 4.43 (benzhydryl proton), 3.42 and 2.40 (2 pairs of bridgehead protons), 2.97 (*N*-methyl group), 2.20 to 1.25 (hydroxyl and methylene protons).

B. A. 0.5-g. sample (0.00139 mole) of *endo*-*N*-methyl-3′,3′-diphenylspiro [norbornane-*syn*-7,2′-oxirane]2,3-dicarboximide (III) was hydrogenated over 0.25 g. of 10% palladium on carbon in 50 ml. of methanol on the Paar shaker. After 6 hr., the reaction was stopped and filtered. Concentration of the filtrate afforded crystals from methanol. The crystals were washed with ether and dried, yielding 0.43 g. (86%) of V, m.p. (245) 272–277°, identical to the previously prepared sample by mixed melting point and infrared spectra.

***endo*-7-Diphenylmethylene-*N*-methyl-2,3-norbornanedicarboximide (IV).**—A solution of 0.45 g. (0.00125 mole) of V in 25 ml. of cold pyridine was treated with 0.135 ml. (0.00187 mole) of thionyl chloride dropwise, with cooling. After standing at room temperature overnight, the solution was diluted with 50 ml. of water and extracted three times with chloroform. The extracts were washed with dilute acid and base, and water, dried over magnesium sulfate, filtered, and concentrated to dryness *in vacuo*, affording 0.45 g. of oil which crystallized from ether–petroleum ether. There was obtained 0.33 g. (77%) of IV, m.p. 148–151° alone, or when admixed with authentic IV.[2] The infrared and ultraviolet spectra were also identical [λ_{max} 246 mμ (ϵ 16,200), λ sh 224 mμ (ϵ 14,900)].

Isomeric *anti*-7-Diphenylmethyl-*syn*-7-hydroxy-2,3-norbornanedicarboxylic Acids (VI).—A 9.8-g. sample of *endo*-[*anti*-7-diphenylmethyl-*syn*-7-hydroxy-*N*-methyl]-2,3-norbornanedicarboximide (V) was added to a solution of 50 g. of potassium hydroxide in 250 ml. of water and 250 ml. of ethanol and refluxed for 6 hr. The solution was then concentrated *in vacuo* to remove ethanol and diluted with 100 ml. of water. The solution was cooled and acidified with dilute hydrochloric acid. The solution was decanted from the gummy solid and extracted six times with methylene chloride. The extracts were added to the gummy solid, which was concentrated and dried by boiling off benzene. The product crystallized from methylene chloride giving 8.1 g. (81.5%), m.p. 135–142° (dec.). A sample was recrystallized from ethanol–benzene, m.p. 143–145° (dec.); λ_{max}^{KBr} 3.34, 5.85, 6.22, 6.65, 6.71, 6.85, 7.05 μ.

(15) We are indebted to Varian Associates for this spectrum.

Anal. Calcd. for $C_{22}H_{22}O_5$: 72.11; H, 6.05. Found: C, 72.23; H, 6.13.

***anti*-7-Diphenylmethyl-*syn*-7-hydroxy-2,3-norbornanedicarboxylic Acid, γ-Lactone (VIIIa) and *endo*-[*anti*-7-Diphenylmethyl-*syn*-7-hydroxy]-2,3-norbornanedicarboxylic Anhydride (VII).**—A 0.09-g. sample of VI was treated with 0.5 ml. of acetyl chloride and warmed at 60° for 2 hr. The acetyl chloride was boiled off and the residual product dried *in vacuo*. The material was then dissolved in chloroform and extracted three times with 5% sodium bicarbonate solution. The chloroform solution was dried and concentrated, affording 0.02 g. (23.4%) of a mixture of neutral products.

The aqueous solution was acidified with dilute hydrochloric acid and the gummy solid was crystallized by adding methylene chloride. The filtrate was decanted and the crystalline product was recrystallized from aqueous ethanol. There was obtained 0.45 g. (53%) of VIIIa, m.p. 190–192.5°. A sample was recrystallized again from aqueous ethanol and melted at 191–192.5°; $\lambda_{max}^{CHCl_3}$ 3.40, 5.62, 5.85, 6.25, 6.75, 6.88, 7.07 μ.

Anal. Calcd. for $C_{22}H_{20}O_4$: C, 75.84; H, 5.79. Found: C, 75.67; H, 6.02.

From a similar reaction, a 79% yield of noncrystalline, neutral product was obtained. The material was crystallized once from petroleum ether and twice from methylene chloride–ether affording a 6.5% yield of VII, m.p. 224–225.5°; λ_{max}^{KBr} 2.90, 3.39, 5.58, 5.71, 6.25, 6.68, 6.88 μ.

Anal. Calcd. for $C_{22}H_{20}O_4$: C, 75.84; H, 5.79. Found: C, 76.00; H, 5.85.

***anti*-7-Diphenylmethyl-*syn*-7-hydroxy-2,3-norbornanedicarboxylic Acid, γ-Lactone (VIIIb).**—A solution of 0.43 g. (0.00115 mole) of *anti*-7-diphenylmethyl-*syn*-7-hydroxy-2,3-norbornanedicarboxylic acid (VI) in 10 ml. of methanol was titrated with an ethereal solution of diazomethane until the yellow color persisted. After standing for 2 hr. at room temperature, the solution was concentrated to dryness.

The product was dissolved in ether and washed with 5% sodium bicarbonate solution. The ether solution was dried over magnesium sulfate, filtered, and concentrated to dryness at the water-pump, affording 0.32 g. (74%) of the oily dimethyl ester of VI $\lambda_{max}^{CHCl_3}$ 2.80, 3.45, 5.82, 6.25, sh. 6.75, 6.95 μ.

The diester (0.3 g., 0.00076 mole) was dissolved in 3.5 ml. of absolute ethanol and added to 3.5 ml. of a sodium ethoxide solution (1 g. of sodium/50 ml. of absolute ethanol). After refluxing for 16 hr., the solution was diluted with 3.5 ml. of water and refluxed for an additional 7 hr.

The solution was then diluted with 3.5 ml. of water, washed three times with ether, acidified with dilute hydrochloric acid and extracted with methylene chloride. The extracts were washed with water, dried over magnesium sulfate, filtered, and concentrated to dryness at reduced pressure. The product was recrystallized once from methylene chloride–ether and once from methanol–benzene, affording 0.18 g. (72%) of the mixture of diacids VI, m.p. 142–145° (dec.); λ_{max}^{KBr} 3.40, 5.87, 6.24, 6.68, sh. 6.73, 6.88 μ.

From a similar reaction, after the isolation of VI, m.p. 140–145°, in 57% yield, there was obtained a 14% yield of a new diacid, m.p. 258–260° (dec.); λ_{max}^{KBr} sh. 3.0, 3.30, 3.40, 5.90, 6.27, 6.69, sh 6.75, 6.90, 7.05 μ.

Anal. Calcd. for $C_{22}H_{22}O_5$: C, 72.11; H, 6.05. Found: C, 71.94; H, 5.98.

A 0.10-g. sample of this diacid, m.p. 258–260°, was treated with 0.5 ml. of acetyl chloride and the mixture was warmed at 60° for 18 hr. The acetyl chloride was evaporated and the crystalline product was dried under vacuum and triturated twice with petroleum ether and dried again affording 0.10 g. of VIIIb, m.p. 252–260°; λ_{max}^{KBr} 3.25, 3.35, 5.58, 5.83, 6.23, 6.65, 6.85, 7.03 μ. A sample recrystallized from methylene chloride–ether and melting at 253–259°, gave the following:

Anal. Calcd. for $C_{22}H_{20}O_4$: C, 75.84; H, 5.79. Found: C, 75.62; H, 5.85.

***exo*-8-Diphenylmethylene-*N*-methyl-3-oxatricyclo[3.2.1.0^{2,4}]-octane-6,7-dicarboximide (X).**—To a solution of 1 g. (0.00294 mole) of *exo*-7-diphenylmethylene-*N*-methyl-5-norbornene-2,3-dicarboximide (IX)[2] in 10 ml. of chloroform in an ice bath was added slowly a solution of 0.405 g. (0.00294 mole) of perbenzoic acid in chloroform. After standing for 24 hr. at room temperature, the solution was washed with 5% sodium carbonate solution, dried over magnesium sulfate, filtered, and concentrated to dryness *in vacuo*. The product was crystallized from methylene chloride–ether, yielding 0.92 g. of X (87.7%), m.p. 176.5–179.5°;

λ_{max}^{KBr} 5.64, 5.89, 6.25 (w), 6.70 6.97, 7.24 μ; λ_{max} 243 mμ (ϵ 13,300).

Anal. Calcd. for $C_{23}H_{19}NO_3$: C, 77.29, H, 5.36; N, 3.92. Found: C, 77.08; H, 5.45; N, 3.94.

A sample of X was recovered unchanged following retreatment with perbenzoic acid.

***endo*-8-Diphenylmethylene-3a,4,7,7a-tetrahydro-2-methyl-4,7-methanoisoindoline *N*-Oxide (XII).**—To 7 g. (0.022 mole) of *endo*-8-diphenylmethylene-2-methyl-3a,4,7,7a-tetrahydro-4,7-methanoisoindoline (XI)[2] in 70 ml. of chloroform in an ice bath was added a chloroform solution of 0.065 mole of perbenzoic acid. After standing for 3 days at room temperature, the solution was washed well with 5% sodium carbonate solution and concentrated to dryness *in vacuo*.

The crude product was dissolved in benzene and shaken with dilute hydrochloric acid, giving three layers—an aqueous layer containing insoluble material, an oily benzene-insoluble layer, and a benzene solution. The latter was separated. The other two layers were combined, made basic with aqueous sodium hydroxide, and extracted with methylene chloride. The extracts were washed with water, dried, and concentrated to dryness *in vacuo*, giving 9.1 g. of oily basic product.

The base was converted to its maleate salt in acetone–ether. There was obtained 6 g. (61%) of salt which after two recrystallizations from methanol, showed m.p. 151–152° (dec.); λ_{max}^{KBr} 2.90, 3.30, 4.30 (br.), 5.85, 6.15, 6.30, 6.90, 7.23 μ; λ_{max} 245 mμ (ϵ 18,300).

Anal. Calcd. for $C_{27}H_{27}NO_5$: C, 72.79; H, 6.11; N, 3.14. Found: C, 72.72; H, 6.25; N, 3.10.

In order to obtain an n.m.r. spectrum, a 0.2-g. sample of XII maleate was suspended in water and the free base was precipitated by the addition of concentrated sodium hydroxide solution. The base was extracted into ether; the extracts were washed once with water, dried over sodium sulfate, filtered, and concentrated. Crystallization from benzene–heptane gave 0.09 g. of XII, m.p. 98–100°. The base readily picks up water on standing; dissolves easily in dilute acid and is precipitated by the addition of dilute base. λ_{max}^{KBr} 2.95 (H_2O?), 3.30, 6.0 (br.), 6.23, 6.66, 6.88 μ. The n.m.r. in deuteriochloroform showed the following values in p.p.m.: 7–7.5 (10 aromatic protons); 6.4, 6.45, 6.48 (2 vinyl protons); 4.35, 3.6, 3.45, 3.2, 2.65 (11 protons-*N*-methyl, methylene and bridgehead).

Because of the hygroscopic nature of the compound, analytical results were inconsistent.

***endo*-2-Benzoyl-8-diphenylmethylene-3a,4,7,7a-tetrahydro-4,7-methanoisoindoline (XIV).**—To 1 g. (0.00334 mole) of *endo*-8-diphenylmethylene-3a,4,7,7a-tetrahydro-4,7-methanoisoindoline (XIII)[2] in 25 ml. of methylene chloride and 50 ml. of 10% sodium hydroxide was added 0.425 ml. (0.00367 mole) of benzoyl chloride. After stirring for 3 hr. at room temperature, the layers were separated and the aqueous solution was washed once with methylene chloride. The combined organic solutions were washed first with water and then with 2 *N* hydrochloric acid. The organic extract was dried over magnesium sulfate, filtered, and concentrated to dryness *in vacuo*, affording 1.4 g. of a viscous oily product. Crystallization occurred slowly from ethanol, giving 1.05 g. (78%) of XIV, m.p. 163–182°. Recrystallization from ethanol afforded 0.85 g. (63%) m.p. 175–180°.

An analytical sample, melting at 177–179°, showed $\lambda_{max}^{CHCl_3}$ 6.19, 6.33, 6.68, 6.97 μ; λ_{max} 244 mμ (ϵ 23,000).

Anal. Calcd. for $C_{29}H_{25}NO$: C, 86.32; H, 6.25; N, 3.47. Found: C, 86.31; H, 6.62; N, 3.55.

The n.m.r. in deuteriochloroform showed the following major peaks (in p.p.m.): 7.4, 7.25 (15 aromatic protons), 6.5, 6.3 (2 vinyl protons), 3.6, 3.5, 3.15, 2.65, 1.75, 1.55 (8 aliphatic protons).

Epoxidation of XIV with 1 Equivalent of Perbenzoic Acid.—To 2 g. (0.005 mole) of XIV in 25 ml. of chloroform was added dropwise with stirring a solution of 0.69 g. (0.005 mole) of perbenzoic acid in chloroform at 0°. After standing at room temperature for 72 hr. the solution was washed twice with 5% sodium carbonate solution, dried over magnesium sulfate, filtered, and concentrated to dryness, affording an oil. The oily product was chromatographed over 40 g. of Merck acid-washed alumina. The column was prepared with ether and the sample was put on in benzene. The following fractions were taken.

Fr.	Vol., ml.	Solvent	Wt., g.	M.p., C°
1	125	Et_2O	0.22	
2	125	Et_2O	.76	165–169.5
3	125	Et_2O	.30	176–178.5
4	125	Et_2O	.18	167/174.5–178
5	100	Et_2O	.06	152.5–156.5
6	125	Et_2O	.04	
7	125	Et_2O–$CHCl_3$(1:1)	.08	139–157
8	125	Et_2O–$CHCl_3$(1:1)	.06	
9	125	Et_2O–$CHCl_3$(1:1)	.24	165–175
		Total:	1.94 g. (92.7%)	

Fractions 2, 3, and 4 were combined and recrystallized from ethanol, affording 1.0 g. (47.6%) m.p. 161–167°; λ_{max}^{KBr} 6.15, 6.35, 6.68, 6.90, 7.02 μ; λ^{CH_3OH} at 245 mμ ϵ 7150 and end absorption.

Anal. Calcd. for $C_{29}H_{25}NO_2$: C, 83.03; H, 6.01; N, 3.34. Found: C, 83.04; H, 6.27; N, 3.37.

The n.m.r. spectrum in deuteriochloroform showed the following major peaks (in p.p.m.): 7.35, 7.3 (15 aromatic protons), 6.4 and 6.25 (*ca.* 1.4 vinyl protons), 3.5, 3.3, 2.45, 2.25, 1.6 (*ca.* 8.9 aliphatic protons).

From the integration of the n.m.r. spectrum, the vinyl proton count indicates the presence of *ca.* 70% of XVI in this mixture, and 30% of XV. This is supported by the ultraviolet spectrum. The absorption at 245 mμ accounts for the presence of 30% of XV in the mixture.

Chromatography fractions 6, 7, 8, and 9 were combined and recrystallized from ethanol–ether, affording 110 mg. (5.2%) m.p. 183–188°; λ_{max}^{KBr} 6.15, 6.25, 6.35, 6.70, 6.92, 7.02 μ; $\lambda_{max}^{CH_3OH}$ 245 mμ (ϵ 21,700) and end absorption.

Anal. Calcd. for $C_{29}H_{25}NO_2$: C, 83.03; H, 6.01; N, 3.34. Found: C, 82.41; H, 6.01; N, 3.27.

The n.m.r. spectrum in deuteriochloroform showed the following major peaks (in p.p.m.): 7.45 and 7.25 (15 aromatic protons), 3.5, 3.25, 2.9 (10.4 aliphatic protons).

Both the n.m.r. and ultraviolet spectra indicate this material is largely compound XV.

Acknowledgment.—The authors are indebted to Mrs. Mary C. Christie for many of the analyses and spectra, to Dr. H. R. Almond, Jr., for the n.m.r. spectra, and to Dr. Janis Plostnieks for helpful discussions.