[CONTRIBUTION FROM THE RESEARCH DIVISION OF ETHICON, INC.]

Stereochemistry of Diels–Alder Adducts. II. The Alkylation of Some Bicyclic Nitriles

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The stereochemistry of some carboxylic acids derived from 2-norbornene* and bicyclo[2,2,2]oct-2-ene was investigated. The reaction of either 5-*endo*cyano-2-norbornene (Ia) or 5-*exo*cyano-2-norbornene (Ib) with methyl chloride in the presence of sodamide and liquid ammonia gave 5-*endo*cyano-5-*exo*methyl-2-norbornene (III). As a by-product of both reactions, there was obtained an amidine fraction which upon saponification gave 2-norbornene-5-*exo*carboxamide (II); II also could be obtained in good yield from Ia by treatment with sodamide and liquid ammonia followed by hydrolysis of the resulting amidine. The Diels–Alder reaction between cyclopentadiene and ethacrylic acid gave predominantly 5-*endo*ethyl-2-norbornene-5-*exo*carboxylic acid which was converted to a carboxamide isomeric with that obtained upon saponification of the reaction product of Ia and ethyl bromide. Thus, the alkylation reaction appears to be a general method for the preparation of the unnatural or minor adducts of the Diels–Alder condensation between cyclopentadiene and α-alkylacrylic acids or their derivatives. The alkylation of 5-*endo*cyanobicyclo[2,2,2]oct-2-ene (VIII), on the other hand, gave a mixture of stereoisomeric 5-cyano-5-methylbicyclo[2,2,2]oct-2-enes (X) and an amidine fraction which was hydrolyzed to bicyclo[2,2,2]oct-2-ene-5-*endo*carboxamide (IXa). The Diels–Alder reaction between 1,3-cyclohexadiene and methacrylic acid gave a mixture of 5-methylbicyclo[2,2,2]oct-2-ene-5-carboxylic acids (XI) from which pure 5-*exo*methylbicyclo[2,2,2]oct-2-ene-5-*endo*carboxylic acid (XIa) was obtained *via* the iodolactone XII. A mechanism is proposed to account for differences in the stereospecificity of alkylation in the 2-norbornene and bicyclo[2,2,2]oct-2-ene series.

As part of a program designed to synthesize some highly hindered trisubstituted acetamides of bicyclic systems, it became necessary to study the stereochemistry of some carboxylic acid derivatives of 2-norbornene and bicyclo[2,2,2]oct-2-ene.

The 5-methyl-2-norbornene-5-carboxylic acids previously have been obtained by the Diels–Alder reaction between cyclopentadiene and methacrylic acid. This reaction results in a mixture of stereoisomers which is difficult to separate into its two pure components.[1] Furthermore, extension of the reaction to higher homologs of methacrylic acid is limited by the availability of these materials[2] and by the high temperatures necessary to effect condensation with cyclopentadiene. Therefore, an alternate route to the 5-alkyl-2-norbornene-5-carboxylic acid derivatives was sought. Alkylation of 5-*endo*cyano-2-norbornene (Ia) with methyl chloride and sodamide in liquid ammonia gave 37% 5-*endo*cyano-5-*exo*methyl-2-norbornene (III) which, upon saponification with alcoholic potassium hydroxide, afforded 5-*exo*methyl-2-norbornene-5-*endo*carboxamide (IV) and the known 5-*exo*methyl-2-norbornene-5-*endo*carboxylic acid[1] (V). The acid V formed an iodolactone and proved to be identical with the minor adduct of the Diels–Alder reaction between cyclopentadiene and methacrylic acid which was reported by Beckmann, *et al.*[1] The major product, on the other hand, formed an iodohydrin. Recently, Meek and Trapp[3] assigned the *endo*-carboxyl configuration to the minor adduct on the basis of iodolactone[4] formation, and the major adduct was assigned the *exo*carboxyl configuration. The latter, in contrast to our results, was reported to be unreactive toward the iodine reagent.[5] When IV was hydrogenated, 2-*exo*methylnorbornane-2-*endo*carboxamide[1] was obtained which could be saponified to 2-*exo*methylnorbornane-2-*endo*carboxylic acid.[1]

In addition to the methylated nitrile III, an amidine fraction was isolated as a by-product of the alkylation reaction, which, upon mild hydrolysis, yielded a carboxamide (II) melting at 182–183°. This carboxamide also was obtained in 73% yield upon hydrolysis of the reaction product of Ia and sodamide in liquid ammonia in the absence of an alkyl halide. Parham, *et al.*,[6] have reported the preparation of a carboxamide melting at 181–183° from 2-norbornene-5-*endo*carboxylic acid. Upon repetition of their work with highly purified material, however, we obtained a carboxamide melting at 202–203°. The Diels–Alder reaction between cyclopentadiene and acrylamide gave two isomeric carboxamides in a ratio of 10:1 melting at 202–203° and at 182–183°, respectively. The former proved to be identical by elementary analysis, mixed melting point and a comparison of infrared spectra with the carboxamide derived from pure 2-norbornene-5-*endo*carboxylic acid[7] and the latter with II. Compound II, which could also be prepared from pure 2-norbornene-5-*exo*carboxylic acid[7] *via* the acid chloride, was saponified readily to the *exo*carboxylic acid with aqueous sodium hydroxide. Saponification of the higher-melting carboxamide, on the other hand, gave 2-norbornene-5-*endo*carboxylic acid which was identified by conversion to its iodolactone.[7] The two isomeric carboxamides upon hydrogenation yielded, respectively, the known norbornane-2-*exo*- and 2-*endo*carboxamides. From these interconversions, it is now evident that the carboxamide II possesses the *exo* configuration and that the higher-melting isomer must be 2-norbornene-5 *endo*carboxamide.

5-*Exo*cyano-2-norbornene (Ib) was prepared by

(*) For the naming of these compounds, see "System of Nomenclature for Terpene Hydrocarbons," Advances in Chemistry Series, No. 14, American Chemical Society, Washington, D. C., 1955.

[1] S. Beckmann, R. Schaber and R. Bamberger, *Chem. Ber.*, **87**, 997 (1954).

[2] The synthesis of higher homologs of methacrylonitrile has been reported recently by W. J. Bailey, F. E. Naylor and J. J. Hewitt, *J. Org. Chem.*, **22**, 1076 (1957).

[3] J. S. Meek and W. B. Trapp, THIS JOURNAL, **79**, 3909 (1957).

[4] C. S. Rondestvedt, Jr., and C. D. Ver Nooy, *ibid.*, **77**, 4878 1955).

[5] The formation of an iodohydrin from 5-*endo*methyl-2-norbornene-6-*exo*carboxylic acid has been reported recently by S. Beckmann and R. Mezger, *Chem. Ber.*, **90**, 1559 (1957).

[6] W. E. Parham, W. T. Hunter and R. Hanson, THIS JOURNAL, **73**, 5068 (1951).

[7] C. D. Ver Nooy and C. S. Rondestvedt, Jr., *ibid.*, **77**, 3583 (1955).

dehydrating II according to the general method of LaForge.[8] Both Ia and Ib upon partial saponification gave a mixture of II, 2-norbornene-5-*endo*-carboxamide and an acidic fraction. Thus, because of their ready isomerization under aqueous alkaline conditions, the hydrolysis products of Ia and Ib could not serve to establish their configurations. Aqueous sulfuric acid at room temperature brought about a hydration of the double bond in Ia with the formation of a hydroxycyanonorbornane. In glacial acetic acid and sulfuric acid both hydration of the cyano group and addition of the elements of acetic acid to the double bond took place in Ia. Two isomeric acetoxynorbornanecarboxamides were isolated from this reaction by fractional crystallization. Under neutral conditions shown to proceed without isomerization, the isomeric 5-cyano-2-norbornenes were characterized as their ureidomethyl derivatives (*vide infra*).

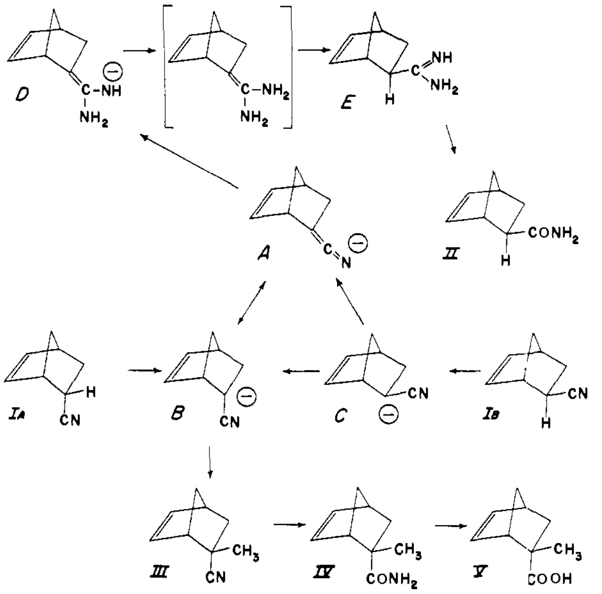
When Ib was alkylated by means of methyl chloride in the presence of sodamide and liquid ammonia, III was isolated unexpectedly in 77% yield. In addition, a basic fraction was obtained which gave II upon hydrolysis.

2-*endo*Cyanonorbornane when subjected to the methylation procedure also gave, analogous to the unsaturated nitriles, both 2-*endo*cyano-2-*exo*methylnorbornane and norbornane-2-*exo*carboxamide. Saponification of this alkylated nitrile yielded 2-*exo*methylnorbornane-2-*endo*carboxylic acid. The reaction of the saturated nitrile with methyl chloride proceeded much more vigorously than did the alkylation of Ia or Ib, an observation that is in agreement with the reduction in I-strain[9] upon hydrogenation of the bicyclic ring.

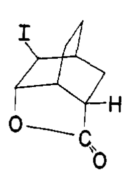
When Ia was alkylated with ethyl bromide by the above procedure, the ethylated nitrile corresponding to III was obtained in 77% yield. Saponification of this product gave both 5-*exo*ethyl-2-norbornene-5-*endo*carboxylic acid, whose configuration was established by conversion to the iodolactone, and 5-*exo*ethyl-2-norbornene-5-*endo*carboxamide. The stereoisomeric 5-*endo*ethyl-2-norbornene-5-*exo*-carboxylic acid was prepared by the Diels–Alder condensation of cyclopentadiene with ethacrylic acid[10] and converted to 5-*endo*ethyl-2-norbornene-5-*exo*carboxamide *via* the acid chloride.

The mechanism[11] by which the isomeric 5-cyano-2-norbornenes are alkylated may proceed through a hybrid carbanion of the type (B–A–C). Form B, the *endo*-carbanion, offers less resistance to the entry of the alkylating agent than does form C, the *exo*-carbanion, in the 2-norbornene series. Hence, the *exo*alkyl-*endo*nitrile III is produced from either Ia or Ib. Amidine formation, on the other hand, involves form A, which by addition of ammonia produces the enamine anion D. This ion, then upon proton addition rearranges to the thermodynamically more stable[12] *exo*-form E.

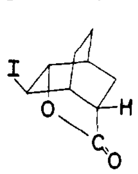
CHART I



Extension of the alkylation reaction to the bicyclo[2,2,2]oct-2-ene series necessitated a prior investigation of the stereochemistry of some 5-substituted derivatives. When 5-*endo*carbethoxybicyclo[2,2,2]oct-2-ene[13] was subjected to the isomerization procedure of Roberts, *et al.*,[14] and hydrolyzed, two acidic components were isolated by fractional crystallization. The higher-melting form (VIa, m.p. 56–57°), which predominated over the lower-melting form (VIb, m.p. 46–47°) by a factor of approximately ten, proved to be identical with the acid[15] obtained by hydrolysis of the Diels–Alder adduct of 1,3-cyclohexadiene and ethyl acrylate. That VIa possessed the expected *endo*-configuration was shown by its conversion to an iodolactone (VIIa, m.p. 81–82°). When the iodolactonization was extended over a longer period of time, however, an isomeric iodolactone (VIIb, m.p. 74–75°) was obtained. From the carbonyl absorption maxima exhibited by these compounds, it might be inferred that VIIa and VIIb represent the isomeric five- and six-membered lactones,[16] respectively.



VIIA



VIIB

The acid VIa also was obtained by saponification of 5-*endo*cyanobicyclo[2,2,2]oct-2-ene[17] (VIII) *via* the corresponding carboxamide IXa. The latter,

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[8] F. B. LaForge, This Journal, **50**, 2477 (1928).

[9] H. C. Brown, *Rec. Chem. Progr.* (*Kresge–Hooker Sci. Lib.*), **14**, 83 (1953); H. C. Brown, J. H. Brewster and H. Schechter, This Journal, **76**, 467 (1954); R. B. Turner, W. R. Meador and R. E. Winkler, *ibid.*, **79**, 4116 (1957).

[10] C. Mannich and E. Ganz, *Ber.*, **55**, 3486 (1922).

[11] For a discussion of the alkylation of nitriles, see A. C. Cope, H. L. Holmes and H. O. House, Chapter 4 in R. Adams, "Organic Reactions," Vol. IX, John Wiley and Sons, Inc., New York, N. Y., 1957; and E. L. Eliel, Chapter 2 in M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons Inc., New York, N. Y., 1956.

[12] R. B. Woodward and H. Baer, This Journal, **66**, 645 (1944).

[13] R. Seka and O. Tramposch, *Ber.*, **75**, 1379 (1942).

[14] J. D. Roberts, E. R. Trumbull, Jr., W. Bennett and R. Armstrong, This Journal, **72**, 3116 (1950).

[15] C. A. Grob, H. Kny and A. Gagneux, *Helv. Chim. Acta*, **40**, 130 (1957).

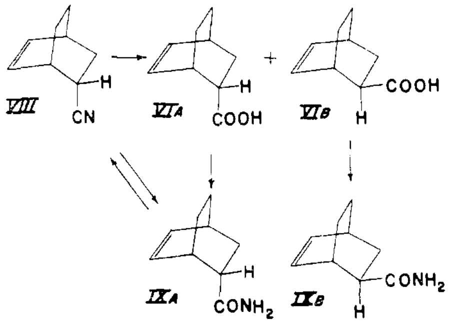
[16] Compare P. Wilder, Jr., and A. Winston, This Journal, **77**, 5598 (1955).

[17] K. Alder, H. Krieger and H. Weiss, *Chem. Ber.*, **88**, 144 (1955).

which could also be prepared from VIa *via* the acid chloride, was dehydrated to VIII without rearrangement.

The acid fraction VIb also was converted to a carboxamide but iodolactonization unexpectedly gave both iodolactones (VIIa and VIIb), dependent upon reaction time; no pure acidic fraction could be recovered in this reaction. While the infrared spectra of VIb and IXb differed considerably from the corresponding *endo*-isomers VIa and IXa (*vide infra*), the lack of chemical evidence makes it impossible at this time to assign the *exo* configuration to VIb and IXb with certainty.

CHART II

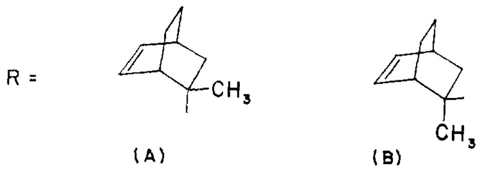


The Diels–Alder reaction between 1,3-cyclohexadiene and methacrylic acid gave upon saponification a mixture of isomeric acids from which no pure isomer could be separated by fractional crystallization, although considerable concentration of a higher-melting material (XIb, m.p. 129–130°) was achieved. When the distilled reaction product (XI) was subjected to iodolactonization, 35% of an iodolactone (XII) and 33% of an acidic fraction were obtained. Thus, in contrast to the analogous reaction with cyclopentadiene, the Diels–Alder reaction between 1,3-cyclohexadiene and methacrylic acid yields 5-*exo*methylbicyclo[2,2,2]oct-2-ene-5-*endo*carboxylic acid as the major product. Whether this difference in configuration indicates the latter reaction to follow the Alder orientation rules[18,19] more closely is uncertain in view of the high reaction temperature necessary to effect condensation.

When the iodolactone XII was subjected to zinc reduction,[20] pure 5-*exo*methylbicyclo[2,2,2]oct-2-ene-5-*endo*carboxylic acid (XIa, m.p. 118–119°) was obtained. This acid and the carboxamide XIIIa derived from it differed considerably in the infrared from the high-melting concentrate XIb and its carboxamide XIIIb.

Reduction of the carboxamides XIIIa and XIIIb with lithium aluminum hydride and subsequent reaction of the products with nitrourea[21] gave the corresponding 5-methyl-5-ureidomethylbicyclo[2,2,2]-oct-2-enes (XVa and XVb).

$$RCOOH \longrightarrow RCONH_2 \longrightarrow RCH_2NH_2 \longrightarrow RCH_2NHCONH_2 \quad (1)$$



These derivatives proved to be useful for the separation of the isomeric 5-methylbicyclo[2,2,2]oct-2-ene-5-carboxylic acids. When the distilled adduct of 1,3-cyclohexadiene and methacrylic acid was converted to the carboxamide and subjected to reaction sequence 1, a mixture of ureidomethyl derivatives was obtained. The components differed sufficiently in solubility to permit a separation into two isomeric 5-methyl-5-ureidomethylbicyclo[2,2,2]oct-2-enes (XVa, m.p. 190°, and XVb, m.p. 145–146°) whose stereoisomeric relationship was shown by catalytic hydrogenation to 2-methyl-2-ureidomethylbicyclo[2,2,2]octane. Conversion of pure XIIIa to the ureidomethyl derivative, however, gave only the higher-melting isomer XVa. On the other hand, the highest melting acidic fraction (XIb) obtained from the Diels–Alder reaction gave a mixture of ureidomethyl derivatives in which XVb predominated. To establish that reaction sequence 1 proceeded without rearrangement, the carboxamide IV and its stereoisomer 5-*endo*-methyl-2-norbornene-5-*exo*carboxamide (m.p. 159–160°) were converted to their ureidomethyl derivatives. In each case, the respective derivative was obtained as the only product of the reaction.

When VIII was subjected to the methylation procedure described for the norbornene analog Ia both a neutral and a basic fraction were isolated. The basic fraction upon saponification yielded only bicyclo[2,2,2]oct-2-ene-5-*endo*carboxamide (IXa) and the corresponding acid VIa. In one instance a small amount of the N-methyl derivative of IXa also was isolated. The neutral fraction consisting of the alkylated nitrile was saponified to a carboxamide and converted to a mixture of isomeric ureidomethyl derivatives from which XVa and XVb were isolated in a ratio of 3:1.

These results indicate that, in contrast to the norbornene series, alkylation of 5-*endo*cyanobicyclo-[2,2,2]oct-2-ene (VIII) is accompanied by a partial inversion about the 5-carbon atom. Thus, it appears that in the bicyclo[2,2,2]oct-2-ene series, both anions corresponding to forms B and C can participate in the displacement reaction. This fact reflects the greater symmetry of the bicyclo[2,2,2]oct-2-ene ring and hence a reduced steric selectivity toward an entering alkylating agent. Since the *endo* configuration would be expected to be the thermodynamically favored one in the 5-substituted bicyclo[2,2,2]oct-2-ene series, the observed absence of inversion in the amidine by-product fits well into the mechanistic scheme proposed in Chart I.

Infrared Spectra.—Because of the difficulties encountered in identifying the isomeric *endo*- and *exo*-substituted bicyclo[2,2,2]oct-2-enes by purely chemical means, a comparison of their infrared spectra with those of their norbornene analogs was employed as an additional criterion for the assignment of configuration. In general, the differences in absorption maxima between the stereoisomeric nor

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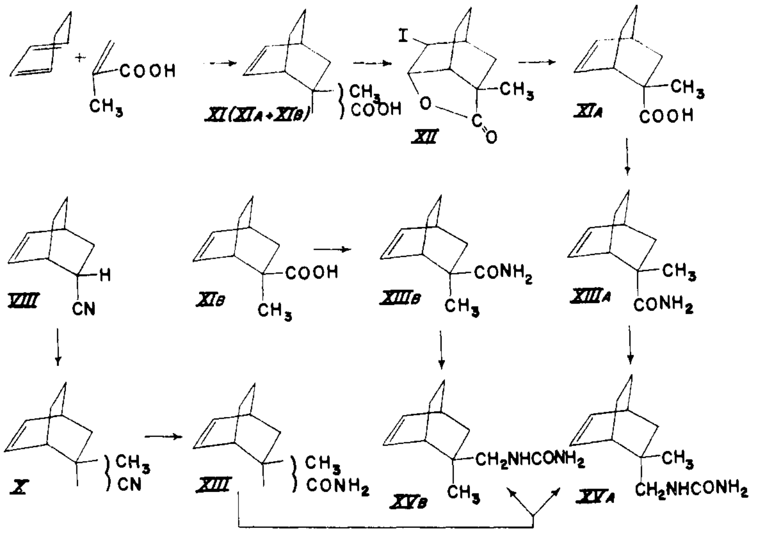
[18] M. C. Kloetzel, Chapter 1 in R. Adams, "Organic Reactions," Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1948.

[19] F. Winternitz, M. Mousseron and G. Rouzier, *Bull. soc. chim. France*, 170 (1955).

[20] K. Alder and F. Brochhagen, *Chem. Ber.*, **87**, 167 (1954).

[21] T. S. Buck and C. W. Ferry, THIS JOURNAL, **58**, 854 (1936).

CHART III



bornenes were greater than in the more symmetrical bicyclo[2,2,2]oct-2-ene series. The most significant differences between stereoisomeric pairs of both series were observed in the 13–15 μ region. In most instances, a remarkable parallel with respect to the direction of shift and in the intensity of the bands was seen when the stereoisomeric pairs of the norbornenes were compared with their bicyclo[2,2,2]oct-2-ene homologs.

Experimental[22]

Methylation of 5-*endo*-Cyano-2-norbornene (Ia).—5-*endo*Cyano-2-norbornene[23] (357 g., 3.0 moles) was added slowly to a stirred suspension of sodamide (from 69.0 g. (3.0 g. atoms) of sodium) in 3.5 l. of liquid ammonia. Gaseous methyl chloride was passed into the reaction mixture for 3.5 hours, 500 ml. of dry toluene then was added and the ammonia was allowed to evaporate overnight. The residue was filtered through a layer of Celite, the filter-cake was washed with toluene and the combined filtrates were washed with 10% hydrochloric acid and with water. The toluene phase was dried superficially by shaking for several minutes with anhydrous potassium carbonate and distilled through a 12″ Vigreux column giving 149.5 g. (37%) of 5-*endo*cyano-5-*exo*methyl-2-norbornene[24] (III), b.p. 105–108° (30 mm.), most of which solidified to a waxy material melting at 46–47°.

Anal. Calcd. for $C_9H_{11}N$: C, 81.16; H, 8.33; N, 10.52. Found: C, 81.07; H, 8.23; N, 10.35.

Sufficient solid sodium hydroxide was added to the aqueous acid washings above to precipitate the amidine as an oil and to give a concentration of 20% sodium hydroxide in the aqueous phase. The mixture was refluxed for 0.5 hour whereupon the oil became crystalline. The cooled suspension was filtered and the precipitate was washed with ice-water. Recrystallization from water gave 112.7 g. (27%) of 2-norbornene-5-*exo*carboxamide (II) as glistening plates, m.p. 182–183.5°; infrared absorption maxima[25]: 11.10(m), 11.57(w), 11.95(m), 12.19(m), 12.80(m), 13.99(s) and 14.60 (m) μ.

Anal. Calcd. for $C_8H_{11}NO$: C, 70.04; H, 8.08; N, 10.21. Found: C, 69.84; H, 8.22; N, 9.95.

5-*exo*Methyl-2-norbornene-5-*endo*carboxamide (IV).—A solution of 26.6 g. of III and 56 g. of potassium hydroxide in 84 g. of 95% ethanol was refluxed for 10 hours. The solvent was distilled under reduced pressure through a Vigreux column while 2 volumes of water was added gradually. The residue was cooled and the crystalline product was filtered, washed with cold water and recrystallized from boiling water. The colorless plates (16.1 g., 53%) melted at 130.5–131.5°; infrared absorption maxima: 10.95(s), 11.22(s), 11.85(s), 12.16(s), 12.84(s), 13.72(s), 14.08(s), 14.95(s) and 15.30(s) μ.

Anal. Calcd. for $C_9H_{13}NO$: C, 71.49; H, 8.67; N, 9.26. Found: C, 71.32; H, 8.70; N, 9.28.

5-*exo*Methyl-2-norbornene-5-*endo*carboxylic Acid (V).—5-*exo*Methyl-2-norbornene-5-*endo*carboxamide (IV, 25.0 g.) was refluxed for 5 days with a solution of 46.2 g. of potassium hydroxide in 150 ml. of water. The cooled solution was filtered from unsaponified IV (9.1 g.) and the filtrate was acidified with 6 *N* hydrochloric acid. The colorless solid precipitate (15.0 g., m.p. 103–104°) was recrystallized twice from hexane and gave 9.2 g. of coarse crystals, m.p. 109–110°. The mixed melting point with a sample of the minor adduct[26] (m.p. 109°) of the Diels–Alder reaction between cyclopentadiene and methacrylic acid was not depressed; infrared absorption maxima: 10.95(s), 11.08(s), 11.82(m), 12.06(s), 12.82(m), 13.36(m), 14.00(s) and 14.71(s) μ.

The S-benzylthiuronium salt (prepared by the method of Vogel[27]) melted at 150–151° when recrystallized from dilute ethanol.

Anal. Calcd. for $C_{17}H_{22}N_2O_2S$: C, 64.12; H, 6.97; N, 8.80. Found: C, 64.16; H, 7.04; N, 8.72.

The iodolactone (prepared according to the method of reference 7 in 91% yield) melted at 86.5–87.5° when recrystallized from hexane–cyclohexane (reported[8] m.p. 83–86°). The carbonyl stretching frequency exhibited a band at 5.64 μ.

2-*exo*Methylnorbornane-2-*endo*carboxamide.—A solution of 27.8 g. of IV in 250 ml. of ethanol was hydrogenated in the presence of palladium oxide catalyst at an initial pressure of 45 lb. Reduction was complete in 45 minutes. The residue, after removal of catalyst and solvent, was recrystallized from water as fine blades (24.1 g., m.p. 126–127.5°). For analysis a sample was again recrystallized, m.p. 127.5–128.5° (reported[1] m.p. 127°).

2-*exo*Methylnorbornane-2-*endo*carboxylic Acid.—Sodium nitrite (32.5 g.) was added in small portions with stirring during 4 hours to a solution of 51.7 g. of 2-*exo*methylnorbornane-2-*endo*carboxamide in 75 ml. of 75% sulfuric acid at 50–60°. The cooled suspension was then diluted with water and extracted with ether. The ether solution was extracted with 10% sodium hydroxide solution and the product was reprecipitated in almost quantitative yield (m.p. 95–97°) by acidification with hydrochloric acid. When recrystallized from water, it melted at 97.5–98.5° (reported[1] m.p. 92–93°). The acid was obtained in 56% yield when the hydrolysis was carried out with isoamyl nitrite and hydrochloric acid in acetic acid solution.[28]

5-*endo*Methyl-2-norbornene-5-*exo*carboxylic Acid,[1] m.p. 82–83°; infrared absorption maxima: 11.00(s), 11.60(s), 11.72(s), 12.21(s), 12.70(m), 13.25(m), 13.48(s), 13.65(s), 13.98(s) and 14.74(s) μ.

The iodohydrin was prepared by dissolving 15.2 g. of the acid in 10% sodium hydroxide solution and adding sodium

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[22] Melting points are uncorrected. Analyses and infrared spectra by Mr. E. R. Hoffmann and Miss Mary Grace Comfort of these laboratories.

[23] This compound was prepared by the method of H. A. Bruson (THIS JOURNAL, **64**, 2457 (1942)) with slight modification to minimize formation of the *exo* isomer. The reaction temperature was maintained at 25° and ether was used as a solvent.

[24] The adduct of cyclopentadiene and methacrylonitrile, which is probably 5-*exo*cyano-5-*endo*methyl-2-norbornene for the most part, has been reported by J. Gillois-Doucet, *Ann. chim.* (*Paris*), **10**, 497 (1955); and by V. G. Yashunskii, A. P. Terent'ev and Ya. G. Nekhlin, *Zhur. Obshchei Khim.*, **26**, 723 (1956); see also reference 3.

[25] Infrared spectra were determined with a model 21 Perkin-Elmer spectrophotometer. Solids were measured as potassium bromide pellets and liquids as capillary films between potassium bromide plates.

[26] We are indebted to Prof. Beckmann for a sample of this material and for a helpful discussion of the problem.

[27] A. I. Vogel, "Textbook of Practical Organic Chemistry," Longmans, Green and Co., London, 1948, p. 359.

[28] N. Sperber, D. Papa and E. Schwenk, THIS JOURNAL, **70**, 3091 (1948).

bicarbonate and iodine stock solution according to reference 7. The product (20.4 g., 68%, m.p. 188°) was recrystallized from acetone–hexane, m.p. 195–196° dec.

Anal. Calcd. for $C_9H_{13}IO_3$: C, 36.50; H, 4.42. Found: C, 36.63; H, 4.72.

The S-benzylthiuronium salt melted at 165–166° when recrystallized from 50% ethanol.

Anal. Calcd. for $C_{17}H_{22}N_2O_2S$: C, 64.12; H, 6.97; N, 8.80. Found: C, 64.32; H, 7.26; N, 8.95.

5-*endo*Methyl-2-norbornene-5-*exo*carboxamide,[1] m.p. 159–160°; infrared absorption maxima: 11.05(m), 11.09(m), 11.65(m), 11.84(s), 12.19(s), 12.47(m), 12.93(s), 13.71(s), 14.00(s) and 15.35(s) μ.

2-Norbornene-5-*exo*carboxamide (II).—(a) 5-*endo*Cyano-2-norbornene (Ia, 59.5 g., 0.5 mole) was added slowly to a stirred suspension of sodamide (from 11.5 g., 0.5 g. atom of sodium) in 750 ml. of liquid ammonia. Dry toluene (100 ml.) was added and the ammonia was allowed to evaporate spontaneously. The residue was decomposed carefully with water and acidified with 10% hydrochloric acid. The aqueous phase was drawn off, washed with toluene and saponified by refluxing for 0.5 hour in 20% sodium hydroxide solution. Recrystallization of the crude product from water gave 50.2 g. (73%), m.p. 181–182°.

(b) 2-Norbornene-5-*exo*carboxylic acid (purified *via* the iodolactonization procedure,[7] m.p. 45–46°) exhibited absorption maxima at 11.10(s), 11.61(m), 11.85(w), 12.60(w), 12.74(w), 14.00(s) and 14.80(m) μ.

The S-benzylthiuronium salt melted at 170–171° dec. when recrystallized from ethanol.

Anal. Calcd. for $C_{16}H_{20}N_2O_2S$: C, 63.13; H, 6.62; N, 9.21. Found: C, 62.85; H, 6.56; N, 9.35.

Ten grams of the acid was refluxed for 3 hours with 11.9 g. of thionyl chloride and 25 ml. of chloroform. Fractional distillation under reduced pressure gave 10.3 g. (90%) of 2-norbornene-5-*exo*carbonyl chloride, b.p. 70–72° (8 mm.). A solution of the acid chloride in 250 ml. of absolute ether was saturated with anhydrous ammonia. The precipitated carboxamide was filtered and washed with ice-water, m.p. 182.5–183.5°. Recrystallization from water gave 7.0 g. (63%), m.p. 182.5–184°.

Norbornane-2-*exo*carboxamide.—A solution of 10 g. of II in 150 ml. of warm ethanol was hydrogenated at 50 lb. pressure in the presence of platinum oxide catalyst. The theoretical amount of hydrogen was absorbed in 0.5 hour. The glistening plates (m.p. 191–192°), which separated after removal of the catalyst and concentration of the solution, were recrystallized from water, m.p. 192.5–193.5° (reported[29] m.p. 187–188°).

2-Norbornene-5-*exo*carboxylic Acid from II.—One-half mole (68.5 g.) of II was refluxed with 500 ml. of 20% sodium hydroxide solution. The liberation of ammonia, which was collected in standard hydrochloric acid, was complete in 2 hours (98% of the calculated amount titrated). The cooled solution was washed with ether, acidified with hydrochloric acid and the precipitated product was extracted with ether. The extract was dried over anhydrous calcium chloride and distilled under reduced pressure giving 61.4 g. (89%), b.p. 127–128° (7 mm.), m.p. *ca.* 36°. The distillate, upon further purification *via* the iodolactomization method[7] and by recrystallization from pentane, gave 34.5 g., m.p. 44–45° (reported[7] m.p. 44–45°).

Diels–Alder Condensation of Cyclopentadiene with Acrylamide.—A suspension of 71.0 g. (1.0 mole) of acrylamide, 79.2 g. (1.2 moles) of freshly distilled cyclopentadiene and 1 g. of hydroquinone in 500 ml. of 50% aqueous ethanol was refluxed for 8 hours with stirring. The cooled mixture was filtered and the filter-cake was washed with water and with pentane. The crude precipitate (140.0 g., m.p. 194–196°) was recrystallized from ethanol giving 89.0 g. (65%) of 2-norbornene-5-*endo*carboxamide as glistening plates, m.p. 200–202°. For analysis a sample was recrystallized from water, m.p. 201–203°; infrared absorption maxima: 10.95(m), 11.92(m), 12.17(m), 12.72(w), 12.96(m), 13.74(s) and 14.43(s) μ.

Anal. Calcd. for $C_8H_{11}NO$: C, 70.04; H, 8.08; N, 10.21. Found: C, 69.86; H, 8.01; N, 10.12.

Concentration of the ethanolic mother liquors from the Diels–Alder reaction gave 8.5 g. (6.5%) of II, m.p. 183–184° when recrystallized from water.

2-Norbornene-5-*endo*carboxylic acid,[7] m.p. 44–45°, exhibited infrared absorption maxima at 10.95(s), 11.04(s), 11.90(s), 12.12(w), 12.29(w), 12.85(m), 13.38(m), 13.50(m), 14.15(s) and 14.86(m) μ.

The S-benzylthiuronium salt melted at 179–180° when recrystallized from ethanol.

Anal. Calcd. for $C_{16}H_{20}N_2O_2S$: C, 63.13; H, 6.62; N, 9.21. Found: C, 62.95; H, 6.76; N, 9.15.

2-Norbornene-5-*endo*carboxamide.—2-Norbornene-5-*endo*carbonyl chloride (prepared by the method for the *exo*-isomer above, b.p. 84–85° (14 mm.), 75–85%) gave the carboxamide (m.p. 198–201°, 74%). A sample melted at 202–203° when recrystallized from water.

Norbornane-2-*endo*carboxamide.—Hydrogenation of 2-norbornene-5-*endo*carboxamide by the method for the *exo* isomer above) gave glistening plates, m.p. 210.5–211.5° when recrystallized from ethanol and from water (reported[30] m.p. 210–211°).

Reduction of 2-Norbornene-5-*endo*carboxylic Acid Iodolactone.—A solution of 8.0 g. of the iodolactone[7] (m.p. 58–59°) in 300 ml. of 95% ethanol was refluxed with 50 g. of zinc dust for 5 hours with stirring. The suspension was filtered and the filtrates were distilled to dryness under reduced pressure. The residue was taken up in dilute sodium hydroxide and filtered. Acidification of the filtrate with hydrochloric acid precipitated 2-norbornene-5-*endo*carboxylic acid, m.p. 44–46°. Recrystallization from pentane raised the m.p. to 45–46°.

The acid (0.75 g.) was converted to the carboxamide *via* the acid chloride. The resulting 2-norbornene-5-*endo*carboxamide melted at 200–202° when recrystallized from water.

Reactions of 5-*endo*Cyano-2-norbornene (Ia). (a) **Isomeric 5(or 6)-Acetoxynorbornane-2-carboxamides (Bertram–Walbaum Reaction).**—A mixture of 47.5 g. of Ia in 250 ml. of acetic acid and 50 ml. of concentrated sulfuric acid was allowed to stand at room temperature for 5 days. The clear reddish solution was diluted with 500 ml. of water and made alkaline with solid sodium carbonate. A tan, granular, somewhat oily solid separated. The product (47.5 g.) crystallized slowly from water, m.p. 202–206°. Four recrystallizations from absolute ethanol gave fine colorless plates, m.p. 207–210° which depressed the m.p. of 2-norbornene-5-*endo*carboxamide. It did not decolorize potassium permanganate in aqueous acetone.

Anal. Calcd. for $C_{10}H_{15}NO_3$: C, 60.89; H, 7.67; N, 7.10. Found: C, 61.02; H, 7.70; N, 7.00.

The aqueous alkaline filtrate above was extracted with ether; the extracts dried over anhydrous potassium carbonate and the solvent was evaporated. The solid residue (6.0 g.) was recrystallized four times from water, m.p. 182–183°. It depressed the m.p. of 2-norbornene-5-*exo*carboxamide.

Anal. Found: C, 61.15; H, 7.67; N, 7.03.

(b) **5(or 6)-Hydroxy-2-cyanonorbornane.**—Twenty grams of Ia was shaken for 5 hours with 200 ml. of 50% sulfuric acid. The nitrile gradually dissolved with the formation of a deep reddish solution. An equal volume of water was added and the solution was made alkaline with solid sodium carbonate. The precipitated oil was extracted with ether, the extracts were dried over anhydrous potassium carbonate and the solvent was evaporated. The residue was distilled twice under reduced pressure yielding 4.5 g. of colorless liquid, b.p. 92–98° (0.15 mm.), $n^{25}\text{D}$ 1.5007. The infrared spectrum exhibited a sharp $C{\equiv}N$ band at 4.46 μ and a broader OH band at 9.24 μ.

Anal. Calcd. for $C_8H_{11}NO$: C, 70.04; H, 8.08; N, 10.21. Found: C, 69.89; H, 8.13; N, 9.95.

2-*endo*Cyanonorbornane.—A solution of 59.5 g. of Ia in 250 ml. of ethanol was hydrogenated at 45 lb. pressure in the presence of palladium oxide catalyst. The product was distilled under reduced pressure yielding 57.2 g., b.p. 90–91° (12 mm.), which solidified to waxy crystals. For analysis a sample was recrystallized from pentane, m.p. 43–44° (reported[17] m.p. 36–37°).

Anal. Calcd. for $C_8H_{11}N$: C, 79.29; H, 9.15; N, 11.56. Found: C, 79.51; H, 9.08; N, 11.25.

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(29) K. Alder, G. Stein, E. Rolland and G. Schulze, *Ann.*, **514**, 211 (1934).

(30) W. R. Boehme, THIS JOURNAL, **80**, 4740 (1958).

Methylation of 2-*endo*Cyanonorbornane.—A solution of 60.5 g. of 2-*endo*cyanonorbornane in 50 ml. of dry toluene was added in 5 minutes to a suspension of sodamide (from 11.5 g. of sodium) in 600 ml. of liquid ammonia. When gaseous methyl chloride was passed into the reaction mixture it reacted vigorously and some material was blown from the flask. The alkyl halide was then passed over the surface of the suspension with stirring for 2 hours. 2-*endo*Cyano-2-*exo*methylnorbornane isolated by the procedure described for the unsaturated analog III was obtained in 32% yield (21.5 g.), b.p. 74–76° (6 mm.), $n^{25}\text{D}$ 1.4770.

Anal. Calcd. for $C_9H_{13}N$: C, 79.95; H, 9.69; N, 10.36. Found: C, 79.96; H, 9.65; N, 10.50.

Saponification of the amidine fraction gave 25.1 g. of crude norbornane-2-*exo*carboxamide (m.p. 182–185°). When the neutral fraction was saponified by the procedure employed for III, there was obtained 11.9 g. of 2-*exo*methylnorbornane-2-*endo*carboxamide, m.p. 125.5–127°. Recrystallization from water yielded 8.8 g., m.p. 127–128°.

5-*exo*Cyano-2-norbornene (Ib).—An intimate mixture of 114 g. of II and 142 g. of phosphorus pentoxide was distilled under a pressure of 33 mm. until the bath temperature reached 220°. Distillation began at a bath temperature of about 150° and gave 34.0 g. (37%), b.p. 107–110° (33 mm.). For analysis, it was redistilled through a short Vigreux column yielding 33.5 g., b.p. 101–103° (29 mm.), $n^{25}\text{D}$ 1.4843.

Anal. Calcd. for C_8H_9N: C, 80.63; H, 7.61; N, 11.76. Found: C, 80.34; H, 7.81; N, 11.88.

Methylation of 5-*exo*Cyano-2-norbornene (Ib).—The *exo*-nitrile (32.5 g.), upon methylation by the procedure employed for Ia with methyl chloride and sodamide (from 6.9 g. of sodium) in 300 ml. of liquid ammonia, yielded 27.8 g. (77%) of 5-*endo*cyano-5-*exo*methyl-2-norbornene (III), b.p. 104–106° (31 mm.), m.p. 46–47.5°.

The methylated nitrile (13.3 g.) was saponified by the procedure employed for III above. The crude IV (11.2 g., m.p. 127–129°) was recrystallized twice from water, m.p. 130.5–131.5°.

From the acid washings of the toluene phase, there was obtained by alkaline hydrolysis 3.3 g. (9%) of II, m.p. 177–178°. Recrystallization from water gave 2.5 g., m.p. 181.5–183°.

Diels–Alder Reaction between Cyclopentadiene and Ethacrylic Acid.—A mixture of 24.0 g. of ethacrylic acid,[10] 18.7 g. of technical dicyclopentadiene and 0.1 g. of hydroquinone was heated in a sealed glass tube at 170–175° for 12 hours. The resulting viscous liquid was extracted with dilute sodium hydroxide solution and the alkaline extract was acidified with hydrochloric acid. The precipitated oil was taken up in ether, dried over anhydrous calcium chloride and distilled under reduced pressure. The distillate, consisting principally of 5-*endo*ethyl-2-norbornene-5-*exo*-carboxylic acid (23.0 g., 59%), boiled at 102–106° (0.5 mm.), $n^{25}\text{D}$ 1.4856.

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.03; H, 8.62.

5-*endo*Ethyl-2-norbornene-5-*exo*carboxamide.—A solution of 18.5 g. of 5-*endo*ethyl-2-norbornene-5-*exo*carboxylic acid and 19.8 g. of thionyl chloride in 25 ml. of chloroform was refluxed for 3 hours and distilled. The acid chloride (14.7 g., 71%, b.p. 75–77° (4 mm.)) was dissolved in 300 ml. of ice-cold absolute ether and the solution was saturated with gaseous ammonia. The precipitated ammonium chloride was filtered and the filtrate was evaporated. Four recrystallizations of the residue from hexane gave 9.5 g. (65%) of colorless plates, m.p. 97–98°; infrared absorption maxima: 10.95(w), 11.03(w), 11.41(w), 11.73(w), 12.18(m), 12.57(w), 12.80(m), 13.10(w), 13.78(s) and 14.10(m) μ.

Anal. Calcd. for $C_{10}H_{15}NO$: C, 72.69; H, 9.15; N, 8.48. Found: C, 72.96; H, 9.11; N, 8.39.

5-*endo*Cyano-5-*exo*ethyl-2-norbornene.—Compound Ia (59.5 g.) was added slowly to a stirred suspension of sodamide (from 11.5 g. of sodium) in 700 ml. of liquid ammonia. A solution of 81.5 g. of ethyl bromide in 125 ml. of dry toluene was added dropwise with stirring during 0.5 hour and the ammonia was allowed to evaporate spontaneously. Water (100 ml.) was added carefully to the residue and the toluene layer was separated, washed with 10% hydrochloric acid and dried superficially by shaking for several minutes with anhydrous potassium carbonate. Distillation under reduced pressure gave 48.4 g. (66%), b.p. 120–122° (8 mm.), $n^{25}\text{D}$ 1.4812.

Anal. Calcd. for $C_{10}H_{13}N$: C, 81.58; H, 8.90; N, 9.52. Found: C, 81.80; H, 8.89; N, 9.47.

5-*exo*Ethyl-2-norbornene-5-endocarboxamide.—A solution of 22.1 g. of 5-*endo*cyano-5-*exo*ethyl-2-norbornene and 42 g. of potassium hydroxide in 63 g. of ethanol was refluxed for 11 hours. The solvent was distilled under reduced pressure while 150 ml. of water was added gradually. The suspension was cooled, filtered and the precipitate was washed well with cold water. Recrystallization of the crude product (21.6 g., 87%, m.p. 143–143.5°) from water gave 17.4 g. of glistening plates, m.p. 142–143°; infrared absorption maxima: 10.90(m), 10.96(m), 11.27(w), 11.73-(m), 12.12(m), 12.44(w), 12.65(w), 12.77(m), 13.78(s) and 14.19(s) μ.

Anal. Calcd. for $C_{10}H_{15}NO$: C, 72.69; H, 9.15; N, 8.48. Found: C, 72.50; H, 9.25; N, 8.30.

5-*exo*Ethyl-2-norbornene-5-*endo*carboxylic Acid.—A solution of 24 g. of 5-*endo*cyano-5-*exo*ethyl-2-norbornene, 50 g. of potassium hydroxide and 10 ml. of water in 250 ml. of ethylene glycol was refluxed for 16 hours. Dilution of the cooled solution with 250 ml. of water precipitated 21.3 g. (79%) of the carboxamide, m.p. 138–140°. The aqueous alkaline glycol solution was washed with hexane and acidified with hydrochloric acid. The liberated acid was then extracted with hexane, the extracts dried over Drierite and distilled to give 2.5 g. (9%), b.p. 150–155° (4 mm.).

The iodolactone (2.6 g.), which was prepared by the procedure of reference 7, formed pale yellow needles, m.p. 88.5–89.5°, when recrystallized from hexane. The carbonyl stretching frequency exhibited a maximum at 5.62 μ.

Anal. Calcd. for $C_{10}H_{13}IO_2$: C, 41.11; H, 4.48. Found: C, 41.15; H, 4.53.

Isomeric Bicyclo[2,2,2]oct-2-ene-5-carboxylic Acids.—A solution of 241 g. of 5-*endo*carbethoxybicyclo[2,2,2]oct-2-ene[13] and 149 g. of sodium methoxide in 440 ml. of methanol was refluxed for one week. Most of the methanol was removed under reduced pressure and the residue was refluxed with 660 ml. of water for 20 hours. The solution was concentrated to 300 ml., filtered, and the filtrate was acidified with hydrochloric acid. The precipitated oil (168 g., 68%) was fractionally crystallized from pentane at low temperature to give 102 g. of a fraction melting at 56–57° (VIa) and 13.6 g. of a fraction melting at 46–47° (VIb); infrared absorption maxima (VIa): 10.68(s), 11.06(s), 11.62(s), 11.80(m), 12.04(m), 12.25(m), 12.53(m), 13.35-(w), 13.58(w), 14.45(s), 15.01(w) and 15.34(m) μ; (VIb): 10.76(s), 11.04(s), 11.58(m), 11.84(m), 12.01(w), 12.24(w), 12.52(m), 13.45(w), 13.60(w), 14.27(s), 14.47(s), 15.04(w) and 15.31(m) μ.

Anal. Calcd. for $C_9H_{12}O_2$: C, 71.02; H, 7.95. Found: (VIa): C, 70.96; H, 8.13. (VIb): C, 71.33; H, 8.17.

Bicyclo[2,2,2]oct-2-ene-5-*endo*carboxylic Acid.—(a) A mixture of 33 g. of 1,3-cyclohexadiene,[31] 40 g. of acrylic acid and 0.25 g. of hydroquinone was heated in a sealed glass tube at 170° for 24 hours. Distillation of the reaction mixture gave 28 g. (45%), b.p. 140–150° (20 mm.), which solidified upon cooling. After several recrystallizations from pentane at −30°, it melted at 56–57°.

(b) A mixture of 5-*endo*cyanobicyclo[2,2,2]oct-2-ene[17] (VIII), 75 ml. of 20% aqueous potassium hydroxide and 75 ml. of ethanol was refluxed for 16 hours. The solution was concentrated to one-fourth of its volume and diluted with 100 ml. of water. A small amount of IXa was filtered off and the filtrate was acidified with hydrochloric acid. The solid (9.2 g.) which separated was recrystallized several times from pentane, m.p. 55–56°.

Bicyclo[2,2,2]oct-2-ene-5-*endo*carboxylic Acid Lactone.—The lactone was prepared from 3 g. of the acid VIa by the procedure of Alder and Stein.[8] The crude lactone (1 g.) was recrystallized several times from pentane–hexane, m.p. 207–208°. The carbonyl absorption maximum exhibited a band at 5.68 μ.

Anal. Calcd. for $C_9H_{12}O_2$: C, 71.02; H, 7.95. Found: C, 70.88; H, 7.89.

Bicyclo[2,2,2]oct-2-ene-5-*endo*carboxylic Acid Iodolactones (VIIa) and (VIIb). (a) VIIa.—The acid VIa was

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[31] K. Ziegler, A. Späth, E. Schaaf, W. Schumann and E. Winkelmann, *Ann.*, **551**, 80 (1942).

iodolactonized[7] for a period of 24 hours in the dark. The iodolactone (75%) was recrystallized from hexane, m.p. 81–82°. The carbonyl absorption maximum occurred at 5.60 μ.

Anal. Calcd. for $C_9H_{11}IO_2$: C, 38.87; H, 3.99. Found: C, 39.18; H, 4.23.

The acid fraction VIb gave iodolactone VIIa in 59% yield.

(b) **VIIb.**—When the reaction time was lengthened to 3 days or more, an iodolactone was isolated from VIa in 55% yield which melted at 74–75° when recrystallized from hexane. The carbonyl absorption maximum occurred at 5.68 μ.

Anal. Found: C, 39.11; H, 4.22.

Approximately the same yields of iodolactone VIIb were obtained under these conditions from VIb and from the crude distilled adduct of 1,3-cyclohexadiene and acrylic acid.

Bicyclo[2,2,2]oct-2-ene-5-*endo*carboxamide (IXa).—Five grams of VIa was converted to the carboxamide *via* the acid chloride by the procedure described for the corresponding norbornene analog. The crude product was recrystallized from ethyl acetate and from water yielding 3.5 g., m.p. 162–163°; infrared absorption maxima: 11.05(s), 11.55(s), 12.06(s), 12.42(s), 12.85(s), 13.85(s) and 14.60(s) μ.

Anal. Calcd. for $C_9H_{13}NO$: C, 71.49; H, 8.67; N, 9.26. Found: C, 71.61; H, 8.55; N, 9.10.

One gram of IXa in 15 ml. of 20% aqueous potassium hydroxide was refluxed for 6 hours. The resulting solution was washed with ether and acidified with hydrochloric acid. The solid (VIa, 0.5 g.) which separated melted at 55.5–56.5° when recrystallized from pentane.

5-*endo*Cyanobicyclo[2,2,2]oct-2-ene (VIII).—The carboxamide (IXa, 1.8 g.) was dehydrated by the procedure described for Ib. The resulting nitrile was recrystallized from pentane, m.p. 58–59° (reported[17] m.p. 58°).

Bicyclo[2,2,2]oct-2-ene-5-*exo*carboxamide (IXb).—The *exo*-acid VIb was converted to the carboxamide *via* the acid chloride as described above; m.p. 158–159° when recrystallized from ethyl acetate; infrared absorption maxima: 11.08(s), 11.58(m), 11.96(s), 12.08(m), 12.43(s), 12.85(s) and 14.44(s) μ.

Anal. Calcd. for $C_9H_{13}NO$: C, 71.49; H, 8.67; N, 9.26. Found: C, 71.58; H, 8.71; N, 9.15.

Diels–Alder Condensation of 1,3-Cyclohexadiene and Ethyl Methacrylate.—A solution of 146 g. of 1,3-cyclohexadiene, 209 g. of ethyl methacrylate and 2 g. of hydroquinone was heated in a glass-lined autoclave at 130° for 22 hours. Distillation of the reaction product gave 48 g. of 5-carbethoxy-5-methylbicyclo[2,2,2]oct-2-ene, b.p. 122–123° (27 mm.). The distillate, which gave a poor analysis, appeared to be contaminated with dicyclohexadiene (b.p. 110° (27 mm.)).

Isomeric 5-Methylbicyclo[2,2,2]oct-2-ene-5-carboxylic Acids (XI), (a) Diels–Alder Condensation.—A mixture of 49 g. of 1,3-cyclohexadiene, 55 g. of methacrylic acid and 1 g. of hydroquinone was heated in a sealed glass tube at 160° for 24 hours. The contents of the tube were distilled under reduced pressure giving 46 g. of distillate, b.p. 150–190° (20 mm.), which solidified on standing. The poorly melting substance was subjected to a series of low temperature fractional recrystallizations from pentane. In addition to numerous intermediate fractions, 5 g. of a material (XIb), m.p. 129–130°, was obtained.

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.47; H, 8.65.

(b) **Hydrolysis of 5-Carbethoxy-5-methylbicyclo[2,2,2]-oct-2-ene.**—A solution of 114 g. of 5-carbethoxy-5-methylbicyclo[2,2,2]oct-2-ene and 71 g. of potassium hydroxide in 325 ml. of 90% ethanol was refluxed for 2 hours. The alcohol was removed under reduced pressure and 350 ml. of ice-water was added. The filtered solution was washed with ether and acidified with hydrochloric acid. The precipitate (78 g., m.p. 105–120°) which separated was subjected to extensive fractional crystallization from pentane at low temperature. In addition to many intermediate fractions, there was obtained 10 g. of the highest melting fraction (XIb, m.p. 129–130°).

5-*exo*Methylbicyclo[2,2,2]oct-2-ene-5-*endo*carboxylic Acid (XIa). (a) Iodolactone.—The acidic fraction (23.2 g.) obtained in the above reactions prior to fractional crystallization was subjected to the iodolactonization[7] procedure. A neutral fraction (4.5 g.) was obtained which was recrystallized several times from pentane, m.p. 112–113°. The carbonyl absorption maximum was observed at 5.65 μ.

Anal. Calcd. for $C_{10}H_{13}IO_2$: C, 41.11; H, 4.48. Found: C, 41.26; H, 4.54.

As a by-product of the iodolactonization reaction, there was obtained 7.7 g. of an acidic fraction. This fraction could be further separated into 4.7 g. of a pentane-soluble portion, but no pure compound could be isolated from either.

When the iodolactonization was applied to the acid fraction XIb, only a small quantity of iodolactone XII was obtained. The acidic fraction contained iodine and probably consisted of a mixture of the *exo*-acid and its iodohydrin, but no separation into pure components was possible.

(b) **Reduction of the Iodolactone XII.**—A suspension of 6 g. of XII and 40 g. of zinc dust in 200 ml. of ethanol was refluxed with stirring for 5 hours. The solid was filtered off and the filtrate was evaporated under reduced pressure. The solid residue (4.0 g.) was taken up in dilute aqueous potassium hydroxide and reprecipitated with hydrochloric acid. The precipitate (3.5 g., m.p. 105–115°) gave 5-*exo*-methylbicyclo[2,2,2]oct-2-ene-5-*endo*carboxylic acid (XIa, m.p. 118–119°) when recrystallized once from pentane; infrared absorption maxima: 10.45(m), 10.60(m), 11.15(w), 11.34(m), 11.75(w), 12.17(w), 12.35(m), 13.32(w), 14.28(s) and 15.30(m) μ.

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.39; H, 8.52.

2-Methylbicyclo[2,2,2]octane-2-carboxylic Acid.—An ethanolic solution of the isomeric acids XI obtained by the Diels–Alder condensation of 1,3-cyclohexadiene with methacrylic acid was hydrogenated at 45 lb. pressure in the presence of palladium catalyst. After removal of the catalyst and solvent, there was obtained a quantitative yield of the reduced acid, m.p. 122–123° when recrystallized from pentane.

Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.31; H, 9.69.

2-Methylbicyclo[2,2,2]octane-2-carboxamide was prepared from the acid *via* the acid chloride, m.p. 125–126° after one crystallization from hexane.

Anal. Calcd. for $C_{10}H_{17}NO$: C, 71.81; H, 10.25; N, 8.38. Found: C, 71.87; H, 10.38; N, 8.40.

5-*exo*Methylbicyclo[2,2,2]oct-2-ene-5-*endo*carboxamide (XIIIa).—The acid (XIa, 1.5 g.) was converted to the carboxamide *via* the acid chloride. The product was recrystallized from water and from hexane to give 0.6 g., m.p. 113–114°; infrared absorption maxima: 11.35(s), 12.03(s), 12.38(s), 12.61(s), 13.80(s) and 14.42(s) μ.

Anal. Calcd. for $C_{10}H_{15}NO$: C, 72.64; H, 9.15; N, 8.48. Found: C, 72.98; H, 9.30; N, 8.55.

5-*endo*Methylbicyclo[2,2,2]oct-2-ene-5-*exo*carboxamide (XIIIb).—The acid (XIb, 5 g.) was converted to the carboxamide *via* the acid chloride. The product was recrystallized several times from hexane to give 1.1 g., m.p. 125–126°; infrared absorption maxima: 11.31(m), 11.50(m), 11.90(m), 11.96(m), 12.15(m), 12.35(m), 12.59(m), 13.82(s), 14.30(s) and 15.28(m) μ.

Anal. Found: C, 72.74; H, 9.00; N, 8.55.

Methylation of 5-*endo*Cyanobicyclo[2,2,2]oct-2-ene (VIII).—Following the procedure described for the preparation of III, 86 g. of VIII gave 56 g. (61%) of 5-cyano-5-methylbicyclo[2,2,2]oct-2-ene, b.p. 129–130° (15 mm.), which solidified on cooling. A sample recrystallized from pentane and sublimed *in vacuo* melted at 74–76°.

Anal. Calcd. for $C_{10}H_{13}N$: C, 81.58; H, 8.90; N, 9.52. Found: C, 81.90; H, 8.81; N, 9.65.

The amidine fraction upon saponification gave 3.5 g. of a carboxamide (m.p. 107–108°) which was extracted with boiling hexane. The hexane-insoluble residue consisted of IXa, m.p. 162–163°. The cooled hexane extracts deposited 1.3 g. of **N-methylbicyclo[2,2,2]oct-2-ene-5-*endo*-carboxamide** which was recrystallized several times from hexane and sublimed *in vacuo*, m.p. 103–105°.

Anal. Calcd. for $C_{10}H_{15}NO$: C, 72.69; H, 9.15; N, 8.48. Found: C, 72.64; H, 9.28; N, 8.65.

When the N-methylcarboxamide above was saponified with aqueous potassium hydroxide, compound VIa, m.p. 56–57°, was obtained as the sole product.

Saponification of X: 5-Methylbicyclo[2,2,2]oct-2-ene-5-carboxamide (XIII).—When 15 g. of X was saponified by the procedure employed for III, there was obtained 12 g. of the carboxamide, m.p. 121–122° after several recrystallizations from hexane. In spite of the sharp melting point and a satisfactory elementary analysis, this material was shown subsequently (*vide infra*) to consist of a mixture of the stereoisomeric carboxamides.

Ureidomethyl Derivatives. General Procedure.—One to 2 g. of the bicyclic carboxamide or nitrile in absolute ether solution was added to a suspension of a 50% molar excess of lithium aluminum hydride[32] in absolute ether and the mixture was refluxed for 2–8 hours. Carboxamides which were only slightly soluble in ether, *i.e.*, II and its stereoisomer, were reduced by the Soxhlet technique. The reaction mixture was then cooled in ice and the complex was decomposed with a minimum volume of water and the same volume of 50% aqueous sodium hydroxide solution. The inorganic salts generally separated as a pasty solid from which the almost anhydrous solution of the amine could be decanted readily. The amine was precipitated with gaseous hydrogen chloride from the ether solution. The amine hydrochloride then was dissolved in aqueous alcohol containing an equimolar amount of sodium hydroxide and nitrourea.[33] The solution was warmed at 70–75° for 1–2 hours and allowed to cool. The ureidomethyl derivative which separated upon cooling or concentrating the solution was recrystallized from water or from aqueous ethanol.

When Ia was reduced with lithium aluminum hydride and the product was treated with nitrourea, **5-*endo*ureidomethyl-2-norbornene** (m.p. 120–121°) was obtained after several recrystallizations from water. This compound also was obtained directly in a high state of purity from 2-norbornene-5-*endo*carboxamide; infrared absorption maxima: 10.77(w), 11.05(w), 11.96(w), 12.11(w), 12.85(w), 13.88(m) and 14.16(m) μ.

Anal. Calcd. for $C_9H_{14}N_2O$: C, 65.03; H, 8.49; N, 16.85. Found: C, 65.12; H, 8.32; N, 16.66.

5-*exo*Ureidomethyl-2-norbornene (m.p. 129–130°) was obtained as the sole product of the reaction from either Ib or II; infrared absorption maxima: 11.00(w), 11.11(w), 11.60(w), 12.09(w), 12.70(w), 12.85(w), 13.22(w), 14.13(m) and 14.28(s) μ.

Anal. Found: C, 65.00; H, 8.54; N, 17.05.

5-*exo*Methyl-5-*endo*ureidomethyl-2-norbornene, m.p. 163–164°, was obtained as the sole reaction product from IV; infrared absorption maxima: 11.17(m), 11.46(m), 11.93(m), 12.20(m), 12.90(m), 13.52(s), 13.87(s), 14.15(m) and 15.07(m) μ.

Anal. Calcd. for $C_{10}H_{16}N_2O$: C, 66.63; H, 8.95; N, 15.54. Found: C, 66.90; H, 9.06; N, 15.55.

5-*endo*Methyl-5-*exo*ureidomethyl-2-norbornene, m.p. 134–135°, was obtained from 5-*endo*methyl-2-norbornene-5-*exo*carboxamide as the sole product of the reaction; infrared absorption maxima: 11.11(s) 11.45(m), 11.87(m), 11.97 (m), 12.19(s), 12.91(s), 13.73(s), 14.00(s) and 14.21(s) μ.

Anal. Found: C, 66.72; H, 8.92; N, 15.45.

Ureidomethyl Derivatives of XIIIa and XIIIb.—To a solution of 4 g. of lithium aluminum hydride in 200 ml. of absolute ether was added with stirring a solution of 11 g. of XIII, the saponification product of 5-cyano-5-methylbicyclo[2,2,2]oct-2-ene (X), in 500 ml. of absolute ether. The mixture was refluxed for 6 hours and the complex was decomposed. Distillation of the extracts gave 8.1 g. of an amine, b.p. 98–100° (20 mm.). The amine was suspended in 250 ml. of 20% ethanol and treated with 12 g. of nitrourea. Upon standing overnight, the solution deposited 12.3 g. of 5-exomethyl-5-endoureidomethylbicyclo[2,2,2]-oct-2-ene (XVa) which melted at 188–189° when recrystallized several times from ethyl acetate; infrared absorption maxima: 10.96(m), 11.14(w), 12.33(w), 12.94(w), 13.72(m), 14.30(s) and 14.95(m) μ.

Anal. Calcd. for $C_{11}H_{18}N_2O$: C, 68.00; H, 9.34; N, 14.42. Found: C, 68.23; H, 9.33; N, 14.60.

The aqueous alcoholic filtrates above were evaporated to dryness under reduced pressure. The residue of 4.3 g. of **5-*endo*methyl-5-*exo*ureidomethylbicyclo[2,2,2]oct-2-ene (XVb)** melted at 146–147° after several recrystallizations from ether; infrared maxima: 10.86(m), 11.12(m), 11.35-(m), 11.90(m), 12.30(m), 12.96(s), 13.79(s), 14.45(s) and 15.10(s) μ.

Anal. Found: C, 68.11; H, 9.46; N, 14.21.

Hydrogenation of either XVa or XVb in ethanol solution at 45 lb. pressure in the presence of palladium catalyst gave fine plates of **2-methyl-2-ureidomethylbicyclo[2,2,2]octane,** m.p. 159–160°.

Anal. Calcd. for $C_{11}H_{20}N_2O$: C, 67.30; H, 10.27; N, 14.27. Found: C, 67.29; H, 10.24; N, 14.50.

Conversion of XIIIb to the ureidomethyl derivative gave XVb (m.p. 145–146°) as the main product together with some higher melting material which could not be purified. When pure XIIIa was employed as the starting material in the above reaction sequence, XVa (m.p. 188–189°) was obtained as the sole product of the reaction.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF DELAWARE]

Thermal Degradation of Carbamates of Methylenebis-(4-phenyl Isocyanate)[1]

BY ELIZABETH DYER AND G. EARL NEWBORN, JR.[2]

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The products of pyrolysis at 300° of the biscarbamates prepared from methylenebis-(4-phenyl isocyanate) and 1-butanol 2,2-dimethyl-1-propanol and benzyl alcohol, and of the polycarbamate from methylenebis-(4-phenyl isocyanate) and 1,6-hexanediol have been determined quantitatively. In all cases carbon dioxide and the parent alcohol or diol were formed. The benzyl biscarbamate and the polycarbamate yielded amine residues, which contained 4,4'-diaminodiphenylmethane. Polymeric carbodiimides were isolated from degradation of the *n*-butyl and neopentyl biscarbamates and were shown to be possible intermediates in pyrolysis of the benzyl biscarbamate and the polycarbamate.

The literature contains little work on the purely thermal degradation of biscarbamates or of polycarbamates. Monomeric carbamates of the type RNHCOOR' are known to be degraded above 200° to the isocyanate and the alcohol,[3] and there are scattered references to the formation of other products, such as carbon dioxide,[4,5] ureas[4,5] and olefins.[4] Studies of thermal degradation of carbamates in the presence of amines and organic acids have been conducted recently by Mukaiyama and

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[1] From the Ph.D. dissertation of G. Earl Newborn, Jr., University of Delaware, 1958.

[2] Armstrong Cork Co., Research Fellow, 1955–1957.

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