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Journal

Journal of the American Chemical Society, 85(8)

ISSN

0002-7863

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Publication Date

1963-04-01

DOI

10.1021/ja00891a027

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[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE UNIVERSITY, EAST LANSING, MICH.]

Two Unusual Reactions Encountered during the Devious Hydrolysis of 3,3-Dimethyl-1,1,2,2-tetracyanocyclopropane to the Corresponding Tetracarboxylic Acid[1]

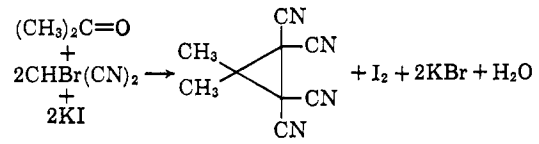
BY HAROLD HART AND FILLMORE FREEMAN

RECEIVED OCTOBER 31, 1962

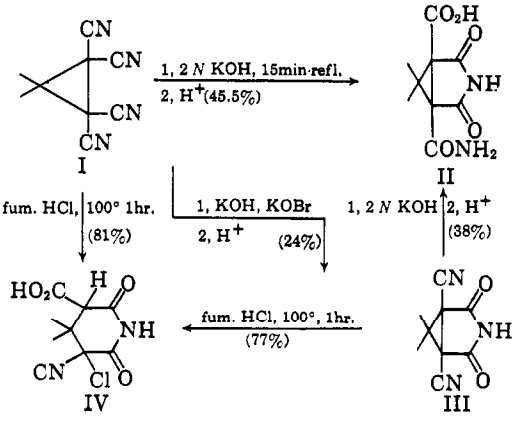
The structure of the first isolable alkaline hydrolysis product of 3,3-dimethyl-1,1,2,2-tetracyanocyclopropane (I) is confirmed as the acid-amide-imide II. Thermal decarboxylation of II proceeds with cleavage of the cyclopropane ring, and probably involves participation by the neighboring *cis*-carboxamido group; mechanisms which would allow decarboxylation without ring opening would require highly strained transition states. Two additional examples of decarboxylation of a cyclopropanecarboxylic acid with ring cleavage are presented. Compound II was converted in four steps and high yield by alternate methylation with diazomethane and hydrolysis with base to the corresponding cyclopropanetetracarboxylic acid (XIII). One of the hydrolytic steps (X → XI) involves a remarkable transformation in which a five-membered imide ring between *cis* substituents is hydrolyzed on one side of the cyclopropane ring plane and formed on the opposite side.

Introduction

The discovery[2] that a crystalline product deposits rapidly when aqueous potassium iodide is added at room temperature to a solution of bromomalononitrile in acetone led to a rather general synthesis of tetracyanocyclopropanes[3] which we propose be called the Wideqvist reaction.[4] By using tetrahydrofuran as solvent, the reaction has been used to prepare tetracyanocyclopropane itself from formaldehyde[5]; and in another modification, alkylidene bismalononitriles were converted with bromine to monoalkyltetracyanocyclopropanes.[6,7]

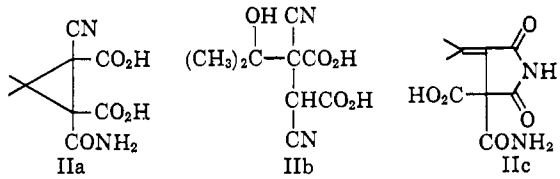


The assignment of the correct structure to I depended upon the isolation of certain of its hydrolysis products and their characterization by independent synthesis.[8] These reactions are summarized in Scheme 1, using structures assigned by Ramberg and Wideqvist. Alkaline hydrolysis of I reportedly liberated one-half of the theoretical nitrogen as ammonia very rapidly; acidification gave a crystalline solid, m.p. 196–197° with CO_2 evolution, to which the acid-amide-imide structure II[9] was assigned. The same product (m.p. and comparison of the crystals in a polarizing microscope) was obtained from the previously known[10,11] III. The alternate structure IIa was discarded primarily on the basis of titration data (>1 but <2 equivalents of base required for neutralization to phenolphthalein) and synthesis from III. Earlier, Birch, Gough and Kon[11] had isolated a presumably identical compound from III but assigned it structure IIb; this was also discarded[8] on reasonable grounds (among others, its failure to lactonize). Hydrolysis of I or III with fuming hydrochloric acid gave a single product, assigned structure IV. Finally, not shown in Scheme 1, Ramberg and Wideqvist hydrolyzed I with concentrated ammonia which contained potassium hydroxide, and obtained on acidification (CO_2 evolved) a dibasic acid, m.p. 165°, originally thought[8] to be impure *cis*-caronic acid, but in fact probably γ,γ-dimethylitaconic acid.[12]



SCHEME I

In view of the simplicity and generality of the Wideqvist reaction as a synthesis of cyclopropanes, and considering also the current interest in polycyano compounds,[13] it seemed worthwhile to re-examine the alkaline hydrolysis[14] of I, not only to establish with modern methods the structure of the first product II, but also to complete the hydrolytic degradation of I. This paper describes a sequence by which I may be converted to the tetraacid in five steps, and discloses two novel reactions discovered along the way.



Results and Discussion

The Structure of II.—The yield of II from I was improved to over 80% by adding methanol to the aqueous potassium hydroxide. Potentiometric titration established that II was dibasic in accord with the assigned structure (pK_A^I 2.45 and pK_A^{II} 8.35). Absence of bands in the 4.4 μ region mitigated against structures

(1) Paper XII in a series on Cyclopropane Chemistry. For the previous paper, see H. Hart and R. A. Cipriani, *J. Am. Chem. Soc.*, **84**, 3697 (1962).

(2) L. Ramberg and S. Wideqvist, *Arkiv. Kemi, Mineral. Geol.*, **12A**, No. 22, 12 (1937).

(3) S. Wideqvist, *ibid.*, **20B**, No. 4, 8 (1945).

(4) The equation is written with iodine as a product, but the initial inorganic product may well be iodine bromide.

(5) R. M. Scribner, G. N. Sausen and W. W. Prichard, *J. Org. Chem.*, **25**, 1440 (1960).

(6) R. P. Mariella and A. J. Roth, III, *ibid.*, **22**, 1130 (1957).

(7) Our own investigations into the scope of the Wideqvist reaction will be described in a separate paper.

(8) L. Ramberg and S. Wideqvist, *Arkiv. Kemi, Mineral. Geol.*, **14B**, No. 37, 13 (1941).

(9) 2,4-Dioxo-5-carboxamido-6,6-dimethyl-3-azabicyclo[3.1.0]hexane-1-carboxylic acid; because the systematic names of most compounds described in this paper are of this length, compounds will be referred to only by number in the text. Systematic names are given in the Experimental part.

(10) I. Guareschi and E. Grande, *Atti R. Accad. Torino*, **34**, 18/6 (June); *Chem. Zentr.*, **70**, *II*, 439 (1899).

(11) S. F. Birch, W. H. Gough and G. A. R. Kon, *J. Chem. Soc.*, **119**, 1315 (1921).

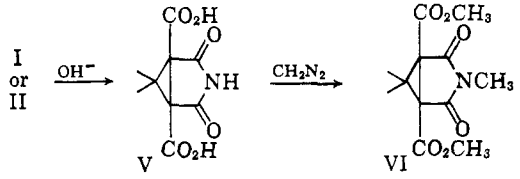
(12) See ref. 6, footnote 9.

(13) See particularly the series of ten papers from the du Pont group, *J. Am. Chem. Soc.*, **80**, 2775–2844 (1958), and subsequent papers.

(14) The acidic hydrolysis to IV has not yet been reinvestigated.

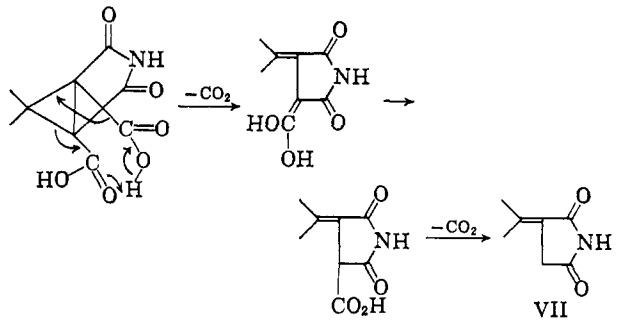
containing the cyano group.[15] The n.m.r. spectrum in D_2O containing NaOD showed two singlets at 8.74 and 8.76 τ with equal areas (C-CH_3). In dimethyl sulfoxide, the n.m.r. showed singlets at −1.14 and 2.39 τ, relative areas 1:2, ascribed to the imide and amide hydrogens, respectively (succinimide and phthalimide, in the same solvent, show imide singlets at −1.00 and −1.13 τ, respectively). These data are consistent only with the formulation of this product as II, the mechanistically unlikely alternative IIc being eliminated by the position of the methyl resonances in the n.m.r.

The amide group of II resisted reaction with nitrous acid or nitrosyl chloride. But prolonged alkaline hydrolysis led to the diacid V in over 80% yield; V was also obtained directly from I (in nearly quantitative



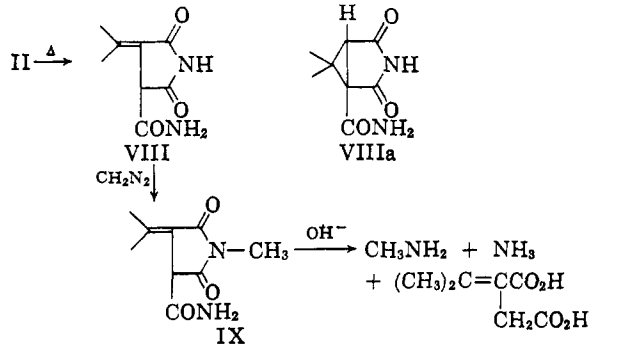
yield, if one allows for the small amount of II also isolated). Diazomethane converted V to the trimethyl derivative VI.[16]

When V was heated above its melting point, carbon dioxide was evolved.[17] Analysis of the crystalline product (obtained in 42% yield) showed that two moles of carbon dioxide had been lost, but its melting point (166–167°) was different from that (120°) reported[18] for caronimide. Furthermore, the infrared showed a carbon–carbon double bond (6.0 μ) which was confirmed by a positive Baeyer test. The product is therefore undoubtedly isopropylidenesuccinimide (VII)[19]; indeed, mechanistic considerations suggest that this is the only plausible decarboxylation product, cleavage of the three-membered ring occurring with loss of the first mole of carbon dioxide. The imide carbonyl is prevented from participating in the decarboxylation because the resulting enolic intermediate would contain a [3.1.0] system with a double bond exocyclic to the three-membered ring. The normal reaction of a *cis*-1,2-cyclopropanedicarboxylic acid, *i.e.*, anhydride formation, is also mitigated against because of strain in the product,[17] but the carbonyl of the *cis*-carboxyl is in a favorable position to assist the decarboxylation. In



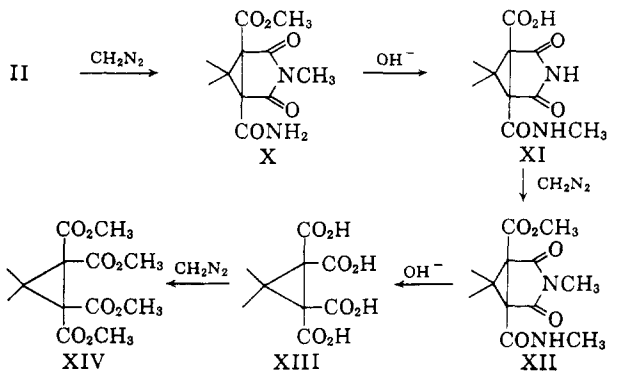
short, forces conspire against all normal paths and favor the one observed.

Two further examples (one presented now and one reserved for a later section of this paper) show that this novel decarboxylation is general and that ring opening occurs with the loss of the first mole of carbon dioxide. When II was heated for a short time just above its melting point, one mole of carbon dioxide was lost and a crystalline product, m.p. 240–241°, was isolated in 87% yield. Its n.m.r. spectrum in 10% sodium hydroxide showed the two allylic methyl groups (singlets at 7.72 and 8.14 τ with equal areas) expected for VIII but at lower field than is permissible for VIIIa (*cf.* II, *vide supra*). The n.m.r. of VIII in dimethyl sulfoxide had



three equal singlets at −1.03 (imide), 2.27 and 2.80 τ; the latter two are amide hydrogens, one of which is apparently hydrogen-bound to the imide carbonyl. The single C–H on the ring carbon holding the carboxamido group is not visible in either solvent. The carbon–carbon double bond in VIII is also evident from its infrared spectrum (6.05 μ) and positive Baeyer test. Treatment of VIII with diazomethane gave IX which, on hydrolysis, gave two moles of nitrogen bases and isopropylidenesuccinic acid.

Conversion of II to Methyl 3,3-Dimethyl-1,1,2,2-tetracarboxylate (XIV).—Compound I was successfully converted, *via* II, to the tetracarboxylic acid XIII by the unusual route shown in Scheme 2. Alkaline hydrolysis of II or V proceeded only very slowly, presumably be-

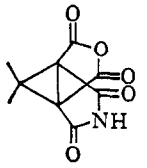


SCHEME 2

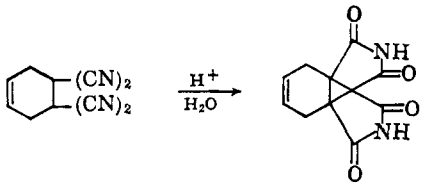
(15) L. J. Bellamy, "Infrared Spectra of Complex Molecules," J. Wiley and Sons, Inc., New York, N. Y., 1958, p. 264.

(16) Imides have previously been converted to N-methyl derivatives with diazomethane; see G. Labruto, *Gazz. chim. ital.*, **63**, 2669 (1933).

(17) Formation of the anhydride apparently would result in excessive strain



Fused five-membered rings of this type are known, if the remaining bridging ring is larger, as in the formation of the diimide



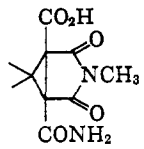
See W. J. Middleton, R. E. Heckert, E. L. Little and C. G. Krespan, *J. Am. Chem. Soc.*, **80**, 2783 (1958).

(18) K. N. Menon and J. L. Simonsen, *J. Chem. Soc.*, 302 (1929).

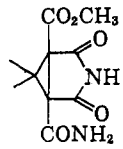
(19) Curiously, this simple compound appears not to have been previously reported.

cause the di- or tri-anions are only sluggishly attacked by base.

Compound II was therefore methylated with two moles of diazomethane to give a nearly quantitative yield of X which, on hydrolysis, gave in 90% yield a product corresponding to loss of one of the two methyl groups. The two obvious structures XIa and XIb are immediately eliminated because the compound was dibasic; the values of the pK_A's (I, 2.65; II, 8.38) suggested a carboxyl and an imide (*cf.* II, *vide supra*), leaving XI as the only reasonable structure. The n.m.r. spectrum in D_2O containing NaOD showed two peaks, at 7.36 and 8.84 τ, with relative areas 1:2, assigned to the N–CH_3 and $C(CH_3)_2$, respectively.

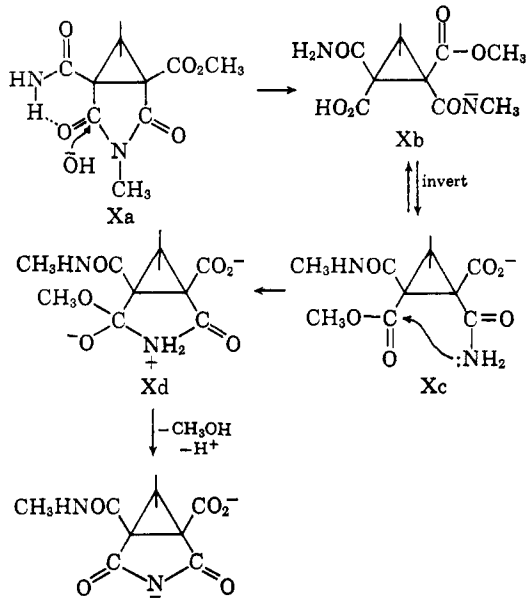


XIa



XIb

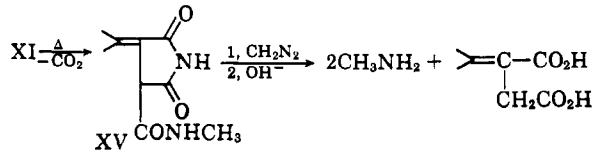
When one considers the multiplicity of hydrolytic reactions which might occur when X is treated with strong base, the formation of XI in excellent yield as the only isolable product is truly remarkable. It clearly arises from opening of the imide ring to produce a carboxyl group and an N-methylamide, followed by reaction of the amide and ester functions intramolecularly on the opposite side of the three-membered ring. Although the mechanistic details are not known, it is possible to rationalize the sole production of XI as



Hydrogen bonding between the amide nitrogen and the imide carbonyl, as shown in Xa, would make that carbonyl the most likely site of attack by base. That such hydrogen bonding can be important has already been shown from the n.m.r. of VIII. Hydrogen bonding between the *cis*-amide and ester functions is less likely than that shown in Xa because it requires a seven- rather than six-membered ring. Similarly, the amide and ester are not free to react intramolecularly for reasons cited above.[17] Because of solubility difficulties, it was not possible to obtain a satisfactory n.m.r. spectrum of X, but in a later paper we will present n.m.r. evidence for hydrogen bonding of the type postulated, in an analog of X. Following the opening of the imide ring (Xb) and equilibration to the carboxylate ion Xc, the amide function is freed from both constraints and reacts intramolecularly *via* an intermediate of the type Xd to furnish the dianion of XI which, because of the accumulated negative charge, is not susceptible to ready further hydrolysis.

As noted in the Experimental part, XI may also be prepared by the alkaline hydrolysis of N-methyl III; this implies that in the conversion of III to II shown in Scheme 1, the imide function of II need not necessarily arise from the imide function of III.

Decarboxylation of XI again led to opening of the three-membered ring, it being converted just above its melting point smoothly to XV.



Reaction of XV with diazomethane followed by hydrolysis allowed the isolation of methylamine (as its hydrochloride) in over 95% yield, thus adding confirmatory evidence to the structure assigned to XI. Isopropylidenesuccinic acid was also isolated from the hydrolysis.

Attempts to hydrolyze XI with alkali failed. With diazomethane, it was converted to XII, which was rapidly hydrolyzed to the tetracarboxylic acid XIII. Because of difficulties with purification, XIII was converted to its tetramethyl ester XIV for analysis. The n.m.r. spectrum of XIV is decisive regarding its structure, consisting of two sharp singlets at 6.42 (O–CH_3) and 8.56 τ (C–CH_3), relative areas 2:1.

The sequence of reactions just described allows the conversion of I to XIV in over-all 43% yield, despite the number of steps. The scheme is general for tetracyanocyclopropanes derived from ketones, as will be described in a separate paper.[20]

Experimental[21]

2,4-Dioxo-5-carboxamido-6,6-dimethyl-3-azabicyclo[3.1.0]-hexane-1-carboxylic Acid (II).—A solution of 2.8 g. (0.016 mole) of 3,3-dimethyl-1,1,2,2-tetracyanocyclopropane (I),[2] m.p. 208–209°, in 30 ml. of 25% aqueous potassium hydroxide and 40 ml. of methanol was refluxed for 3 hours, the alcohol removed (Rinco rotary evaporator) and the remaining liquid extracted continuously with ether for 4 hours to remove non-acidic materials. The aqueous solution was then acidified (congo red) with dilute hydrochloric acid and extracted continuously with ether for 24 hours. Removal of the solid from the extract by filtration, and recrystallization from water gave 2.81 g. (80.1%) of white crystals of II, m.p. (dec.) 196–197° (lit. value[8] 196–197°). In order to be certain of its identity with the product described by Ramberg and Wideqvist,[8] a sample was analyzed.

Anal. Calcd. for $C_9H_{10}N_2O_6$: C, 47.79; H, 4.46; N, 12.39. Found: C, 47.68; H, 4.49; N, 12.33.

Aqueous potentiometric titration gave a neutralization equivalent of 112.3 (theory 113.1) with pK_A^I 2.45 and pK_A^{II} 8.35. The infrared spectrum in Nujol had characteristic bands at 2.85, 2.95 (N—H), 5.50, 5.70, 5.85 μ (C=O) and no absorption from 4.40–4.45 (C≡N); the n.m.r. in D_2O (containing NaOD) had singlets at 8.74 and 8.76 τ with equal areas and in dimethyl sulfoxide there were singlets at −1.14 and 2.39 τ, relative areas 1:2. Compound II was recovered in >90% yield from reactions with sodium nitrite and hydrochloric acid (0°, 1 hour) and with isoamyl nitrite, ethanol and sulfuric acid (0°, 12 hours).

2,4-Dioxo-3,3-dimethyl-3-azabicyclo[3.1.0]hexane-1,5-dicarboxylic Acid (V). From II.—A solution of 1.13 g. (5 mmoles) of II in 30 ml. of 10% sodium hydroxide was refluxed for 3.25 hours. During reflux, the evolved ammonia was swept by a stream of nitrogen into standard hydrochloric acid, which, at the end of this period, indicated that nearly one mole of ammonia had been produced. The alkaline solution was acidified with

(20) H. Hart and F. Freeman, unpublished results.

(21) Melting points are uncorrected. Analyses are by Spang Microanalytical Laboratories, P. O. Box 1111, Ann Arbor, Mich. Nuclear magnetic resonance spectra were obtained on a Varian model A-60 or HR-60 instrument at 60 Mc. Band positions are in τ-units (G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958)), and relative areas were obtained by electronic integration.

dilute hydrochloric acid and extracted continuously with ether for 36 hours. The ether extract was dried (sodium sulfate), evaporated, ethyl acetate added and, after treatment with Norit, the product was isolated and recrystallized from ethyl acetate–pentane, yielding 0.92 g. (80.7%) of V, m.p. 168–169° dec. Potentiometric titration gave pK_A^I 2.4, pK_A^{II} 5.15, pK_A^{III} 9.75. The n.m.r. spectrum in D_2O containing NaOD had singlets with equal areas at 8.62 and 8.68 τ.

Anal. Calcd. for $C_9H_9NO_6$: C, 47.58; H, 3.99; N, 6.16; neut. equiv., 75.7. Found: C, 47.36; H, 4.22; N, 6.05; neut. equiv., 75.1.

From I.—A solution of 1.70 g. (0.01 mole) of I in 40 ml. of 2 *N* potassium hydroxide was refluxed for 9 hours, acidified (congo red) with hydrochloric acid and extracted continuously with ether for 36 hours. Filtration of the ether layer gave 0.39 g. (17.2%) of II, m.p. 196–197° dec. after recrystallization from water. The ether solution was then dried over anhydrous sodium sulfate, treated with Norit, and the solvent evaporated (Rinco). Recrystallization of the crude residue from ethyl acetate–pentane gave 1.88 g. (82.8%) of white crystals of V, m.p. and m.m.p. 167–168° dec.

Methyl 2,4-Dioxo-3,6,6-trimethyl-3-azabicyclo[3.1.0]hexane-1,5-dicarboxylate (VI).—To a solution of 2.27 g. (0.01 mole) of V in 50 ml. of absolute methanol cooled in an ice-bath was added an ethereal solution of diazomethane in small portions until gas evolution ceased and the solution acquired a pale yellow color. Solvent and excess reagent were evaporated, and the residue recrystallized from methanol, giving 2.49 g. (91.1%) of VI, m.p. 106–107°. Its infrared spectrum (CCl_4) showed carbonyl bands at 5.60, 5.75 and 5.85 μ and no N–H stretching band near 3 μ.

Anal. Calcd. for $C_{12}H_{16}NO_6$: C, 53.52; H, 5.62; N, 5.20. Found: C, 53.47; H, 5.70; N, 5.16.

Decarboxylation of V.—A flask containing 2.27 g. (0.01 mole) of V was swept with a dry nitrogen stream, and immersed in an oil-bath at 168°, whereupon V melted and evolved carbon dioxide. After 1 minute the flask was removed from the oil-bath and cooled to room temperature. The yellow residue was dissolved in methanol, treated with Norit, the solvent evaporated and the residue recrystallized from water, giving 0.59 g. (42.2%) of isopropylidenesuccinimide (VII), m.p. 167–168°. The compound gave a positive Baeyer test for unsaturation and showed bands at 2.95 (N—H), 5.65 and 5.85 (C=O) and 6.0 μ (C=C) in chloroform solution.

Anal. Calcd. for $C_7H_9NO_2$: C, 60.42; H, 6.52; N, 10.07. Found: C, 60.40; H, 6.60; N, 10.00.

Decarboxylation of II.—The procedure was the same as that just described for decarboxylation of V, except that the oil-bath temperature was 197°. From 2.26 g. (0.01 mole) of II there was obtained 1.58 g. (87.1%) of 3-isopropylidene-4-carboxamidosuccinimide (VIII), white needles from water, m.p. 240–241° dec. Its infrared spectrum had bands at 2.95 and 3.15 μ (N—H), 5.70, 5.85, 5.96 μ (C=O) and 6.05 μ (C=C). The n.m.r. spectrum in dimethyl sulfoxide had singlets with equal areas at −1.03, 2.27 and 2.80 τ; in 10% sodium hydroxide, the n.m.r. spectrum showed singlets with equal areas at 7.72 and 8.14 τ.

Anal. Calcd. for $C_8H_{10}N_2O_3$: C, 52.74; H, 5.53; N, 15.37. Found: C, 53.06; H, 5.56; N, 15.27.

Preparation and Hydrolysis of 4-Carboxamido-3-isopropylidene-1-methylsuccinimide (IX).—Methylation of VIII with diazomethane (as in the preparation of VI) gave IX in 86.4% yield, m.p. 229–230° from methanol.

Anal. Calcd. for $C_9H_{12}N_2O_3$: C, 55.09; H, 6.17; N, 14.28. Found: C, 55.29; H, 6.26; N, 14.19.

A mixture of 0.70 g. (3.5 mmoles) of IX and 30 ml. of 10% sodium hydroxide was refluxed for 5 hours during which time volatile products were swept by nitrogen into standard hydrochloric acid. Titration after this time showed nearly two moles of volatile base had evolved. The alkaline solution was cooled, acidified with dilute hydrochloric acid and cooled overnight in the refrigerator. The solid was filtered and recrystallized from water, giving 0.21 g. (38.2%) of isopropylidenesuccinic acid, m.p. 164–165° (lit. value[22] 161.5–162°), neut. equiv. 79.15 (theory 79.07).

Methyl 2,4-Dioxo-5-carboxamido-3,6,6-trimethyl-3-azabicyclo-[3.1.0]hexane-1-carboxylate (X).—The procedure was identical with that described above for the preparation of VI. From 2.26 g. (0.01 mole) of II there was obtained 2.4 g. (98%) of X, recrystallized from methanol, m.p. 195–195.5°. It had characteristic infrared bands in chloroform at 2.87 and 2.95 μ (N—H) and 5.63, 5.70, 5.85 (C=O).

Anal. Calcd. for $C_{11}H_{14}N_2O_5$: C, 51.96; H, 5.55; N, 11.02. Found: C, 51.93; H, 5.58; N, 11.16.

(22) C. G. Overberger and C. W. Roberts, *J. Am. Chem. Soc.*, **71**, 3618 (1949).

2,4-Dioxo-5-(N-methyl)-carboxamido-6,6-dimethyl-3-azabicyclo[3.1.0]hexane-1-carboxylic Acid (XI). From X.—A solution containing 2.54 g. (0.01 mole) of X, 35 ml. of methanol and 25 ml. of 10% sodium hydroxide was refluxed for 30 minutes then cooled, the methanol removed (Rinco evaporator), the residue made strongly acidic with dilute hydrochloric acid and placed in the refrigerator overnight. Filtration of the white crystals gave 2.15 g. (90%) of XI, m.p. 204–205° dec. Compound XI had, by potentiometric titration in water, pK_A^I 2.65 and pK_A^{II} 8.38. Its n.m.r. spectrum in D_2O containing NaOD had singlets at 7.36 and 8.84 τ, relative areas 1:2.

Anal. Calcd. for $C_{10}H_{12}N_2O_6$: C, 49.99; H, 5.04; N, 11.66; neut. equiv., 120.11. Found: C, 49.98; H, 5.04; N, 11.66; neut. equiv., 118.03.

From III.—3,3-Dimethyl-1,2-dicyanocyclopropane-1,2-carboximide (III)[11] (m.p. 242° dec., equal singlets at 8.50 and 8.57 τ in acetonitrile) was methylated with diazomethane by the usual procedure. From 1.9 g. (0.01 mole) of III there was obtained 2.0 g. (98.8%) of 3,3-dimethyl-1,2-dicyanocyclopropane-1,2-N-methylcarboximide, white needles from methanol, m.p. 235–236° dec. Its n.m.r. had three equal singlets at 7.16 (N–CH_3), 8.43 and 8.70 τ (C–methyl's).

Anal. Calcd. for $C_{10}H_9N_3O_2$: C, 59.10; H, 4.46; N, 20.68. Found: C, 59.23; H, 4.54; N, 20.61.

A solution of 2.03 g. (0.01 mole) of this N-methylimide in 15 ml. of 10% sodium hydroxide, after 30 minutes reflux followed by acidification with hydrochloric acid and cooling in the refrigerator overnight, gave 1.99 g. (83.1%) of XI, m.p. 204–205° dec., identical with material obtained from X. In an attempt to hydrolyze XI further, 2.0 g. (8.3 mmoles) was refluxed for 3 hours with 30 ml. of 10% sodium hydroxide, cooled, acidified to congo red with hydrochloric acid and extracted continuously with ether for 24 hours. The extracted mixture was filtered to give 1.53 g. (76.5%) of tan crystals which, on recrystallization from methanol, gave recovered XI, m.p. and m.m.p. 205–206° dec. No crystalline product could be isolated from the ether extract.

Decarboxylation of XI.—The procedure was analogous to that described above for V. 4-(N-Methyl)-carboxamido-3-isopropylidenesuccinimide (XV), m.p. 131–132° from water, was obtained from XI in 89% yield.

Anal. Calcd. for $C_9H_{12}N_2O_3$: C, 55.09; H, 6.17; N, 14.28. Found: C, 55.18; H, 6.25; N, 14.31.

Compound XV gave a positive Baeyer test and, when treated as above with diazomethane, gave 4-(N-methyl)-carboxamido-3-isopropylidene-1-methylsuccinimide, m.p. 69–70° from methanol, in 85.7% yield.

Anal. Calcd. for $C_{10}H_{14}N_2O_3$: C, 57.12; H, 6.71; N, 13.33. Found: C, 57.19; H, 6.87; N, 13.09.

Quantitative hydrolysis of the latter demonstrated that both nitrogens had methyl groups attached to them. A sample (0.26 g., 1.25 mmoles) in 15 ml. of 10% sodium hydroxide was refluxed for 6 hours, evolved gases being swept by a nitrogen stream into hydrochloric acid. The latter was then evaporated to dryness and the white residue dissolved in 10 ml. of refluxing absolute ethanol. On cooling, there was obtained 0.162 g. (95.4%) of methylamine hydrochloride, m.p. and m.m.p. 226–227°. Continuous extraction of the acidified reaction mixture with ether for 24 hours allowed recovery of 0.066 g. (33.6%) of isopropylidenesuccinic acid, m.p. 164–165° from water (lit. value[17] 161.5–162°).

Methyl 2,4-dioxo-5-(N-methyl)-carboxamido-3,6,6-trimethyl-3-azabicyclo[3.1.0]hexane-1-carboxylate (XII) was prepared from XI and diazomethane in the usual way. From 1.20 g. (5 mmoles) of XI there was obtained 1.25 g. (93.3%) of XII, m.p. 154–155°, from methanol. Compound XII had an N–H band at 2.95 μ and carbonyl bands at 5.70, 5.88 and 5.95 μ. Its n.m.r. spectrum in chloroform showed singlets at 6.22, 7.05, 8.42 and 8.75 τ and a doublet at 7.13 τ, all with equal areas.

Anal. Calcd. for $C_{12}H_{16}N_2O_6$: C, 53.72; H, 6.01; N, 10.44. Found: C, 53.82; H, 6.15; N, 10.31.

3,3-Dimethyl-1,1,2,2-tetracarboxylic Acid (XIII).—A solution of 1.34 g. (5 mmoles) of XII in 13 ml. of 10% sodium hydroxide and 20 ml. of methanol was refluxed for 30 minutes, then cooled and the alcohol removed by evaporation (Rinco). The remaining solution was extracted continuously for 6 hours with ether. This extract was discarded, the aqueous solution acidified with dilute hydrochloric acid and again extracted continuously with ether (36 hours). The ether extract was dried over anhydrous sodium sulfate and the solvent partially evaporated. To the remaining solution there was added 10 ml. of ethyl acetate; the whole was treated with Norit and the product isolated (0.87 g., 70.7%) by recrystallization from ethyl acetate–pentane; m.p. 166–169°. Further attempts at purification led to decomposition, so the acid was converted to its tetramethyl ester for analysis.

Methyl 3,3-Dimethylcyclopropane-1,1,2,2-tetracarboxylate (XIV).—Compound XIII (0.98 g., 4 mmoles) was methylated

with diazomethane in the usual fashion, yielding 0.96 g. (80%) of XIV, m.p. 154.5–155°. Its infrared spectrum in carbon tetrachloride showed a sharp intense carbonyl band at 5.75 μ and its n.m.r. spectrum in chloroform showed two sharp singlets at 6.42 and 8.56 τ, relative areas 2:1.

Anal. Calcd. for $C_{13}H_{18}O_8$: C, 51.65; H, 6.00. Found: C, 51.81; H, 6.12.

Acknowledgment.—We are indebted to the Office of Ordnance Research (Contract No. DA-20-018-ORD-16492) and to the Petroleum Research Fund of the American Chemical Society (Grant 488-C) for financial support of this research. H. H. also thanks his hosts at Cambridge University for their hospitality and discussions during preparation of this manuscript, and the National Science Foundation for a Senior Postdoctoral Fellowship. Finally, we thank Mr. John S. Fleming for certain of the n.m.r. spectra.