After cooling in an ice bath, it was extracted ten times each with an equal volume of chloroform. The combined chloroform extracts were dried over Na_2SO_4 and evaporated *in vacuo* leaving a solid residue.

Compound 27.—The crude product was dissolved in *ca.* 10 ml of methanol; the solution was treated with Norit, and then filtered. After addition of an equal volume of ether and chilling, it gave short white needles: yield 290 mg (28.5%), mp 138–142°.

Anal. Calcd for $C_7H_{10}N_2O_3$: C, 49.40; H, 5.92; N, 16.46. Found: C, 49.68; H, 6.13; N, 16.32.

Compound 30.—The yield of crude product was 500 mg (54.5%). It was recrystallized similarly from methanol–ether as white needles melting at 140–142°.

Anal. Calcd for $C_8H_{12}N_2O_3$: C, 52.16; H, 6.57; N, 15.21. Found: C, 52.23; H, 6.57; N, 15.22.

5-Methoxymethyl-1,3-dimethyluracil (28).—Chromatographic examination of the aqueous phase after extraction of **27** with chloroform indicated the presence of partially methylated products.

In all three systems A–C it gave four well-separated ultraviolet-absorbing spots. The corresponding R_f values were the following: in A 0.70, 0.60, 0.49, 0.39; in B 0.56, 0.48, 0.32, 0.24; and in C 0.76, 0.64, 0.50, 0.36. In all cases the fastest and slowest moving spot corresponded to the product (**27**) and starting material (**26**), respectively. From the chromatogram developed in system A, the spots with R_f's 0.60 and 0.49 were eluted with water and the ultraviolet absorption of the solutions was examined. The spectrum of the extract of the spot with R_f 0.60 resembled that of 3-methyluracil while that of the extract of the spot with R_f 0.49 was similar to that of 1-methyluracil. After the solvent was evaporated *in vacuo*, the residue was dried and extracted repeatedly with hot methanol until no more ultraviolet-absorbing material remained. The combined alcoholic extracts were taken to dryness and the crystalline residue was remethylated following the procedure described above for **27** and **30**. The solid thus recovered from the chloroform extract was recrystallized twice from methanol–ethyl ether to give 270 mg of short white needles, which on slow heating gave a "wet" solid at 125° that melted at 273–275°.

Anal. Calcd for $C_8H_{12}N_2O_3$: C, 52.16; H, 6.57; N, 15.21. Found: C, 52.19; H, 6.45; H, 15.46.

Registry No.—**3a**, 14181-27-2; **3b**, 14181-50-1; **4**, 14181-28-3; **5**, 14181-29-4; **6**, 14271-28-4; **7**, 14181-30-7; **7** (2,4-dinitrophenylhydrozone), 14181-31-8; **8**, 14181-32-9; **9**, 14181-33-0; **10**, 14181-34-1; **11**, 14181-35-2; **12**, 14181-36-3; **13**, 14181-37-4; **14**, 14181-38-5; **15**, 14181-39-6; **16**, 14181-40-9; **17**, 14181-41-0; **18**, 14181-42-1; **19**, 14181-43-2; **20**, 14181-44-3; **22**, 14181-45-4; **24**, 14271-29-5; **27**, 14181-46-5; **28**, 14181-47-6; **30**, 14181-48-7; **32**, 10082-51-6.

Acknowledgment.—The authors are indebted to Dr. George Bosworth Brown for his encouragement and continued interest, Dr. Robert Cushley for many discussions regarding the interpretation of the nmr spectra, and Mr. Marvin Olsen for recording these spectra.

Schmidt Reaction of Hydroxyquinones

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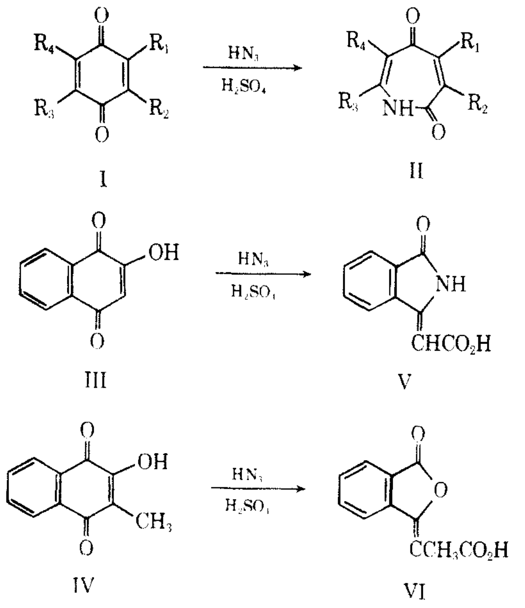
The reactions of 2-hydroxy-1,4-naphthoquinone and 2-hydroxy-3-methyl-1,4-naphthoquinone with hydrazoic acid were investigated. Both quinones reacted, giving ring contracted products; the former gave 3-oxo-$\Delta^{1\alpha}$-isoindolineacetic acid (V) and the latter gave phthalidine-2-propinoic acid (VI). Mechanisms for these transformations are presented in the text.

In earlier publications it was shown that various alkyl-substituted 1,4-benzoquinones and 1,4-naphthoquinones react with hydrazoic acid in concentrated sulfuric acid to give azepinediones (II).[1–4] Reported here are the results of an investigation of the Schmidt reaction on 2-hydroxy-1,4-naphthoquinone (III) and 2-hydroxy-3-methyl-1,4-naphthoquinone (IV). This study was initiated with the idea of preparing hydroxy-substituted azepinediones which would be attractive synthetic intermediates to the illusive azatropolone ring system. However, instead of the expected ring expansion, ring contraction was realized giving 3-oxo-$\Delta^{1\alpha}$-isoindolineacetic acid (V) from 2-hydroxy-1,4-naphthoquinone (III) and the γ-lactone (VI), phthalidine-2-propionic acid, from 2-hydroxy-3-methyl-1,4-naphthoquinone (IV) (see Scheme I).

Compound V and its decarboxylation product, 2-methylenephthalimidine, have previously been synthesized by a more complex method and were shown to be important synthetic intermediates in the preparation of tetrabenzoporphins.[5–8] The conversion of

Scheme I



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[1] D. Misiti, H. W. Moore, and K. Folkers, *Tetrahedron Letters*, No. 16, 1071 (1965).

[2] D. Misiti, H. W. Moore, and K. Folkers, *Tetrahedron*, **22**, 1201 (1966).

[3] R. W. Richards and R. M. Smith, *Tetrahedron Letters*, No. 22, 2361 (1966).

[4] G. R. Bedford, G. Jones, and B. R. Webster, *ibid.*, No. 22, 2367 (1966).

[5] C. E. Dent, *J. Chem. Soc.*, 1 (1938).

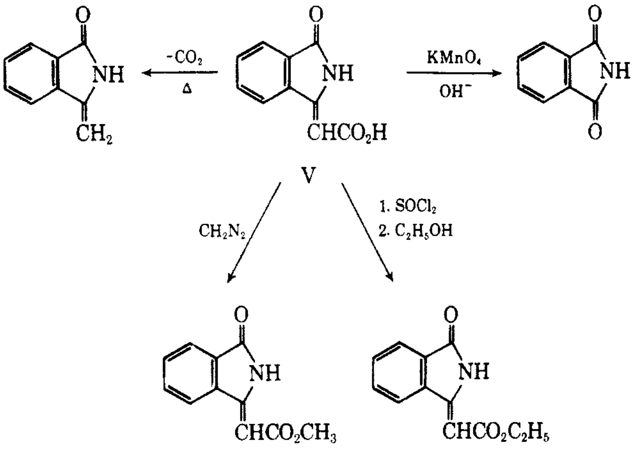
[6] R. P. Linstead and G. A. Rowe, *ibid.*, 1070 (1940).

[7] P. A. Barrett, R. P. Linstead, J. J. Leavett, and G. A. Rowe, *ibid.*, 1076 (1940).

[8] P. A. Barrett, R. P. Linstead, F. G. Rundall, and G. A. P. Tuey, *ibid.*, 1079 (1940).

the quinone, III, to the acid, V, was readily accomplished by the previously reported technique,[1,2] *i.e.*, slow addition of sodium azide to a cold solution of the quinone in concentrated sulfuric acid. The structure of the major product, V (formed in 80% yield), was assigned on the basis of the following chemical and spectral data. The infrared spectrum of V (Nujol) showed characteristic absorptions at 3385 (O—H stretch), 3250 (N—H stretch), 1730 and 1710 cm^{-1} (C=O stretch). The nmr spectrum of a dimethyl sulfoxide-d_6 solution of V showed absorptions at τ -2.5 (1) s, O-H; -0.12 (1) s, N-H; 1.95–2.45 (4) m, aromatic protons; and 3.02 (1) s, vinyl proton. These spectral data are interpreted in terms of structure V, but do not completely rule out other possibilities. For example the azepinedione, II (R_1 = OH; R_2 = H; R_3 and R_4 = CH=CHCH=CH) might also be an expected product which would have similar spectral properties. This ambiguity was eliminated by chemical degradation of the product and synthesis of V by a known sequence of reactions.[6] Compound V readily decolorized bromine and was immediately oxidized with basic permanganate to give phthalimide, identified by comparison with an authentic sample. At its melting point, 235°, the acid decomposed with the evolution of carbon dioxide which was detected and identified by gas chromatographic analyses on a silica gel G column run isothermally at room temperature. Compound V showed characteristic solubility properties for a carboxylic acid being soluble in both 5% sodium hydroxide and 5% sodium bicarbonate. A titrimetric equivalent weight determination gave a value of 190 compared with the calculated value of 189 for V. Reaction of the acid with diazomethane gave the methyl ester, mp 126°.[6] The ethyl ester was also prepared by reaction of the corresponding acid chloride with ethanol, mp 98–99° (see Scheme II).

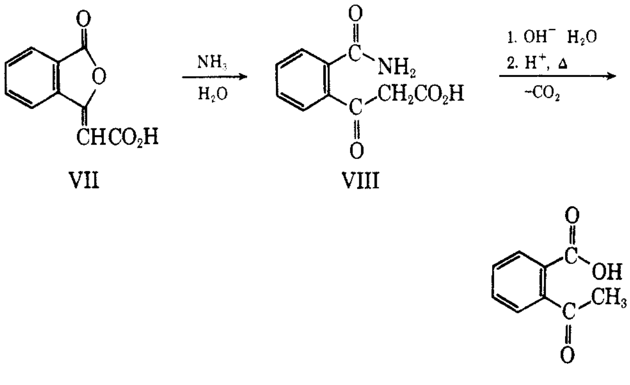
SCHEME II



V

XIII

The literature regarding 3-oxo-$\Delta^{1\alpha}$-isoindolineacetic acid (V) shows some anomalies. Dent[5] reported the acid as being formed as a dihydrate from the reaction of phthalimidineacetic acid (VII) with concentrated aqueous ammonia. Linstead and Rowe[6] later prepared V by the condensation of iminophthalimidine with malonic ester followed by hydrolysis and decarboxylation. Their compound differed markedly from that of Dent, leading Linstead to suggest that the Dent acid was actually *o*-carbamylbenzoylacetic acid (VIII) on the basis of its resistance to oxidation, ease of decarboxylation, and facile conversion to V under acid conditions.



VII

VIII

IX

The exact structure of the Dent acid was of interest to us since it seemed a likely intermediate in the conversion of the quinone, III, to the acid, V. The acid, VIII, was therefore made according to Dent's method and its structure was confirmed as VIII on the basis of spectral (see Experimental Section) and chemical data. Hydrolytic decarboxylation of the acid, VIII, in aqueous sodium hydroxide gave the known compound, *o*-acetylbenzoic acid[9] (IX). Treatment of VIII with cold concentrated sulfuric acid followed by precipitation with water (same conditions as were used for the Schmidt reaction on III except for the absence of sodium azide) gave 3-oxo-$\Delta^{1\alpha}$-isoindolineacetic acid (V) in 84% yield (see Scheme III). Comparison of this product with that obtained from the quinone, III, showed them to be identical in all respects, thus establishing the structure of VIII as well as lending credence to the proposed mechanistic scheme presented above.

Further support for this sequence of reactions was obtained by the isolation and characterization of the azide, X, and its subsequent conversion to V under the Schmidt reaction conditions. The azide was obtained as the major product (69% yield) when the reaction of 2-hydroxy-1,4-naphthoquinone with hydrazoic acid was accomplished by the slow addition of the quinone to a cold solution of excess sodium azide in concentrated sulfuric acid. Precipitation of the reaction products by the addition of water gave only two isolated products, the azide, X, and the acid, V. The proposed structure of the azide is in complete agreement with its spectral data. The infrared spectrum of X (Nujol) showed characteristic absorptions at 3315 (O—H stretch), 2130 (N=N=N stretch), 1720 (C=O stretch), and 1650 cm^{-1} (C=N stretch). The lack of typical carboxylic acid absorption between 2900 and 2500 cm^{-1} is also significant in eliminating structures with the isoindoline nucleus. The nmr spectrum of a pyridine solution of the azide showed the enolic hydroxyl proton as a broad singlet at τ 4.97 and the vinyl proton absorption as a sharp singlet at τ 4.00.

Trapping of the carbonium ion (XII) by sodium azide to give the organic azide, X, is significant in understanding the reaction sequence leading from III

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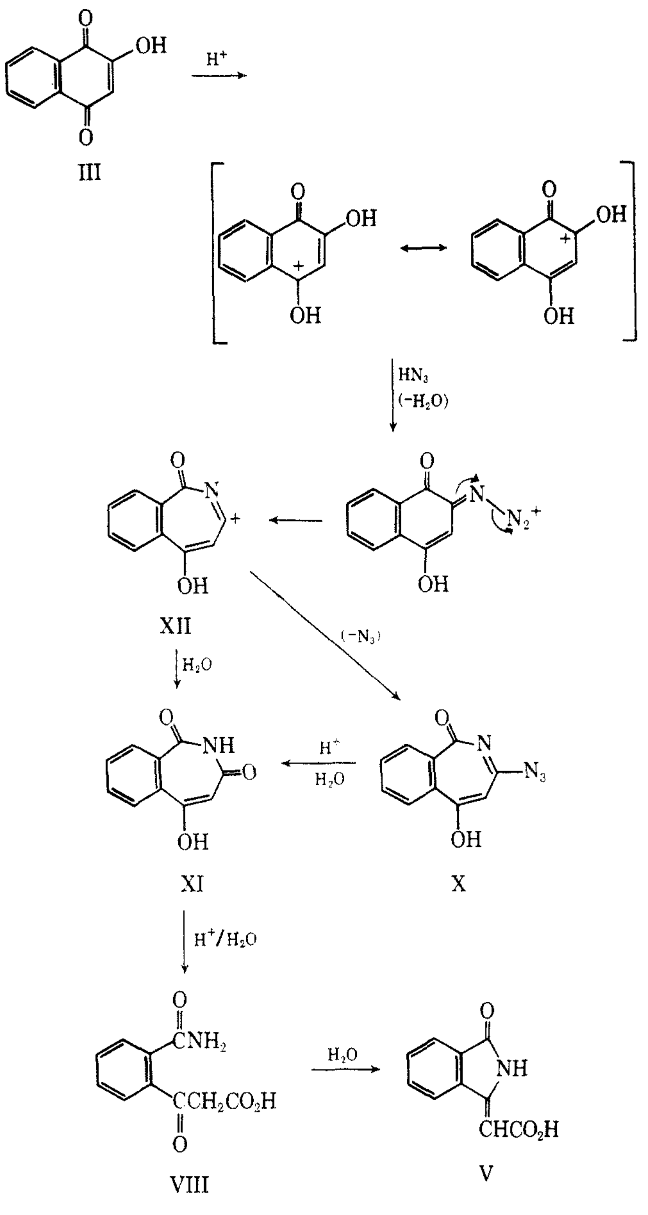
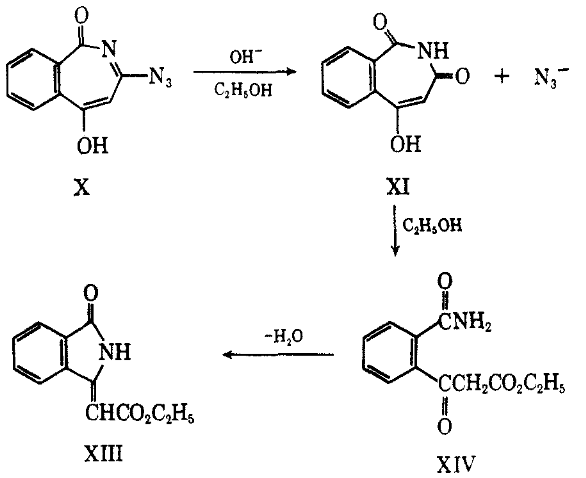
[9] W. Davies, and H. G. Poole, *J. Chem. Soc.*, 2661 (1927).

to V, particularly since the azide itself is converted into V under the reaction conditions. When the azide was dissolved in cold concentrated sulfuric acid and allowed to stand for a few minutes with water being added, the acid, V, precipitated in a nearly quantitative yield. The imide, XI, and Dent's acid, VIII, are presumed to be intermediates in this transformation. Several attempts have been made to convert the azide to the imide, XI, but thus far all attempts have resulted in either no reaction or complete conversion into V or a derivative of this acid. One of these experiments does, however, give evidence for the intermediacy of the imide. When the azide was treated with ethanolic potassium hydroxide it was converted in high yields into the ethyl ester of 3-oxo-$\Delta^{1\alpha}$-isoindolineacetic acid (XIII). Such a transformation could easily come about in the following way. Conversion of the azide into the imide followed by ethanolysis would give the ester, XIV. This ester would then ring close and dehydrate to give the observed product, XIII (see Scheme IV).

SCHEME III



SCHEME IV



When 2-hydroxy-3-methyl-1,4-naphthoquinone (IV) was subjected to Schmidt reaction conditions analogous to those described above for III, the reaction took a somewhat different course. The rate of the reaction was appreciably slower than that observed for III, and after several hours of reaction time the only isolated product, in addition to unreacted starting quinone, was the phthalidine derivative, VI. That hydrazoic acid is involved in this transformation was shown by model experiments in which the quinone, IV, was subjected to the reaction conditions in the absence of sodium azide. No apparent reaction took place under these conditions—the starting quinone being quantitatively recovered. The structure of the product, phthalidine-2-propionic acid (VI) was readily assigned on the basis of spectral data and comparison of its physical properties with those reported in the literature.[10] The γ-lactone ring system is evident from the infrared spectrum of VI which shows carbonyl absorption at 1780 cm^{-1}. The α,β-unsaturated carboxylic acid carbonyl shows an absorption at 1680 cm^{-1}. The nmr spectrum of a dimethyl sulfoxide-d_6 solution of VI shows a single aromatic proton absorption at low field, τ 1.49, and a complex multiplet corresponding to the other three aromatic protons between τ 1.97 and 2.45. The allylic methyl group absorbs as a singlet at τ 7.82.

A mechanistic pathway which explains the formation of VI follows. It should be noted that all steps leading to the formation of the acid, XV, are analogous to those described above for the conversion of the unsubstituted hydroxyquinone III, to the intermediate acid, VIII. However, apparently the more sterically hindered ketone function in XV retards its reaction with the amide nitrogen. This retardation allows amide hydrolysis to take place first to give the dicarboxylic acid (XVI) which subsequently undergoes acid-catalyzed lactone formation and dehydration giving the observed product, VI (see Scheme V).

Continued investigations of the reactions of hydroxyquinones with hydrazoic acid should be fruitful. Of particular interest would be the possible synthesis of a variety of naturally occurring benzylidine-substituted γ-lactones and lactams from the corresponding terphenylhydroxyquinones. For example, the

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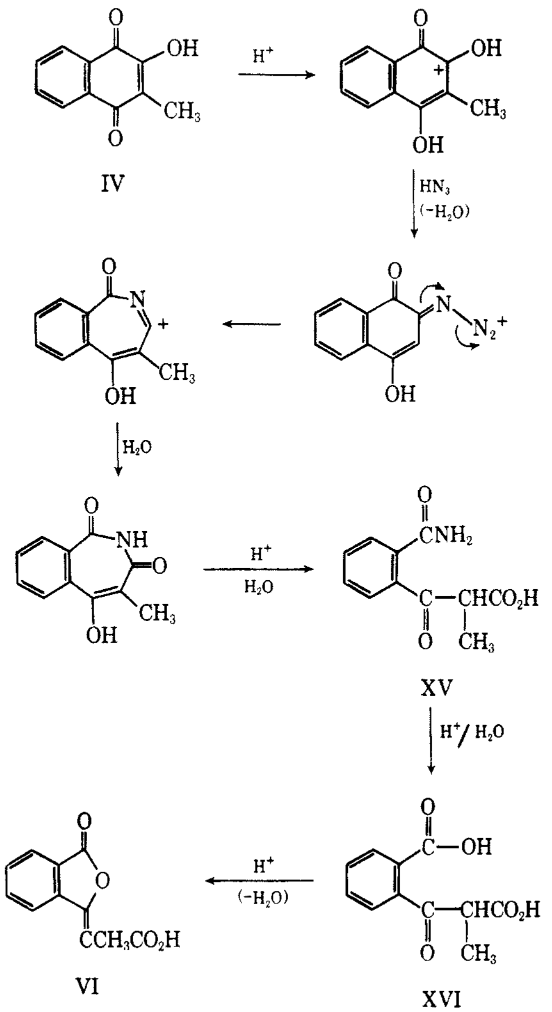
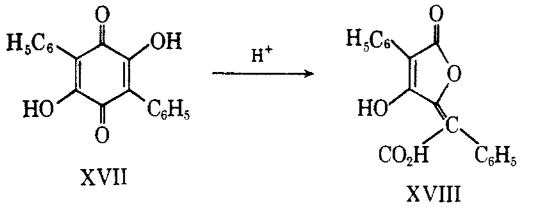
[10] Gabriel, Michael, *Chem. Ber.*, **10**, 1553 (1877).

SCHEME V



conversion of polyporic acid (XVII) into pulvinic acid (XVIII) is currently being investigated.



Experimental Section[11]

3-Oxo-$\Delta^{1\alpha}$-isoindolineacetic Acid (V).—A solution of 15 g (0.086 mole) of 2-hydroxy-1,4-naphthoquinone (III) in 100 ml of concentrated sulfuric acid was cooled to 0°. To this solution was added slowly 11.1 g (0.17 mole) of sodium azide at such a rate as to maintain the reaction temperature between 5 and 10°. The resulting reaction solution was then allowed to warm to room temperature and to stand for an additional 2 hr, at which time no further evolution of nitrogen was observed. The reaction solution was then poured into approximately 500 ml of water. The resulting precipitate was collected by filtration and recrystallized from 95% ethanol giving 13 g (80% yield) of 3-oxo-$\Delta^{1\alpha}$-isoindolineacetic acid, mp 235° dec.

Anal. Calcd for $C_{10}H_7NO_3$: C, 63.49; H, 3.70; N, 7.40. Found: C, 63.75; H, 3.85; N, 7.44.

The product, V, showed typical carboxylic acid solubility characteristics being soluble in both 5% sodium hydroxide and 5% sodium bicarbonate. Bromine in carbon tetrachloride readily reacted with V indicating the presence of carbon-carbon unsaturation.

At its melting point, 235°, 3-oxo-$\Delta^{1\alpha}$-isoindolineacetic acid (V) readily decomposed with the evolution of a gas. A sample of V was pyrolyzed and the gas was trapped in a vacuum line. This gas was then transferred directly to a gas chromatograph, analyzed on a silica gel G column run isothermally at room temperature, and thus identified as CO_2 by comparison of retention times with that of an authentic sample.

Phthalimide.—3-Oxo-$\Delta^{1\alpha}$-isoindolineacetic acid (V, 1 g, 0.0052 mole) was dissolved in 50 ml of 10% sodium bicarbonate. A 1% solution of potassium permanganate was then added dropwise until a permanent permanganate color persisted. The solution was then acidified with 3 *N* sulfuric acid and 5 g of sodium sulfite was added. The solution was heated on the steam bath for a few minutes and then filtered. When the resulting solution cooled, a white crystalline solid, mp 233°, precipitated. This solid was shown to be phthalimide by mixture melting point and comparison of its infrared spectrum with that obtained from an authentic sample.

Methyl 3-Oxo-$\Delta^{1\alpha}$-isoindolineacetate.—The methyl ester of V was prepared in 93% yield by the reaction of an ethereal solution of diazomethane with the acid. The observed melting point for the ester was 126° (lit[6] mp 124–125°).

Ethyl 3-$\Delta^{1\alpha}$-Isoindolineacetate (XIII).—The ethyl ester of V was readily prepared by the reaction of the acid chloride (prepared from the reaction of V with thionyl chloride) with absolute ethanol, mp 98–99°.

***o*-Carbamylbenzoylacetic acid (VIII)** was prepared according to the method reported by Dent.[5]

***o*-Acetylbenzoic Acid (IX).**—*o*-Carbamylbenzoylacetic acid (VIII, 500 mg, 2.5 mmoles) was dissolved in 5 ml of 10% sodium hydroxide. This solution was refluxed for 30 min during which time the evolution of ammonia was detected by odor and by litnus. The solution was then made acid to litnus. Upon cooling, a white crystalline precipitate, *o*-acetylbenzoic acid, formed, mp 112° (lit.[9] mp 114°). An infrared spectrum of the product in Nujol showed O–H stretching at 3200 and between 2700 and 2500 cm^{-1}. Carbonyl absorption was detected as a broad peak centered at 1720 cm^{-1}.

3-Oxo-$\Delta^{1\alpha}$-isoindolineacetic Acid from *o*-Carbamylbenzoylacetic Acid.—Five-hundred milligrams (2.5 mmoles) of *o*-carbamylbenzoylacetic acid was dissolved in approximately 10 ml of cold (0°) concentrated sulfuric acid. After 30 min the solution was poured into ice water resulting in the precipitation of 400 mg (84% yield) of 3-oxo-$\Delta^{1\alpha}$-isoindolineacetic acid. The product was shown to be identical (melting point, mixture melting point, and infrared spectrum) with an authentic sample of the acid, V.

Preparation of the Organic Azide (X).—A solution of 9 g (0.14 mole) of sodium azide in 50 ml of concentrated sulfuric acid was prepared and kept at 0°. To this solution was then added 2.6 g (0.015 mole) of 2-hydroxy-1,4-naphthoquinone over a period of 15 min. The solution was then immediately poured into ice water and the resulting mixture was filtered. The precipitate thus collected consisted mainly of unreacted quinone and 3-oxo-$\Delta^{1\alpha}$-isoindolineacetic acid. The azide, X, slowly formed as a light yellow crystalline solid in the aqueous mother liquor. The azide, X, mp >300°, was recrystallized from ethanol to give 2.2 g (69% yield). One sample of X, submitted for microanalyses, was reported to explode violently upon combustion.

Anal. Calcd for $C_{10}H_6N_4O_2$: C, 56.10; H, 2.81; N, 26.10. Found: C, 56.10; H, 2.84; N, 26.11.

3-Oxo-$\Delta^{1\alpha}$-isoindolineacetic Acid from the Azide, X.—The azide, X (30 mg), was dissolved in 2 ml of cold (0°) sulfuric acid. The solution was allowed to stand for a few minutes and then water was slowly added until a precipitate formed. This product was collected by filtration and shown to be identical (melting point, mixture melting point, and infrared spectrum) with an authentic sample of the acid, V.

Ethyl 3-Oxo-$\Delta^{1\alpha}$-isoindolineacetate (XIII) from the Azide, X.—A solution of 5% potassium hydroxide in 95% ethanol was prepared and 100 mg (0.46 mmoles) of the azide, X, was added. The resulting solution was allowed to stand at room temperature and then acidified with aqueous hydrochloric acid. This solution was poured into water causing the precipitation of a white crystalline solid. The product was collected giving 60 mg (60% yield) of ethyl 3-oxo-$\Delta^{1\alpha}$-isoindolineacetate (XIII). This product was shown to be identical (melting point, mixture

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[11] Melting points are uncorrected. Microanalyses were carried out by Spang Microanalytical Laboratory, Ann Arbor, Mich.

melting point, and infrared spectrum) with an authentic sample of the ethyl ester of V.

Phthalidin-2-propionic Acid (VI).—A solution of 3.5 g (0.018 mole) of 2-hydroxy-3-methyl-1,4-naphthoquinone (IV) in 30 ml of concentrated sulfuric acid was cooled to 0°. To this solution was added 1.7 g (0.026 mole) of sodium azide at such a rate as to maintain the reaction temperature between 5 and 10°. The resulting solution was then allowed to warm to room temperature and stand for an additional 2 hr. The reaction solution was then poured into water causing the precipitation of a yellow solid. This mixture was immediately filtered. The collected solid was mainly unreacted quinone, recovered in excess of 1.5 g. The lactone, VI, precipitated from the mother liquor as a white crystalline solid. Recrystallization from ethanol gave 300 mg (8.3% yield), mp 253° (lit.[10] mp 248°).

Anal. Calcd for $C_{11}H_8O_4$: C, 64.70: H, 3.92. Found: C, 64.71; H, 4.11.

Nmr Spectroscopy.—The nmr spectra were recorded on a Varian Associates high resolution spectrometer (A-56/60) at a frequency of 60 Mcps. Chemical shifts are expressed as shielding values, τ, as defined by G. V. D. Tiers.[12]

Registry No.—III, 83-72-7; IV, 483-55-6; V, 4403-34-3; VI, 14120-20-8; VIII, 14120-21-9; IX, 577-56-0; X, 14120-22-0; XIII, 14120-23-1.

Acknowledgment.—The authors are grateful to the National Science Foundation for partial support of this work from Grant GP 5945.

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[12] G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

Small Charged Rings. X.[1] Expansion of the Aziridinium Ring by Reaction with Nitrones[2]

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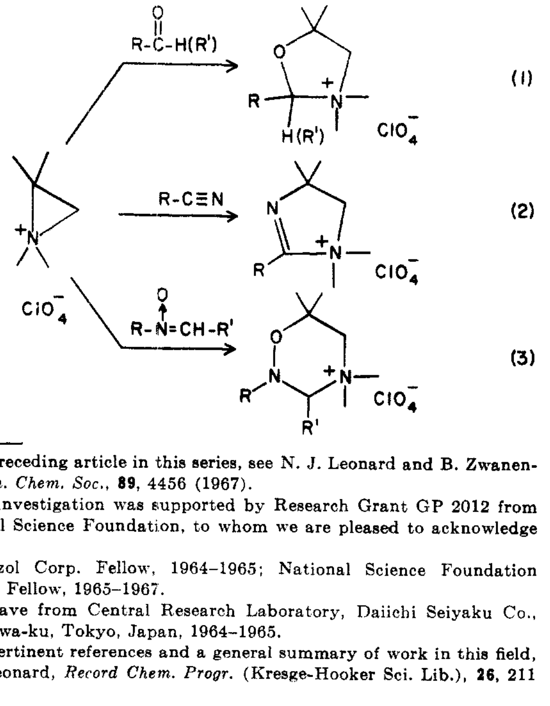
1,1,2,2-Tetramethylaziridinium perchlorate (**3**) has been shown to react with substituted Δ^1-pyrroline 1-oxides (**2**) to yield 1:1 adducts (**4**) containing the 2-oxa-1-aza-5-azoniabicyclo[4.3.0]nonane ring system. The ring expansion thus effected is representative of a new type, expressed as ③$^+$ + 3 → ⑥$^+$, in which a three-membered charged ring combines with a 1,3-dipolar moiety to form a six-membered charged ring. The structures of the adducts were established by catalytic hydrogenolytic cleavage of the 5,6 bond, followed by reductive cleavage of the 1,2 bond with zinc and acetic acid, with attendant spectroscopic and chemical identification of the sequential degradation products. Similar adducts (**15**) were obtained from 1-benzyl-1-ethyl-1-azoniaspiro[2.5]octane perchlorate (**14**) and substituted Δ^1-pyrroline 1-oxides. In this case, cleavage of the 5,6 bond in the adduct was effected with lithium aluminum hydride and cleavage of the 1,2 bond with zinc and acetic acid to complete the establishment of structure.

Previous papers in this series[5] have described the expansion of the aziridinium ring with aldehydes and ketones to form oxazolidinium salts (eq 1) and with nitriles to form imidazolinium salts (eq 2). These reactions may be represented generally by the expression ③$^+$ + 2 → ⑤$^+$, descriptive of a broad type in which a charged, three-membered cycle is increased in size to a charged, five-membered cycle.[6-8] They appear to proceed by opening of the aziridinium ring to the more stable of two possible tertiary β-aminocarbonium ions, which combines with the polarized carbonyl or nitrile group to form the appropriate five-membered heterocycle. We now report an extension of the scope of such ring enlargements to include a new type, ③$^+$ + 3 → ⑥$^+$, where the adding group is a 1,3-dipole in general, a nitrone (azomethine N-oxide) in this particular case (eq 3). The 1,3-dipolar cycloaddition of nitrones to olefinic and acetylenic bonds to form isoxazolidine derivatives is well documented.[9-12] We be-



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[1] For preceding article in this series, see N. J. Leonard and B. Zwanenburg, *J. Am. Chem. Soc.*, **89**, 4456 (1967).

[2] This investigation was supported by Research Grant GP 2012 from the National Science Foundation, to whom we are pleased to acknowledge our thanks.

[3] Lubrizol Corp. Fellow, 1964–1965; National Science Foundation Cooperative Fellow, 1965–1967.

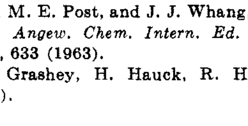
[4] On leave from Central Research Laboratory, Daiichi Seiyaku Co., Ltd., Edogawa-ku, Tokyo, Japan, 1964–1965.

[5] For pertinent references and a general summary of work in this field, see N. J. Leonard, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **26**, 211 (1966).

[6] N. J. Leonard, J. V. Paukstelis, and L. E. Brady, *J. Org. Chem.*, **29**, 3383 (1964).

[7] N. J. Leonard and L. E. Brady, *ibid.*, **30**, 817 (1965).

[8] E. Pfeil and U. Harder, *Angew. Chem.*, **77**, 505 (1965). The tautomeric structure and the name used in this reference to represent the product of reaction of a nitrile with unsubstituted aziridinium tetrafluoborate are very likely in error, since the vigorous conditions employed by Pfeil and Harder would certainly be expected to bring about equilibration to the more stable, symmetrical amidinium type structure



[9] For two recent reviews of the chemistry of nitrones, see (a) J. Hamer and A. Macaluso, *Chem. Rev.*, **64**, 473 (1964); (b) G. R. Delpierre and M. Lamchen, *Quart. Rev.* (London), **19**, 329 (1965).

[10] (a) N. A. LeBel and J. J. Whang, *J. Am. Chem. Soc.*, **81**, 6334 (1959); (b) N. A. LeBel, G. M. J. Slusarczuk, and L. A. Spurlock, *ibid.*, **84**, 4360 (1962); (c) N. A. LeBel, M. E. Post, and J. J. Whang, *ibid.*, **86**, 3759 (1964).

[11] (a) R. Huisgen, *Angew. Chem. Intern. Ed. Engl.*, **2**, 565 (1963); (b) R. Huisgen, *ibid.*, **2**, 633 (1963).

[12] I. Brüning, R. Grashey, H. Hauck, R. Huisgen, and H. Seidl, *Org. Syn.*, **46**, 127 (1966).