[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

THE ACTION OF DIAZOMETHANE UPON DUROQUINONE*

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Until the recent work of Fieser and his students,[1] there had been very little study of the reaction between quinones and aliphatic diazo compounds. v. Pechmann[2] found that two molecules of diazomethane added readily to benzoquinone, and he formulated the product as a dipyrazolinoquinone. Rotter and Schaudy[3] found that diazomethane and xyloquinone gave an unstable, explosive substance which also was formed by addition of two molecules of the diazo compound to one of quinone. Fieser and Peters[1a] found that benzoquinone and diphenyldiazomethane reacted to give a yellow addition product in nearly quantitative yield, but thermal decomposition of this material did not lead to products suitable for further study.

The reaction between 1,4-naphthoquinones and aliphatic diazo compounds produces in general pyrazoloquinones, and Fieser, studying the reaction between 1,4-naphthoquinone and diazoacetic ester, outlined the reaction as involving four steps leading to the pyrazole. Using diphenyldiazomethane (a diazo compound with no hydrogen atoms on the methane carbon atom), Fieser and Peters[1a] were able to obtain the pyrazoline and from this, by thermal decomposition, a cyclopropane derivative as well as 2-benzohydryl-1,4-naphthoquinone. When the quinone nucleus carried substituents however, the reaction with aliphatic diazo compounds was not so regular. Macbeth and Winzor[4] found that 2-methyl-1,4-naphthoquinone was unreactive toward diazomethane, and Fieser and Hartwell[1c] found that this quinone was also unreactive toward hydrazoic acid. However, these authors showed that the analogous 2-benzohydryl-1,4-naphthoquinone readily added diazomethane to give a pyrazoline

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* Abstracted from a thesis by Wilbur Bennett Pings, submitted to the Graduate Faculty of the University of Minnesota, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, July, 1936.

[1] FIESER *et al.*, (*a*) *J. Am. Chem. Soc.*, **53**, 4080 (1931); (*b*) *ibid.*, **56**, 2690 (1934); (*c*) *ibid.*, **57**, 1479, 1482 (1935).

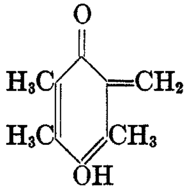
[2] v. PECHMANN, (*a*) *Ber.*, **28**, 855 (1895); (*b*) v. PECHMANN AND SEEL; *ibid.*, **32**, 2292 (1899).

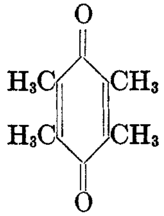
[3] ROTTER AND SCHAUDY, *Monats.*, **47**, 493 (1926).

[4] MACBETH AND WINZOR, *J. Chem. Soc.*, **1935**, 334.

which on thermal decomposition, gave 2-benzohydryl-3-methyl-1,4-naphthoquinone. Finally Fieser and Seligman[1b] discovered that two molecules of 2,6-dimethyl-1,4-naphthoquinone reacted with one of diazomethane to produce a dinaphthylmethane derivative.

In a series of papers from this laboratory[5] duroquinone (B) has been shown to behave as a pentad-enol system toward various enolates, and to react as though it had the structure A. As yet it has not been possible to prepare any simple derivatives of this structure, and from what is known concerning methylene quinones, it seems likely that any simple reaction involving them, in order to give a definite product, would have to proceed very rapidly or else the methylene quinone would simply polymerize. Formula A, however, represents a hydroxy derivative of a methylene quinone. If, in solutions of duroquinone, there is present a small amount of A together with a very reactive methylating agent, it might be possible to obtain from A a methyl derivative sufficiently stable to investigate, provided the reagent used would react with B extremely slowly or not at all. Although diazomethane reacts with double bonds to form pyrazolines it appeared from the work of others that substituents attached to the quinone nucleus exerted a pronounced hindrance to the addition of the reagent to the double bond and that duroquinone (B) would not, therefore, react to give pyrazolines or pyrazoles. Hence, if a reaction occurred, the quinone would have to react in the form A, or else the reaction would have to involve the carbonyl groups of B. The latter reaction had not been shown to occur in the case of paraquinones, although it is the common reaction in the case of orthoquinones and leads to ethers of the hydroquinone or to spiro ethylene oxide derivatives.[6,1a,b,c,2b] Diazomethane therefore appeared to be a promising reagent to use for the detection of any A in duroquinone, for either the hydroxyl group, or the unsubstituted heterogeneous conjugated system of A would be expected to react with this reagent much more rapidly than the double bonds or the carbonyl groups of B.


A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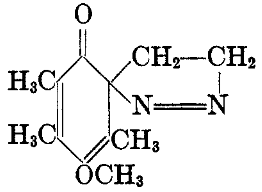
F

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[5] Smith and Johnson, *J. Am. Chem. Soc.*, **59**, 673 (1937) and previous papers.

[6] (*a*) Biltz and Paetzold, *Ann.*, **433**, 64 (1923); (*b*) Arndt, Amende, and Ender, *Monats.*, **59**, 202 (1932); (*c*) Allesandri, *Atti. R. accad. Lincei* [5] **22**, I, 517 (1913).

Duroquinone reacted slowly but completely with diazomethane in cold ethereal solution, and from the reaction mixture four products were isolated. These consisted of two isomeric compounds $C_{11}H_{14}N_2O_2$ (I, an unstable oil and II, a stable yellow crystalline compound melting at 103–104°) formed by addition of one molecule of the reagent to one of quinone, and two isomeric products $C_{12}H_{16}N_4O_2$ both colorless solids (III melting at 124–125°, decomp., and IV, melting at 143–144°, decomp.) formed by addition of two molecules of the reagent to one of quinone.

TABLE I

Products Obtained by Addition of Diazomethane to Duroquinone

(Diazomethane from 10 g. nitrosomethylurea added to 5.5 g. of duroquinone, at −15°)

SOLVENT	TIME (DAYS)	I + II (G.)	III (G.)	IV (G.)
Ether, 250 cc.	18	4.0	1.35	
Ether, 75 cc.	12	2.3	5.68 (III + IV)	
Ether, 125 cc.	12	2.3	5.39 (III + IV)	
Ether, 100 cc. (absolute)	5	—	3.47	
Benzene, 100 cc.	14	3.2	3.24 (III + IV)	
*Ether, 100 cc. + chloroform, 50 cc.	25	2.4 + 1.23 g. from steam distillate + 7.08 g. of quinone.		
Ether 75 cc. + chloroform 20 cc.	12	4.0	2.65	
Ether 100 cc. + acetone 50 cc.	11	2.5	1.34	1.55
Ether 100 cc. + ligroïn 50 cc.	26	3.0	—	3.45 + 0.5 g. duroquinone
Ether 100 cc. + methanol 10 cc.	11	3.0	—	3.43

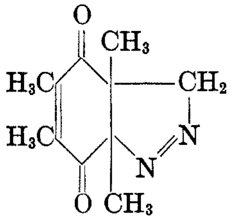
* Eleven grams of quinone used in this experiment with diazomethane from 10 g. nitrosomethylurea.

The mono addition products.—The unstable oily product I was never obtained in a completely pure condition, although analysis agreed well with that required by the composition $C_{11}H_{14}N_2O_2$. Further reaction of I with diazomethane led to IV. The substance I was completely destroyed when oxidized by cold dilute permanganate or by bromine, but when oxidized by ferric chloride, the product was duroquinone (B). Hence the original duroquinone nucleus was intact in I. Attempted acetylation of I gave duroquinone as the only isolable product, and reductive acetylation gave the diacetate of hydroduroquinone. Thermal decomposition of I led to a faintly yellow, stable product (V) melting at 60–61°, having the composition $C_{11}H_{14}O_2$, and which formed a dioxime. The substance

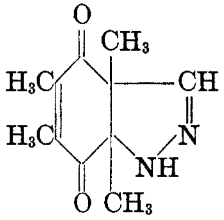
V was unaffected by hydrochloric or sulfuric acid, and was not oxidized by chromic acid or dilute nitric acid. The action of permanganate, or of ozone, upon V caused complete destruction.

In contrast to the behavior of I, the isomeric compound II was completely stable to heat and was recovered unchanged even after it was liquefied and then boiled. The substance (II) was yellow, but it did not have the physical properties characteristic of quinones. It was not volatile with steam, could not be sublimed, and was odorless. Further action of diazomethane upon II, as in the case of I, led to IV. No definite products could be obtained by reduction of II, but the duroquinone skeleton was intact in this compound also, for it gave duroquinone when treated with acetic anhydride followed by sodium bicarbonate, and also when the reduction product was subjected to the action of ferric chloride.

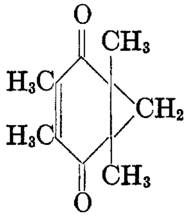
The existence of isomeric mono addition products derived from duroquinone and diazomethane is capable of but two explanations. The compounds might be pyrazolines, in which case the position of the double bond could vary (C and D).



C



D



E

But in this case, conversion of the Δ^1 isomer (C) to the Δ^2 isomer (D) should be possible[7] and such conversion has not been observed for these compounds. Moreover, C and D, by thermal decomposition, should lead to the same product, which is contrary to the observed behavior of I and II. That the decomposition product V obtained from I is not a cyclopropane derivative (E) follows from its stability toward hydrochloric acid, its complete destruction by permanganate and ozone[8] and from the fact that V forms a dioxime.[9] Further evidence against the formulation of I, II and V as C, D, and E respectively is found in the fact that duroquinone can be obtained from either I or II, which would not be the case if these substances were the pyrazolines C and D.

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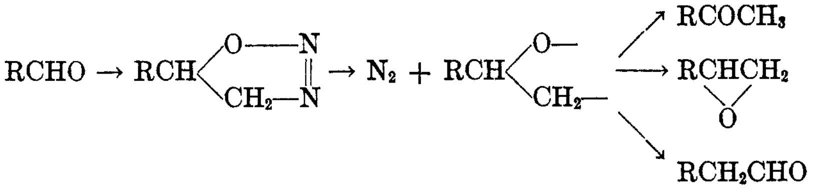
[7] (*a*) v. Auwers and Cauer, *Ann.*, **470**, 284 (1929); (*b*) v. Auwers and Konig, *ibid.*, **496**, 27, 252 (1932); (*c*) v. Auwers and Ungemach, *Ber.*, **66**, 1198 (1933).

[8] Kohler *et al.*, *J. Am. Chem. Soc.*, **39**, 1404, 1699, 2405 (1917); **41**, 1093 (1919).

[9] Kehrmann, *Ber.*, **21**, 3315 (1888).

If I and II are not pyrazolines, they must be formed by a mode of addition of diazomethane which has not yet been observed in the case of paraquinones. Had duroquinone reacted according to formula A, the product would most likely have been a monomethoxy spiro compound, such as F, which not only does not have the composition of I or II, but which, on thermal decomposition, would almost certainly have given a derivative of trimethylethylquinone. No such substances were ever encountered. It follows, then, that the attack of the reagent was confined to the carbonyl groups in the quinone.

Meyer[10] and Schlotterbeck[11] found that certain aldehydes behaved toward diazomethane as though they contained active hydrogen. Nitrogen was evolved, and methyl ketones were formed. Arndt and his collaborators[12] showed that this reaction was not of general application, since in some cases ethylene oxides were formed, the ketone and a homolog of the aldehyde appearing only as by-products. The mechanism put forth by Arndt for these reactions involved a primary 1,3 addition of the reagent to the carbonyl group to give furo-α-β-diazolines which, by loss of nitrogen then gave rise to transient radicals rearranging into the stable products obtained.



Meerwein and Burneleit[13] discovered that although ketones do not react with diazomethane under ordinary conditions, they do so in the presence of certain catalysts (water, alcohols, metallic salts) yielding ethylene oxides and higher ketones. This reaction was formulated as also involving furo-α,β-diazolines as primary products. When applied to cyclic ketones, Mosettig and Burger[14] found that cyclohexanone reacted vigorously with diazomethane in the presence of methanol to give cycloheptanone and even larger ring ketones. Ring expansion in reactions of cyclic dicarbonyl

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[10] Meyer, *Monats.*, **26**, 1295 (1905); *Ber.*, **40**, 847 (1907).

[11] Schlotterbeck, *Ber.*, **40**, 479 (1907).

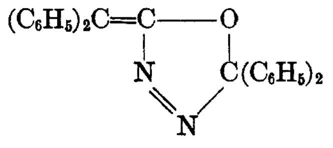
[12] Arndt *et al.*, (*a*) *Z. angew. Chem.*, **40**, 1099 (1927); (*b*) *Ber.*, **60**, 446 (1927); (*c*) *ibid.*, **61**, 1107 (1928); (*d*) *ibid.*, **61**, 1118 (1928); (*e*) *ibid.*, **61**, 1952 (1928); (*f*) *ibid.*, **62**, 44 (1929).

[13] Meerwein and Burneleit, (*a*) *Ber.*, **61**, 1840 (1928); (*b*) *ibid.*, **62**, 999 (1929).

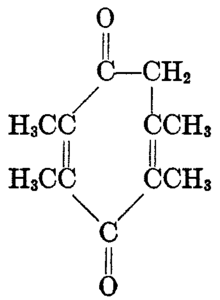
[14] Mosettig and Burger, *J. Am. Chem. Soc.*, **52**, 3456 (1930).

compounds with aliphatic diazo compounds had been noted by others previously.[15]

Although all these reactions between carbonyl compounds and aliphatic diazo compounds were supposed to involve furo-α,β-diazolines, in which a new carbon-to-carbon linkage was established, in no case was the diazoline isolated. Theoretically two modes of addition of aliphatic diazo compounds to carbonyl groups are possible, leading to furo-α,β- and furo-β,β'-diazolines, and it is interesting that in the one case in which the diazoline was actually isolated, Staudinger[16] assigned to it the structure of a furo-β,β'-diazoline (G)

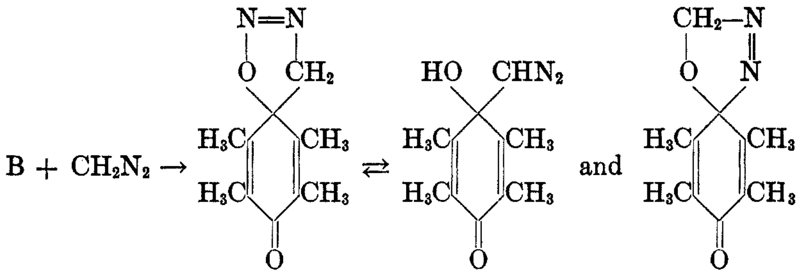


G



V

If the reaction between diazomethane and duroquinone is confined to the carbonyl groups of the quinone, since two modes of addition are possible, two mono addition products should result—the spiro-furo-α,β-diazoline I, and the spiro-furo-β,β'-diazoline II.



I II

While these structures for the mono addition compounds I and II are of necessity based upon rather indirect evidence, at the present time they best represent the behavior of the substances. Although formulas II and IIa, as well as I and Ia, were considered as structures for compounds I and

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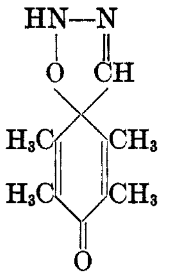
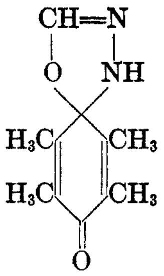
[15] (a) Heller, *Ber.*, **52**, 741 (1919); (b) *ibid.*, **59**, 704 (1926); (c) Hantzsch and Czapp, *ibid.*, **63**, 566 (1930); (d) Arndt, *ibid.*, **63**, 1180 (1930).

[16] Staudinger, *Helv. Chim. Acta*, **4**, 3 (1921).



Ia



IIa

II, respectively, formulas I and II were preferred because of the fact that I could not be converted into II, or vice versa, and because of the difference in thermal stability of compounds I and II. The formulas I and II readily account for the persistence of the original nucleus of duroquinone in these compounds. Moreover, I, being a diazo anhydride, would be tautomeric with the β-hydroxy diazomethane derivative as shown. Such a substance should be unstable and should lose the nitrogen, passing into a larger ring ketone via a spiroethylene oxide (or radicals) as is the case with simple ring ketones such as cyclohexanone. The decomposition product (V) of I is therefore assigned the structure 2,3,5,6-tetramethylcycloheptadiene-2,5-dione-1,4.

The thermal stability of compound II indicates that it must have a structure essentially different from that of I. Although no exact analogy can be drawn, it is known that the aromatic disubstituted β-β′-diazoles are very stable substances.[17] While the conversion of II into duroquinone by action of acetic anhydride followed by sodium bicarbonate is rather obscure for such a stable substance, nevertheless a compound of the structure II would be expected to yield duroquinone as a degradation product.

The di addition products (*III and IV*)—Compound III separated from the reaction mixture in clear rectangular prisms melting at 124–125° with evolution of gas. Analysis indicated the composition $C_{12}H_{16}N_4O_2$. Thermal decomposition caused quantitative loss of nitrogen and led to a colorless substance (VI) $C_{12}H_{16}O_2$ which melted at 142–143° and which formed a dioxime. Substance III reacted with hydrochloric acid or hydrobromic acid to give salts which could be titrated; duroquinone was formed when attempts were made to regenerate III from these salts, or when aqueous solutions of the salts were warmed. No oxime was formed from III, but

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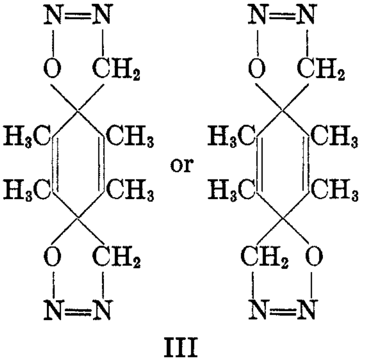
[17] (*a*) Pinner, *Ber.*, **26**, 2130 (1893); (*b*) *ibid.*, **27**, 988, 1006 (1894); (*c*) *Ann.*, **297**, 237 (1897); (*d*) *ibid.*, **298**, 16 (1897); (*e*) Günther, *ibid.*, **252**, 61, 64 (1889); (*f*) Stolle, *J. prakt. Chem.*, [2], **68**, 137 (1903); (*g*) *ibid.*, **70**, 395, 414 (1904); (*h*) *ibid.*, **73**, 279 (1906); (*i*) *ibid.*, **74**, 11, 15, 20, 22 (1906); (*j*) *ibid.*, **88**, 317 (1913).

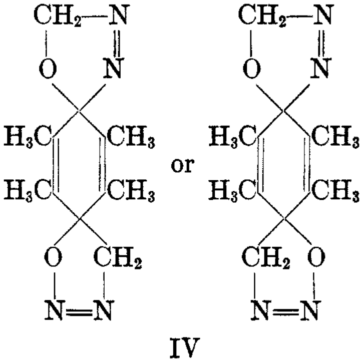
it reacted with phenylhydrazine to give a compound having the composition $C_{18}H_{22}N_6O$. A silver salt was obtained by adding silver nitrate to a solution of III in ammonium hydroxide.

The isomeric compound IV was obtained in clusters of fine needles melting at 143–144° with decomposition. Thermal decomposition of IV was smooth; only about half of the nitrogen was lost, and two unstable isomeric nitrogenous compounds $C_{12}H_{16}N_2O_2$ (VII and VIII) were isolated, along with some duroquinone. Treatment of IV with hydrochloric acid or hydrobromic acid gave salts apparently identical with those obtained from III. Attempts to form an oxime or a semicarbazone from IV gave only duroquinone, and the quinone also resulted when IV was gently warmed with dilute acids. Derivatives were obtained from IV by action of phenylhydrazine or phenylisocyanate, but 1-naphthylisocyanate was without action. A silver salt was obtained from IV in the same manner as from III.

On the basis of these reactions, III is assigned the structure a bisfuro-α,β-diazoline, while IV is given the structure in which one of the hetero rings is a furo-α,β- and the other a furo-β,β'-diazoline. As in the case of compounds I and II, various tautomeric modifications of formulas III and IV (analogous to Ia and IIa) were considered for the di addition products. While the evidence against such formulas for III and IV is much weaker than is the case with compounds I and II—in fact, there is some evidence for such a relationship between III and IV—the bulk of the evidence pointed to two different types of ring structures in substances III and IV and such tautomeric formulas were rejected, at least for the present. Structures III and IV account for the behavior of these compounds upon thermal decomposition, for III, with two unstable furo-α,β-diazoline rings should lose nitrogen quantitatively while IV, with one stable and one unstable ring, should lose only half of the nitrogen. The fact that IV can



III

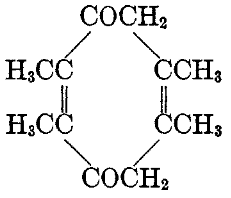


IV

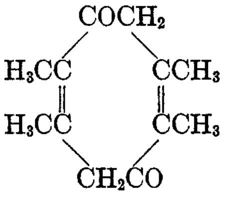
be obtained by addition of diazomethane to either I or II is also an indication that IV must contain one hetero ring of each kind. The difference in behavior of the two compounds on thermal decomposition is an indication that they cannot be represented simply as a pair of *cis-trans* isomers, although such isomerism is possible in the case of compounds having either structure III or IV. Finally, structures III and IV, as well as I and II, account for the easy conversion of the two substances to duroquinone.

The formation of identical salts from III and IV with hydrochloric acid or hydrobromic acid cannot be explained satisfactorily at present. Analyses of the salts indicated a carbon to hydrogen ratio of 1 to 2, and since III and IV have the composition $C_{12}H_{16}N_4O_2$, it appeared that a reduction had occurred. The formation of silver salts from III and IV is just as obscure, for while it is known that furo-β-β' diazoles in many cases form double salts with silver nitrate[17] it is not possible to write such a formula consistent with the analyses of the silver salts of III and IV.

In analogy with structure V, the substance VI obtained by thermal decomposition of III is assigned the structure 2,3,6,7-tetramethylcyclooctadiene-2,6-dione-1,4 (VIa) or 2,3,6,7-tetramethylcycloöctadiene-2-6-dione-1,5 (VIb), while the decomposition product of IV

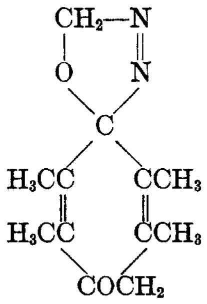


VIa



VIb

is assigned the structure of a spiro-cycloheptadiene-furo-β,β'-diazoline (VII). Two isomeric compounds were obtained by thermal decomposition of IV, but at present the relationship between these is not known. Both VII and VIII were unstable and decomposed on standing to give uncrystal-



(VII)

lizable yellow oils; both reacted with acetic anhydride, giving the same unstable acetyl derivative.

EXPERIMENTAL*

The addition reaction.—The reaction between duroquinone and diazomethane was carried out in a number of solvents. In general either III or IV was obtained, along with varying amounts of the mono addition products I and II. However, it was not possible to predict which of the products would be formed except when methanol was present. Under these circumstances, if any di addition product was obtained, it was invariably IV. In other solvents no such regularity was noticed, and two experiments, apparently identically performed, rarely gave the same results. In general the yields of di addition products ranged from about 30–60%; while the yields of mono addition products ranged from about 75–35%. A typical experiment will be described, and the results of others will be given in tabular form. A solution of diazomethane (2.8 g., 0.067 moles; obtained from 10 g. nitrosomethylurea) in ether (100 cc.) was added to a solution of duroquinone (5.5 g., 0.034 moles) in ether (125 cc.) and methanol (20 cc.). The solution, after standing at −5 to −10° for 11 days, deposited clusters of fine needles (4 g., IV) which were removed, washed with ether, and recrystallized from methanol or chloroform-petroleum ether. The substance (IV) melted at 143–144° with evolution of gas. It was insoluble in cold water, but soluble in hot water, dilute hydrochloric acid, 10% sodium hydroxide, concentrated ammonium hydroxide, and acetic acid. It was decomposed violently by concentrated sulfuric acid.

Anal. Calc'd for $C_{12}H_{16}N_4O_2$: C, 58.04; H, 6.50; N, 22.58.
Found: C, 58.33; H, 6.47; N, 22.77.

Evaporation of the ethereal filtrate from IV and steam distillation of the residue gave only a trace of duroquinone in the distillate. The non-volatile oil (3.2 g., 47%) remaining in the distilling flask was a mixture of I and II.

Anal. Calc'd for $C_{11}H_{14}N_2O_2$: C, 64.04; H, 6.85.
Found: C, 64.63; H, 7.10.

The oils, from four reactions (16 g.) were combined and decomposed by heating gently in a distilling flask. After the vigorous evolution of gas had subsided, water was added and steam was passed through until no more yellow oily material collected in the distillate. The distillate was saturated with salt and extracted with ether. Evaporation of the solvent left a clear yellow oil (2 g.) which solidified on standing. Crystallized several times from dilute acetone, dilute methanol, or low boiling petroleum ether, the substance (V) was nearly colorless and melted at 60–61°. It was insoluble in water, dilute hydrochloric acid, or dilute sodium hydroxide, but was soluble in concentrated sulfuric acid (orange-red solution), and reprecipitated on dilution. Permanganate in dilute acetone was readily reduced by the substance, but bromine in chloroform, as well as acetyl chloride, were without action.

Anal. Calc'd for $C_{11}H_{14}O_2$: C, 74.11; H, 7.92.
Found: C, 74.48; H, 8.11.

The residue remaining after V had been steam-distilled was a dark oil (6.1 g.) which could not be crystallized. When distilled under reduced pressure there was obtained 4.4 g. of a clear yellow oil (b.p. 160–170° 13 mm.) which solidified on cooling. Crystallized from water, dilute methanol, ethanol, acetone, or petroleum ether, the

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* Microanalyses by Mr. J. W. Opie.

substance formed bright-yellow prisms melting at 102–103° (II), and soluble in dilute hydrochloric acid or in concentrated sulfuric acid, insoluble in 10% sodium hydroxide. Cold dilute alkaline permanganate, as well as bromine in chloroform, were instantly decolorized by the substance.

Anal. Calc'd for $C_{11}H_{14}N_2O_2$: C, 64.04; H, 6.85; N, 13.59; mol. wt., 206.
Found: C, 63.74; H, 6.93; N, 13.24, 13.62; mol. wt. (Rast) 221, 212.

The mixture of mono addition products I and II could also be separated by long-continued steam distillation, the yellow product II remaining as a non-volatile residue while the decomposition product (V) of I slowly distilled over.

The di addition product III was obtained by conducting the addition reaction as described above, *omitting the methyl alcohol.* The product (4.26 g., 57%) separated in clear rectangular prisms which were removed and crystallized from methanol. The substance melted at 123° with evolution of gas. It was insoluble in cold water, but soluble in hot water although it decomposed partially, giving a yellow viscous oil. It dissolved in dilute sodium hydroxide, concentrated ammonium hydroxide, and in dilute hydrochloric acid, and was violently decomposed by cold concentrated sulfuric acid.

Anal. Calc'd for $C_{12}H_{16}N_4O_2$: C, 58.04; H, 6.50; N, 22.58.
Found: C, 58.23; H, 6.51; N, 22.64.

The filtrate from III, handled in the say as that from IV, gave a trace of duroquinone and 2.2 g. (35%) of a mixture of the mono addition products I and II.

Addition of diazomethane to II.—The yellow mono addition product II (0.45 g.) in dry ether (25 cc.) was added to diazomethane (0.9 g.) in ether (35 cc.). After standing at 0–5° for 10 days, the products were 0.2 g. of IV, m.p. and mixture m.p. 141–142° (decomp.) and 0.1 g. of unchanged II.

Addition of diazomethane to I.—The oily addition product I (1.8 g.) (from which duroquinone was removed by steam distillation) in ether (25 cc.) and methanol (1 cc.) was added to diazomethane (from 3.5 g. nitrosomethylurea) in ether (30 cc.). After standing at 5–10° for 3 days, the solution deposited colorless needles (0.55 g.) of IV melting at 138–140° (decomp.).

Reactions of I. (*a*) *Ferric chloride.*—The oily product I (0.8 g.) (freed of all volatile material by steam distillation) was dissolved in a little ethanol, and a warm concentrated solution of ferric chloride was added. Gas was evolved, and after standing two hours the yellow precipitate was removed. It weighed 0.33 g., and was duroquinone (m.p. and mixture m.p. 110–111°).

(*b*) *Acetic anhydride.*—The oily product I (0.9 g.) and sodium acetate (1 g.) were dissolved in acetic anhydride (3 cc.) and warmed on the steam bath for 30 minutes. The black solution, when poured into water and made alkaline with sodium hydroxide, precipitated 0.175 g. of duroquinone.

(*c*) *Reductive acetylation.*—The product I (0.92 g.) and sodium acetate (1 g.) were dissolved in acetic acid (10 cc.) and acetic anhydride (5 cc.). The solution was heated to boiling and zinc dust (3 g.) was added in small portions over the course of an hour. The product (0.18 g.) crystallized from ethanol, melted at 197–200° and was the diacetate of hydroduroquinone.

Anal. Calc'd for $C_{14}H_{18}O_4$: C, 67.16; H, 7.25.
Found: C, 67.45; H, 7.09.

The original filtrate from the diacetate was extracted with ether and chloroform. The extracts were washed with bicarbonate solution and dried. Evaporation of the solvents left 0.49 g. of a black intractable oil.

Reactions of V. (*a*) The *oxime*, prepared in the usual way and crystallized from dilute acetone, darkened at 220° and melted at 241–242°.

Anal. Calc'd for $C_{11}H_{16}N_2O_2$ (dioxime): C, 63.42; H, 7.75; N, 13.45.
Found: C, 64.37; H, 7.96; N, 13.21.

No phenylhydrazone or *p*-nitrophenylhydrazone of V could be made. The only product isolated was impure starting material.

(*b*) *Acetylation* of V was unsuccessful, and only unchanged material was recovered after treatment of V in the usual way with acetyl chloride, or with acetic anhydride in the presence or absence of sulfuric acid.

(*c*) *Hydrochloric acid* in ether at −10° failed to react with V in the course of an hour.

(*d*) *Oxidation.*—To a solution of V (178 mg.) in acetone (5 cc.) and water (5 cc.) there was added potassium hydroxide (75 mg.) and then, with cooling, a solution of permanganate (421 mg.) in water (10 cc.) was added dropwise. The color was immediately discharged. A little bisulfite was added, and the solution was extracted with ether. Evaporation of the ether left only a trace of oily residue. The alkaline aqueous layer was evaporated to 15 cc., cooled, acidified with dilute sulfuric acid and saturated with salt. Extraction with ether removed only a trace of oily material.

Repetition of the oxidation with the use of 534 mg. of V, 1.263 g. of permanganate and 223 mg. of potassium hydroxide gave essentially the same results, although a very small amount (about 15 mg.) of material melting at 128–131° was obtained when the alkaline solution was extracted with ether.

Chromic acid (0.5 g.) in acetic acid (1 cc.) and water (0.5 cc.) was without action upon V (0.3 g.) in acetic acid (2 cc.), and even after two days at room temperature the substance was recovered unchanged. Likewise heating of V to 100° for an hour with dilute nitric acid (1:10, 5 cc.) produced no change.

(*e*) *Ozonolysis.*—When subjected to the action of ozonized oxygen (5% O_3) for eleven minutes a cold (−10 to −15°) solution of V (0.5 g.) in carbon tetrachloride (80 cc.) absorbed 85% of the amount of ozone calculated for two double bonds. The ozonide was decomposed by adding the solution dropwise to a boiling mixture of water (100 cc.), zinc dust (2 g.) and a small crystal each of silver nitrate and hydroquinone.[18] The product was a small amount of yellow oil which could not be crystallized and which gave no reaction with *o*-phenylenediamine.

Repetition of the ozonolysis (1 g. of V) with chloroform as the solvent and 3% ozonized oxygen gave only a small amount of yellow oil although 95% of the theoretical amount of ozone was absorbed in 22 minutes. The yellow oil was not oxidized by alkaline hydrogen peroxide, and although the iodoform reaction was immediately positive, no organic acid could be isolated.

In a third experiment, the ozonide from 1.5 g. of V was decomposed by boiling the solution with alkaline hydrogen peroxide with no better results.

Reactions of II.—(*a*) A small amount of II was heated in a test-tube. There was no evolution of gas, even after fusion, followed by boiling of the liquid. The melt solidified on cooling; it was remelted and then boiled for 3 minutes. The substance was recovered completely unchanged.

(*b*) Hydroxylamine hydrochloride (0.5 g.), sodium acetate (0.5 g.), and II (0.34 g.) were dissolved in water (3 cc.) and ethanol (7 cc.), and the mixture was refluxed for 48 hours. The product (45 mg.) was a slightly yellow solid which after several crystallizations first from dilute ethanol and then from chloroform-petroleum ether, melted at 201–203°. (Decomp.) The substance was still impure, but the analysis indicated a monoxime.

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[18] (*a*) WHITMORE AND CHURCH, *J. Am. Chem. Soc.*, **54,** 3711 (1932); (*b*) CHURCH, WHITMORE, AND MCGREW, *ibid.*, **56,** 176 (1934).

Anal. Calc'd for $C_{11}H_{15}N_3O_2$: C, 59.70; H, 6.84; N, 19.00.
Found: C, 58.68, 59.10, 60.21; H, 6.72, 8.30, 7.81; N, 18.92.

(*c*) *Bromination.*—A solution of bromine in chloroform (10%) was added dropwise to a cold solution of II (0.2 g.) in chloroform (10 cc.) until the color of bromine was permanent. The solution after washing with bisulfite and then with water was dried. Evaporation of the solvent left a small amount of yellow oil which solidified when rubbed with a little cold methanol. The solid was crystallized several times; first from dilute methanol, then from dilute acetone, and finally from petroleum ether. It was light yellow and melted at 83-84°.

Anal. Found: C, 47.23; H, 4.83; N, 9.53.

(*d*) *Reduction.*—A solution of II (0.61 g.) in acetic acid (10 cc.) and water (5 cc.) was boiled for three hours with granulated zinc (1.5 g.). The product (0.2 g.) was nearly colorless and melted at 250-256° with some sublimation. Acetylation with acetic anhydride and a drop of sulfuric acid gave 60 mg. of a brown solid melting at 115-125°.

Repetition of the experiment gave a colorless product melting at 198-200° (decomp.). When this product was suspended in a solution of ferric chloride, it was not oxidized to duroquinone nor to II. Acetylation of the compound melting at 198-200° gave a light tan solid (0.17 g.) which melted at 130-138° after it was crystallized twice from dilute methanol.

Reduction of II by stannous chloride and hot hydrochloric acid gave colorless needles which melted at 213-215°. The compound contained no nitrogen, and when oxidized by ferric chloride, the product was duroquinone.

Anal. Found: C, 70.56; H, 7.95.

(*e*) *Acetylation.*—A small amount of II was boiled with acetic anhydride for 5 minutes, and the mixture was poured into ice water. No solid appeared after the anhydride had all decomposed. Excess bicarbonate was added, and the solution, after standing overnight, deposited duroquinone. Boiling saturated bicarbonate solution was without effect upon II, nor was any duroquinone formed when II (0.1 g.) was boiled with acetic anhydride (2 cc.) for 20 minutes, or when water (4 cc.) was added and boiling was continued for 30 minutes longer. But when an excess of bicarbonate was added to this (warm) solution, duroquinone was precipitated immediately.

Reactions of III. (*a*) *Thermal decomposition.*—The reaction was followed quantitatively by measuring the nitrogen evolved, sweeping it out by a current of carbon dioxide and collecting it over 50% potassium hydroxide solution. With chlorobenzene (b.p., 132°) as the solvent, the figures (percentage of the theoretical value for $C_{12}H_{16}N_4O_2$) for the nitrogen evolved were: 100.54; 101.04; 97.88; 96.60. Evaporation of the solvent *in vacuo* left a yellow residue (VI) which partially solidified. The substance was pressed on a clay plate, and the solid was then crystallized several times from dilute ethanol or dilute acetone. It was white, melted at 143-144° and contained no nitrogen. The substance was insoluble in water, dilute sodium hydroxide, and dilute hydrochloric acid. It was soluble in cold concentrated sulfuric acid, and reprecipitated on dilution. The acetone solution of VI did not decolorize permanganate, even when it was boiled. Phenylhydrazine was without action.

Anal. Calc'd for $C_{12}H_{16}O_2$: C, 74.95; H, 8.40; mol. wt., 192.
Found: C, 74.82; H, 8.34; mol. wt., (Rast) 191.

The *oxime* of VI was obtained in 73% yield by the usual procedure. It was white and melted above 260° (very dark at 250°).

Anal. Calc'd for $C_{12}H_{18}N_2O_2$: C, 64.82; H, 8.17; N, 12.60.
Found: C, 64.34; H, 8.23; N, 12.26.

(*b*) *Phenyl isocyanate.*—The substance III (0.2 g.) was heated with several cc. of phenyl isocyanate. No reaction was apparent, but the solid dissolved. The solution was cooled, extracted with ligroïn, and the solvent was evaporated. The residue, crystallized from methanol, melted at 138–139° (decomp.) and was identified as IV by determining the mixture melting point. Repetition of the experiment did not give the same results; instead, a compound melting at 160–161° was obtained which was identical with the product of the action of phenyl isocyanate upon IV. In addition to this product, there resulted a somewhat larger quantity of a colorless solid melting at 127–128° (decomp.) but which was not unchanged III.

Anal. (Substance melting at 127–128°.) Found: C, 67.51; H, 5.39; N, 14.72.

1-Naphthyl islcyanate was without action upon III.

(*c*) *Hydroxylamine* gave no oxime with III; the only product that could be obtained from the reaction was a small amount of red oil.

(*d*) *Phenylhydrazine.*—A solution of III in dilute ethanol gave an immediate precipitate when phenylhydrazine and a little acetic acid were added. The solid, crystallized twice from dilute ethanol, was white and melted at 144–145° (decomp.).

Anal. Calc'd for $C_{18}H_{22}N_6O$ (mono phenylhydrazone): C, 63.87; H, 6.55; N, 24.84.

Found: C, 64.03; H, 6.68; N, 24.60.

(*e*) *Acetylation of III* with acetic anhydride and a drop of sulfuric acid gave a diacetate which melted above 260° after crystallization from ethanol-ethyl acetate.

Anal. Calc'd for $C_{16}H_{20}N_4O_4$: C, 57.80; H, 6.07; N, 16.87.

Found: C, 58.09; H, 6.28; N, 16.57.

(*f*) *Silver salt.*—The substance III (0.5 g.) was allowed to stand with concentrated ammonium hydroxide (15 cc.) until solution was complete. The excess ammonia was removed under reduced pressure, and a solution of silver nitrate (0.7 g.) in water (5 cc.) was added. The light-tan precipitate was filtered and washed with water, ethanol and ether. The product weighed 0.67 g., and melted with decomposition at 128–129°.

Anal. Found: Ag, 34.94, 34.57, 34.59, 34.16.

(*g*) *Hydrochloric acid.*—Concentrated hydrochloric acid (3 cc.) and III (0.1004 g.) were placed on a watch glass and allowed to stand in a vacuum desiccator until the liquid evaporated. The white hygroscopic product weighed 0.1496 g. and melted with decomposition at 112–113°. The material did not depress the melting point of a similar product obtained from IV. The weight of the product indicated a molecular weight of 370. Titration with standard alkali gave values of 328 and 332 for the neutral equivalents, assuming two acid groups were titrated. The titrated solutions gave duroquinone when steam distilled. When hydrochloric acid was allowed to act upon III in the presence of dimedon, the solution did not deposit any precipitate —hence formaldehyde was apparently not eliminated.

(*h*) *Hydrobromic acid.*—By the use of the procedure described above, there was obtained from III (0.1012 g.) and 40% hydrobromic acid (2 cc.), a light-brown solid (0.1734 g.) which darkened at 145° and melted with decomposition at 155–156°. From the quantities of material involved, a molecular weight of 425 was indicated. When the material was suspended in ethanol-ether, it became colorless, and the solid then melted with decomposition at 139–140°. This material did not depress the melting point of a product obtained by the action of hydrobromic acid upon IV.

Anal. (Sample melting at 139–140°.) Found: C, 39.65; H, 6.11; N, 14.52.

Reactions of IV. (*a*) *Thermal decomposition.*—This was carried out as described under III, with bromobenzene (b.p. 156°) as the solvent. The percent of nitrogen evolved in two experiments was 60.65 and 63.28 respectively. The substance IV (2 g.) was decomposed by heating small portions of it in a nickel crucible. Decomposition occurred at 155–160°. When there was no further evolution of gas, the bath was held at 175–180° for 15 minutes. Upon cooling the melt partially solidified. The hot acetone solution filtered, diluted and cooled, deposited 0.27 g. of a light-brown solid melting with decomposition at 128–129°. Four similar thermal decompositions gave the following products: (*a*) 3 g. of IV gave 0.625 g. of nearly colorless material melting at 115°; (*b*) 4 g. of IV gave 0.4 g. of colorless material, melting at 124–127°, and 0.61 g. of buff-colored material melting at 103–105°; (*c*) 5 g. of IV gave 1.15 g. of solid melting at 103–113°; the acetone filtrate, when steam distilled, gave 0.6 g. of duroquinone and 0.8 g. of a black non-volatile residue; (*d*) 5 g. of IV gave 0.51 g. of material melting at 125–129°, 0.38 g. melting at 102–104°, 0.34 g. of duroquinone, and 1.485 g. of non-volatile residue.

Analysis indicated that the two decomposition products (VII and VIII) were isomers, formed by loss of one mole of nitrogen from IV.

Anal. Calc'd for $C_{12}H_{16}N_2O_2$: C, 65.41; H, 7.32; N, 12.72; mol. wt., 220.

Found: (substance melting at 124–127°) C, 65.65; H, 6.87; N, 12.41; mol. wt. (Rast), 250, 258.

Found: (substance melting at 103–113°) C, 65.62; H, 7.33; N, 12.63.

Upon standing, both solids decomposed to yellow oils which could not be solidified. The substance melting at 103–113° (0.2 g.) was heated for 4 hours on the steam bath with acetic anhydride and a drop of sulfuric acid. The solution was diluted, cooled, made alkaline with carbonate and extracted with ether. Evaporation of the ether left 0.16 g. of material melting at 90–117°. Crystallized once from ether-petroleum ether, the substance melted at 138–143°; and when an attempt was made to crystallize this from dilute methanol, the substance decomposed. The decomposition product melting at 124–127° apparently gave the same acetyl derivative, but this also decomposed during attempted recrystallization.

The low-melting isomer (103–113°) gave no oxime when treated with hydroxylamine in the usual manner, nor could any of the starting material be recovered. When the low-melting isomer (0.5 g.) in acetic acid (10 cc.) and water (7 cc.) was boiled for 7 hours with zinc (2 g.) it gave 0.22 g. of material melting at 124–128° and showing no depression in melting point when mixed with the high-melting (124–127°) decomposition product.

(*b*) *2,4-Dinitrophenylhydrazine.*—No phenylhydrazone was obtained by the customary procedure, and from 0.5 g. of IV, 0.38 g. of unchanged material was recovered.

(*c*) *Hydroxylamine.*—The usual procedure for preparation of oximes converted IV (0.4 g.) into duroquinone, and a similar result was obtained when an attempt was made to prepare a semicarbazone of IV.

(*d*) *Methyl sulfate* and alkali completely destroyed IV; only a trace of brown oil could be isolated.

(*e*) *Potassium cyanate.*—To a cold solution of IV (1 g.) in acetic acid (60 cc.) there was added with shaking solid potassium cyanate (5 g.) in small portions. The solution, after standing at 5° for 3 days, was made alkaline with potassium carbonate, and the colorless precipitate was removed. It was dissolved in hot acetic acid, the solution was filtered and the substance was reprecipitated by neutralizing the filtrate with dilute sodium hydroxide. The substance (a urea?)[19] was white, darkened at 245° and melted with decomposition at 251°.

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[19] LOCQUIN AND HEILMAN, *Compt. rend.*, **180**, 1757 (1925).

Anal. Found: C, 49.50; H, 5.62; N, 24.19.

(*f*) *Oxidation.*—A cold (10°) solution of IV (0.5 g.) in sodium hydroxide (10 cc., 10%) and water (40 cc.) was oxidized by addition of permanganate (50 cc., 2%) in 2 cc. portions. The color was immediately discharged. After standing over night at 0°, the precipitated oxides were removed and the alkaline filtrate was extracted with ether and with chloroform. Nothing was removed by the organic solvents. The aqueous solution was acidified with dilute sulfuric acid and again extracted; again nothing was removed. The aqueous layer was then made alkaline and evaporated to dryness. The solid residue (0.5 g.) was dissolved in water (3 cc.), hydrochloric acid (2 drops) was added and the solution was refluxed with *p*-nitrobenzyl bromide (0.5 g.) and alcohol (7 cc.) for 2 hours. The cooled and diluted solution deposited a solid which, when crystallized from alcohol was colorless and melted at 77–78°. The reported melting point of *p*-nitrobenzyl acetate is 78°.[20]

Oxidation of IV (1 g.) in warm (60°) sodium hydroxide (15 cc., 10%) by slow addition of iodine (6.25 g.) in potassium iodide (12.5 g.) and water (50 cc.) gave, when the reaction mixture was diluted with water (15 cc.), a small amount (ca. 15 mg.) of a colorless solid melting at 144–145°, but which was not IV.

Anal. Found: C, 63.58; H, 7.90; N, 24.79.

Extraction of the alkaline filtrate with ether removed 25 mg. of colorless material melting at 106–109°. After crystallizing the substance several times from water, the melting point was 107–108. The water solution, when hot, had a strong phenolic odor.

Anal. Found: C, 49.92; H, 5.95; N, 21.47.

No other products could be isolated.

(*g*) *Phenyl isocyanate.* When heated with several cc. of phenyl isocyanate, the substance IV (0.2 g.) dissolved. Methanol was added to decompose the excess reagent, the hot solution was filtered and the filtrate, on cooling, deposited a colorless solid melting with decomposition at 160–161°. This substance was identical with the substance obtained from III by the same procedure.

Anal. Calc'd for $C_{19}H_{21}N_5O_3$: C, 62.10; H, 5.77; N, 19.06.
Found: C, 62.40; H, 5.82; N, 19.42.

As in the case of III, 1-naphthyl isocyanate was without action upon IV.

(*h*) *Aniline.*—The substance IV (1 g.) was warmed on the steam bath for 5 hours with aniline (0.465 g.) and acetic acid (1.5 cc.). The black liquid was poured into excess sodium bicarbonate, and the solution was extracted with ether. The ether was washed with dilute hydrochloric acid (to remove aniline), then dried and evaporated. The residue was 60 mg. of duroquinone, and steam distillation of the acid washings gave an additional 70 mg. of the quinone. No other material could be isolated, and no triazole was apparently formed.[21]

(*i*) *Silver salt.*—By the same procedure as that used in the case of III, a silver salt (0.45 g.) was prepared from IV (0.5 g.). The substance was a heavy, white solid, which melted at 136–137° with decomposition.

Anal. Found: C, 26.57, 25.99, 25.40, 26.43; H, 3.48, 3.68, 4.42, 3.99; N, 16.78; Ag, 35.20, 34.69, 34.10, 34.53.

The silver salt was unaffected by boiling it for 10 hours with methyl iodide in ether. When methanol was used as the solvent, the product was an orange oil which could not be solidified.

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[20] KAMM, "Qualitative Organic Analysis," John Wiley & Sons, Inc., New York, **1932**, p. 180.

[21] WOLFF, *Ann.*, **325**, 163 (1902); *ibid.*, **394**, 26 (1912).

(*j*) *Hydrochloric acid.*—Substance IV (0.1006 g.) was converted to the hydroscopic salt (0.1511 g.) by the same procedure as that used in the case of III. The salt melted with decomposition at 112–114°, and from the weight of the product, the molecular weight was 373.

Anal. Found: C, 37.53; H, 6.28, N.E. (two acid groups) 300, 312.

When the titrated solutions were steam distilled, duroquinone was obtained. Hydrolysis of the salt to duroquinone by alkali was carried out in the presence of benzaldehyde in an attempt to detect any hydrazine that might have formed. The result was negative, and blanks showed that one drop of dilute hydrazine hydrate gave a positive reaction. Similarly, a test for formaldehyde was made by subjecting IV to the action of hydrochloric acid in the presence of dimedon. This test was also negative, while the blanks were positive.

When IV (0.2 g.) was refluxed for 1.5 hours in alcohol (10 cc.) containing 3–4 drops of hydrochloric acid, the product was duroquinone.

(*k*) *Hydrobromic acid.*—Substance IV (0.1017 g.) was converted to the bromide (0.1765 g.) by the same procedure as that used in the case of III. The crude product, almost white, darkened at 145° and melted with decomposition at 153–154°. When shaken with a mixture of alcohol and ether, cooled, filtered, washed with ether and dried *in vacuo*, the salt was colorless, melted at 139–140° (decomp.) and was identical with the salt obtained by action of hydrobromic acid upon III. From the relative weights of IV and salt, the molecular weight was indicated as 430.

Anal. Found: C, 41.05; H, 5.99; N, 14.46; N.E. (two acid groups) 418, 428; Br. (addition of HNO_3 to the solutions after determining N.E., and titrating for Ag in the usual way), 36.92, 34.58.

When a small amount of the salt was dissolved in water and shaken with freshly precipitated silver oxide, there was an immediate precipitation of silver halide. The silver compounds were removed and the filtrate, after standing for an hour, was extracted with ether. Nothing was removed by the ether. After standing for 4 hours longer, the filtrate deposited a yellow solid which was identified as duroquinone.

SUMMARY

1. Diazomethane has been added to duroquinone, a completely substituted quinone.

2. Four products resulted; two isomeric compounds formed by addition of one molecule of diazomethane to one molecule of the quinone, and two isomeric products formed by addition of two molecules of diazomethane to one of the quinone.

3. The properties and reactions of these substances have been described, and structures have been proposed for them, as well as for the products of their thermal decomposition.

4. The reaction between duroquinone and diazomethane, unlike that of any other *p*-quinone, is confined entirely to the carbonyl groups and no pyrazolines are formed.