

unchanged glyoxalate and much tar. The former was distilled twice more for the preparation of a sample which had the following properties, b.p. 73–74°/0.3 mm., n_D^{25} 1.4806. This sample did not have a satisfactory carbon-hydrogen analysis, possibly because of contamination with unchanged glyoxalate X_{II}. However, XIII formed a 2,4-dinitrophenylhydrazone (see below) which gave highly acceptable analytical data.

Anal. Calcd. for C₈H₁₂O₂: C, 64.27; H, 7.19. Found: C, 62.04; H, 7.19.

The 2,4-dinitrophenylhydrazone, prepared in the usual manner, separated as orange-yellow needles from ethanol-ethyl acetate, m.p. 129–130°.

Anal. Calcd. for C₁₂H₁₄N₄O₆: C, 51.72; H, 4.63. Found: C, 51.86; H, 4.66.

Butylidene acetoacetic ester. This compound was prepared in 76% yield by the method of Cope and Hoffman.²² A

carefully redistilled sample had the following characteristics: b.p. 56°/0.1 mm., n_D^{25} 1.4515. It gave no color with ferric chloride solution; ultraviolet: λ_{\max} 220 m μ , ϵ_{\max} 6800; infrared: bands at 5.80, 5.98, 6.11 μ , shoulder 6.20 μ . The compound formed a 2,4-dinitrophenylhydrazone, m.p. 131–133°, orange-yellow needles from ethanol.

Acknowledgment. The author wishes to express his appreciation to Prof. E. E. van Tamelen for the suggestion of this problem and for much helpful advice.

MADISON, WIS.

(22) A. C. Cope and C. M. Hoffman, *J. Am. Chem. Soc.*, **63**, 3456 (1941).

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

Some Exploratory Syntheses of Benzosuberans and Tetrahydrobenzazepinones and Some Related Diazoöxides

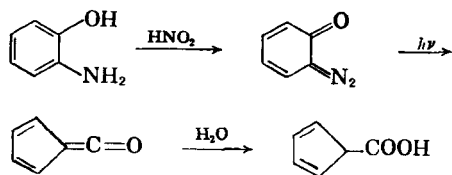
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Received May 5, 1960

The following new diazoöxides have been investigated in exploration of the feasibility of their ring contraction as a general laboratory preparative method: benzosuberan-5-ol-2,3-diazoöxide, benzosuberan-3,2-diazoöxide, 4,5-dihydro-1-benzazepin-2(3H)-one-7,8-diazoöxide, acetophenone-3,4-diazoöxide, acetanilide-3,4-diazoöxide, benzophenone-3,4-diazoöxide, and diphenylmethane-3,4-diazoöxide. Irradiation with ultraviolet light of intensities available without unusual equipment led to mixtures of dyes presumably arising from coupling of ring-contraction products with the parent diazoöxides. Thermal rearrangement was successful for converting naphthalene-1,2-diazoöxide to indenecarboxylic acid derivatives, but similar treatment was not successful with diazoöxides derived from the benzene ring. Naphthalene-1,2-diazoöxide is reduced to β -naphthol in preparative yields by heating with benzyl alcohol or benzylamine. Several synthetic sequences leading to benzosuberan and 3,4-dihydrobenzazepinone derivatives are reported.

INTRODUCTION

In 1944 S \ddot{u} s reported² the first example of the extension to *o*-diazoöxides of the Wolff rearrangement³ of α -diazo ketones. This process accomplishes the remarkable result of shrinking a benzene ring, as it exists in the *o*-aminophenols from which *o*-diazoöxides are prepared, to cyclopentadiene-carboxylic acid derivatives. As reported by S \ddot{u} s and extended⁴ by him and by De Jonge and Dijkstra,⁵ the conversion is brought about by radiation in the near ultraviolet.



(1) From the doctoral thesis of W.L.B., Edgar C. Britton, Fellow in Organic Chemistry, 1953–1955. Present address: American Cyanamid Co., Bound Brook, N. J.

(2) O. S \ddot{u} s, *Ann.*, **556**, 65 (1944).

(3) W. E. Bachmann and W. S. Struve, *Org. Reactions*, **1**, 38 (1942).

(4) O. S \ddot{u} s, *Ann.*, **593**, 91 (1955).

(5) J. De Jonge and R. Dijkstra, *Rec. trav. chim.*, **67**, 328 (1947).

We were interested in exploring the compatibility of the benzene ring-shrinking process to compounds containing carbonyl and amide groups, particularly in cases where the benzene ring is fused to a seven-membered ring. At the same time, we were interested in adapting the reaction as a preparative procedure capable of being accomplished with ordinary equipment. As it has been reported, the reaction requires exceptionally intense ultraviolet radiation for success in synthetic applications; the lower intensities ordinarily available lead to appreciable quantities of dyes derived from coupling of yet unphotolyzed diazoöxide with the cyclopentadiene system. The work reported here consists of the synthesis and investigation of some derivatives of benzene *o*-diazoöxide, some investigations of experimental techniques for rearranging them and also naphthalene-1,2-diazoöxide, and some synthetic schemes leading to diazoöxides in the benzosuberan and 3,4-dihydrobenzazepinone series.

RESULTS AND DISCUSSION

Acetophenone-3,4-diazoöxide was prepared as a highly unstable, explosive solid by diazotizing 3-amino-4-hydroxyacetophenone and liberation of

the product with sodium carbonate. The originally extremely dark red substance exploded when heated to 96°, and showed infrared absorption characteristic of the diazooxide structure. Deterioration was rapid, however, even on storage *in vacuo* in the dark, and a lighter red, nonexplosive substance was produced; it was not further investigated.

For the preparation of acetanilide 3,4-diazo-oxide, 3-nitro-4-hydroxyacetophenone was first converted to 3-nitro-4-hydroxyacetanilide by the Schmidt reaction. Reduction to 3-amino-4-hydroxyacetanilide and diazotization gave the diazooxide as an explosive orange solid.

The conversion of 3-amino-4-hydroxybenzophenone to benzophenone-3,4-diazooxide, an explosive red solid, was accomplished satisfactorily only in the presence of copper sulfate. 3-Amino-4-hydroxydiphenylmethane could not be converted to the diazooxide in as simple a manner as the foregoing substances, but by extraction into ether as fast as the diazooxide was liberated from the diazonium solution by the addition of sodium carbonate, it was obtained as explosive, golden flakes.

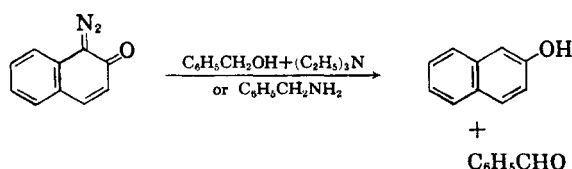
Photolyses of the foregoing diazooxides and of naphthalene-1,2-diazooxide were carried out near 0° in dilute, acidic aqueous solution with a lamp delivering 15.5 watts in the 380–500 mμ region, in which diazooxide absorption bands lie.⁶ These conditions are essentially those of Süs, except that our radiation source, which is near the maximum intensity obtainable with simple apparatus and compatible with cooling needs, was much less intense. Under these conditions, coupling to give dyes predominated with naphthalene-1,2-diazooxide, and only a poor yield of indenecarboxylic acid was obtained. With the other diazooxides, only coupling products were obtained; the addition of heavy metal salts or changing the acidity did not help. These were complex mixtures, as shown by chromatography and partial fractional crystallization, and only from benzophenone-3,4-diazooxide could a tentatively identifiable compound be isolated.

We next turned attention to the catalytic agents effective with α-diazo ketones. The silver benzoate-triethylamine catalyst developed by Newman and Beal⁷ did not cause noticeable gas evolution from naphthalene-1,2-diazooxide, but instead converted it to a black gum. Copper powder was similarly ineffective.

There remained thermal rearrangement, for which there was the encouraging precedent of the formation of indene compounds from the pyrolysis of naphthalene-1,2-diazooxide.⁸ These substances presumably arose from the ketene formed initially, in which case it might be intercepted before un-

desirable reactions by pyrolyzing the diazooxide in the presence of an amine or alcohol. Such an event was realized by dropping naphthalene-1,2-diazooxide into aniline, *p*-toluidine, or phenol at 180°; indene-1-carboxanilide was obtained in 32% yield, the *p*-toluidide in 34%, and phenyl indene-1-carboxylate in 57% yield. Unfortunately, the analogous reaction could not be realized with the other diazooxides studied; cyclopentadienecarboxylic acids could not be isolated, and complex mixtures of dyes similar to those resulting from photolysis were obtained. It appears that the diazo coupling reaction is a faster reaction with cyclopentadienes as contrasted to indenenes, and we reluctantly conclude that the ring-shrinking rearrangement is not likely to be a useful preparative method unless exceptional facilities for high intensity radiation are available.

A potentially useful reaction was observed when thermal rearrangement of naphthalene 1,2-diazo-oxide was attempted in benzyl alcohol instead of phenol. Instead of an ester, β-naphthol was produced in 47% yield, accompanied by benzaldehyde. When tributylamine was also present, reaction took place spontaneously at room temperature to produce a 44% yield of β-naphthol. Benzoyl peroxide did not initiate reaction at 83°. With benzylamine alone the diazooxide was converted to β-naphthol at either room temperature or 184° in 50–53% yields. When the benzyl alcohol reaction was tried with diphenylmethane-3,4-diazo-oxide or benzophenone-3,4-diazooxide, only gums and amorphous colored solids could be isolated. It appears that the reaction might nevertheless have usefulness in the naphthalene series as an alternative when conventional deamination⁹ gives unsatisfactory results.



4,5-Dihydro-1-benzazepin-2(3H)-one-7,8-diazo-oxide (V) was prepared from 7-hydroxy-1-tetralone (I) as outlined in Chart A, which also shows some related transformations which provide support for the assigned structures. The Schmidt reaction was used to convert I to II, followed by nitration to give III. Catalytic reduction yielded an amine (IV) with the reducing properties to be expected of an *o*-amino phenol. Diazotization was satisfactory only in strongly acidic solution, and the diazooxide V could not be isolated from its salt without rapid decomposition.

(6) L. C. Anderson and M. Roedel, *J. Am. Chem. Soc.*, **67**, 955 (1945); J. D. C. Anderson, R. J. W. Le Fevre, and I. R. Wilson, *J. Chem. Soc.*, 2082 (1949).

(7) M. S. Newman and P. F. Beal, III, *J. Am. Chem. Soc.*, **72**, 5161 (1950).

(8) L. Horner, E. Spietschka, and A. Gross, *Ann.*, **573**, 17 (1951); P. Yates and E. W. Robb, *J. Am. Chem. Soc.*, **79**, 5760 (1957).

(9) N. Kornblum, *Org. Reactions*, **II**, 262 (1944).

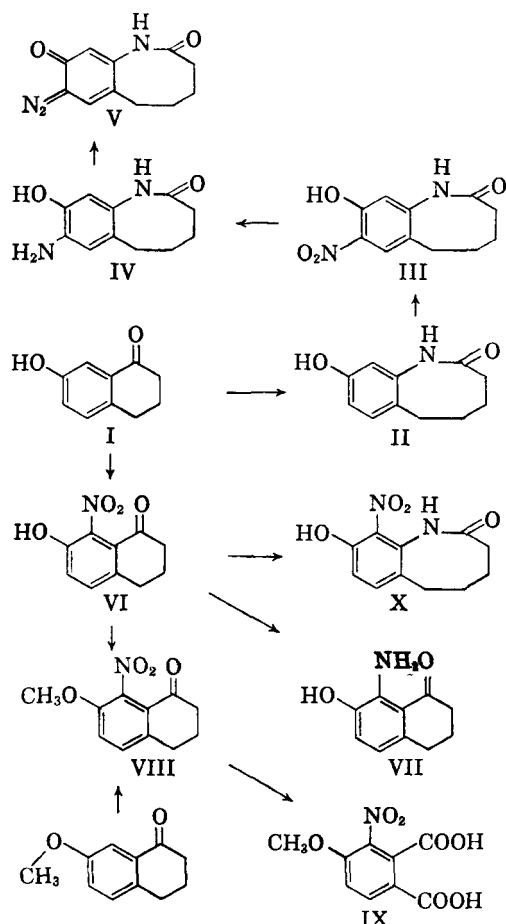


Chart A

The assignment of structure III was confirmed by the synthesis of the isomeric *o*-nitro phenol, X. Nitration of I gave a nitrophenol (VI) which was reduced to the aminophenol VII, which showed the reducing properties of an *o*-aminophenol. Methylation of VI gave the same nitromethoxy-tetralone (VIII) as was obtained by the direct nitration of 7-methoxy-1-tetralone; oxidation to 3-nitro-4-methoxyphthalic acid (IX) established the position of the nitro group. The Schmidt reaction converted VI into the nitrophenolic lactam X, whose melting point and infrared spectrum showed it to be distinct from its isomer, III. The methoxy-nitrotetralone VIII was also converted to a lactam by the Schmidt reaction; this compound is soluble without hydrolysis in 10% sodium hydroxide, as is characteristic of *o*- and *p*-nitroanilides.¹⁰

The phenolic lactam II was also approached from 7-nitro-1-tetralone. Although this route was abandoned in favor of that in Chart A, our initial work on it disclosed an erroneous identification in the literature. The Schmidt reaction converted 7-nitro-1-tetralone unequivocally to 8-nitro-4,5-dihydro-1-benzazepin-2-one, m.p. 220–222°. This

compound had already been reported by von Braun¹¹ and Rawicz as the product, m.p. 225°, obtained by the direct nitration of the lactam 4,5-dihydro-1-benzazepin-2-one. We repeated this preparation and confirmed the melting point, but found that the melting point is depressed by 8-nitro-4,5-dihydro-1-benzazepin-2-one prepared from 7-nitro-1-tetralone. Accordingly, the product obtained by nitrating the lactam must be the 7-nitro isomer, not the 8-nitro as previously reported, and is thus the result of nitration *para* to the amide grouping, as is reasonable to expect as a result of normal orientation behavior.

Methanesulfonic acid was found to be the catalyst-solvent of choice for the foregoing several Schmidt reactions on phenolic acetophenones and tetralones. Trichloroacetic acid¹² in some cases gave little amide and much decomposition, perhaps as a result of the higher temperature (50°) needed. Trifluoroacetic acid, which allows operation at room temperature, gave erratic results and a product usually contaminated with polymeric material.

In view of our successful conversion of cyclic ketones to lactams by means of the Schmidt reaction, we reexamined the report by Huisgen¹³ that benzosuberan-5-one gives mostly tetrazole and only 10% lactam. The experimental conditions reported were such as would favor tetrazole formation. Under the general conditions we have been using, however, benzosuberan-5-one is converted to the lactam 3,4,5,6-tetrahydro-1-benzazocin-2-one in high yield (82% as the trichloroacetic acid addition compound), and an anomaly is thus resolved.

Benzosuberan diazoöxides were first approached by a route involving the Demyanov ring expansion of appropriate tetralin derivatives, but when an alternate route proved more attractive, this one was discontinued. It was carried to the stage of 1-aminomethyl-7-methoxytetralin, prepared by the Curtius degradation of ethyl 7-methoxytetralin-1-acetate, obtained from 7-methoxy-1-tetralone by the Reformatsky reaction, dehydration, and hydrogenation. An attempt to prepare 1-amino-methyl-7-methoxy-1-tetralol for utilization in the Tiffeneau-Demyanov ring expansion failed when formation of the hydrazide from ethyl 7-methoxy-1-hydroxytetralin-1-acetate could not be accomplished without dehydration.

The successful alternative synthesis starts with benzosuberanone (XI), and is outlined in Chart B. Nitration gave 3-nitrobenzosuberan-5-one (XII), which was reduced first to the nitro alcohol (XIII) and then to the amino alcohol (XIV), which was converted to benzosuberan-3,5-diol (XV) by hy-

(10) V. Meyer and P. Jacobson, *Lehrbuch der Organischen Chemie*, Vol. II, Verlag von Veit and Co., Leipzig, 1902, p. 216; S. Kleemann, *Ber.*, 19, 334 (1886).

(11) J. von Braun and M. Rawicz, *Ber.*, 49, 799 (1916).

(12) J. R. Dice and P. A. S. Smith, *J. Org. Chem.*, 14, 179 (1949).

(13) R. Huisgen, *Ann.*, 574, 171 (1951).

drolyzing its diazonium salt. Nitration gave a nitrophenol (XVI), which was reduced to the aminophenol (XVII), diazotization of which gave the diazoöxide XVIII as an explosive, yellow-brown solid.

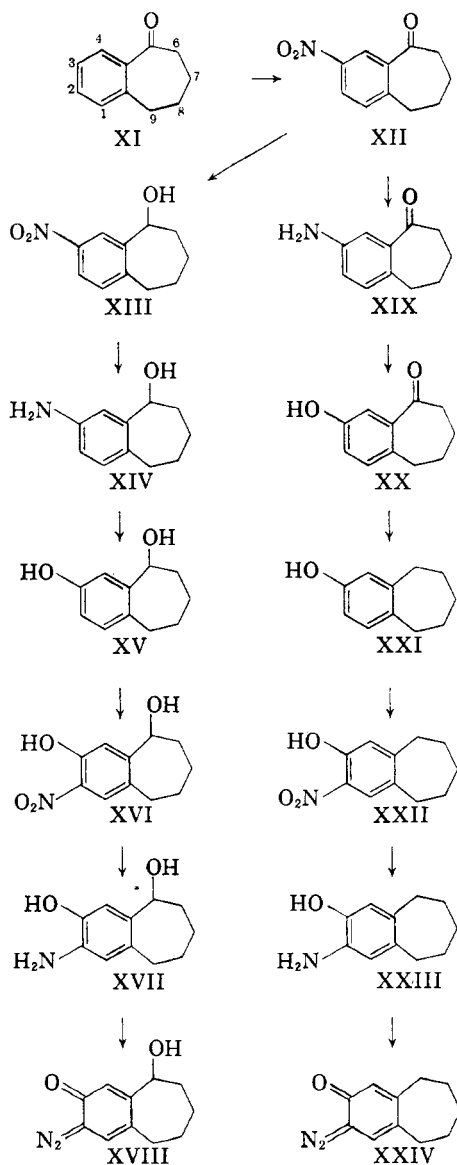


Chart B

The position of the nitro group in XII was effectively established by oxidation of XII to 4-nitrophthalic acid, which strictly shows only that the nitro group is in either the 2- or 3-position. However, the 3-position, *meta* to the carbonyl group, is the only one consistent with orientation rules, and is analogous to the positions in which α -hydrindanone¹⁴ and α -tetralone¹⁵ are nitrated.

The position taken by the nitro group in XVI would be either 2- or 4- according to orientation

effects and the successful conversion to a diazoöxide. The vicinal position, 4-, is improbable on steric grounds; examination of scale models (Courtauld) shows that a nitro group can only be attached at the 4-position when the 5-hydroxyl group is axial, and even then crowding is sufficient to prevent the nitro group becoming coplanar with the benzene ring. The infrared spectrum of XVI in dilute solution in chloroform showed two bands in the O—H stretching region. One, at 3570 cm^{-1} , is properly located for unassociated aliphatic hydroxyl. The other somewhat wider band centered on 3225 cm^{-1} is properly located for a chelated phenol and is superimposable on the band at the same position in the spectrum of *o*-nitrophenol. As effective chelation requires coplanarity of the nitro group with the benzene ring and the phenolic hydroxyl group and only the 2-position is uncrowded enough to allow this, the structural assignment of XVI follows.

The synthesis of the unsubstituted benzosuberone diazoöxide XXIV is also shown in Chart B. 3-Nitrobenzosuberone (XII) was reduced catalytically to the amino ketone XIX, which was diazotized and hydrolyzed to obtain the phenolic ketone XX. Reduction of XX afforded an alternate route to the phenolic alcohol XV. Clemmensen reduction of XX failed, but the Huang-Minlon modification of the Wolff-Kishner reduction gave 2-hydroxybenzosuberone (XXI), which showed the same physical properties as those reported by Prelog, Ruzicka, and Metzler,¹⁶ who prepared it by a more complex route. Nitration to XXII and reduction of XXII to the *o*-aminophenol XXIII were accomplished without complication, and diazotization of XXIII gave the benzosuberone 2,3-diazoöxide (XXIV) as an explosive light brown solid.

The position of the nitro group in XXII is inferred by analogy with 3,4-xyleneol,¹⁷ hydrindanol-5,¹⁸ and 6-hydroxytetralin,^{18,19} all of which have been shown to undergo nitration at the nonvicinal position *ortho* to the hydroxyl group. That the nitro group is *ortho* to the hydroxyl group is also shown by ultimate conversion to a diazoöxide, and by the properties of the aminophenol XXIII, which reduces Tollens' reagent instantly.

The several nitrations of phenolic compounds mentioned in the foregoing discussion were in most cases tried with conventional solvents (sulfuric or glacial acetic acids), but the results were often poor in yield and quality. With trifluoroacetic acid as the reaction medium, however, high yields of

(16) V. Prelog, L. Ruzicka, and O. Metzler, *Helv. Chim. Acta*, **30**, 1741 (1947).

(17) E. Diepolder, *Ber.*, **42**, 2916 (1909); G. D. Parks, *J. Chem. Soc.*, 2143 (1948).

(18) R. T. Arnold and R. L. Evans, *J. Am. Chem. Soc.*, **62**, 556 (1940).

(19) H. Thomas and W. Kross, *Arch. Pharm.*, **265**, 336 (1927).

(14) C. K. Ingold and H. A. Piggott, *J. Chem. Soc.*, **123**, 1469 (1923).

(15) G. Schroeter, *Ber.*, **63**, 1317 (1930).

clean products were uniformly obtained, and this solvent is strongly to be recommended.

The infrared spectra of Nujol mulls of the diazo-oxides described here are in agreement with the observations of Le Fevre, Sousa, and Werner²⁰; diazo absorption was found in the region 2120–2200 cm^{-1} , and that of the flanking carbonyl group at 1580–1640 cm^{-1} , and was always clearly distinguishable from ketone or amide carbonyl. Splitting of the diazo absorption into two bands separated by 50 cm^{-1} was observed with benzo-suberan-2,1-diazo-oxide and acetanilide-3,4-diazo-oxide.

EXPERIMENTAL²¹

Acetophenone-3,4-diazo-oxide. A solution of 1.0 g. (0.0058 mole) of 3-amino-4-hydroxyacetophenone²² (prepared by hydrogenation of 3-nitro-4-hydroxyacetophenone²³) in 175 ml. of 10% hydrochloric acid was diazotized at 2° with a solution of 0.42 g. (0.0061 mole) of sodium nitrite. Cold sodium carbonate solution was added until the solution was basic, and the dark brown mixture was extracted with three 100 ml. portions of chloroform. The combined dried chloroform extracts were evaporated in the dark in a stream of nitrogen, leaving 0.40 g. (62%) of reddish-black solid, m.p. 96° with explosion. The infrared spectrum obtained immediately showed absorption bands at 2150, 1700, and 1630 cm^{-1} , consistent with the structure acetophenone-3,4-diazo-oxide, but decomposition was rapid, even *in vacuo* in the dark. A nonexplosive red solid was formed which was not further investigated. Because of this instability, elementary analyses of this diazo-oxide could not be obtained.

3-Nitro-4-hydroxyacetanilide. To a solution of 18.1 g. (0.10 mole) of 3-nitro-4-hydroxyacetophenone in 200 ml. of technical grade methanesulfonic acid at room temperature was added 11 g. (0.15 mole) of sodium azide in small portions during 4 hr. with stirring. Ten hours after the completion of the addition, the black mixture was poured on cracked ice and neutralized with sodium bicarbonate. A yellow solid, 15.0 g., m.p. 147–152°, precipitated. The filtrate was extracted with three portions of chloroform. Treatment of the extracts with charcoal and evaporation gave an additional 2.1 g.; total yield, 17.1 g. (82%). Recrystallization from aqueous alcohol gave 15.0 g., m.p. 154–156° (reported²⁴ m.p. 157–158°).

Acetanilide-3,4-diazo-oxide. Hydrogenation of 3-nitro-4-hydroxyacetanilide in methanol solution in a Parr apparatus over Adams' Catalyst, concentration of the filtered solution and saturation with hydrogen chloride gave 3-amino-4-hydroxyacetanilide²⁵ as its hydrochloride, m.p. 218–221° dec., in quantitative yield. A solution of 1.5 g. (0.0074 mole) of the hydrochloride and 1.0 ml. of concd. hydrochloric acid in 100 ml. of water was diazotized at 4° with 0.75 g. (0.011 mole) of sodium nitrite, added all at once in a little water. After 15 min. the resulting dark brown solution was made basic with cold sodium carbonate solution and extracted with three 75-ml. portions of chloroform. The combined

extracts were dried and evaporated to incipient crystallization, and then diluted with petroleum ether (b.p. 60–70°). On standing in a refrigerator, 0.68 g. (52%) of orange solid precipitated; m.p. 120° expl., infrared absorption at 2200, 2150, 1690, and 1640 cm^{-1} .

Anal. Calcd. for $\text{C}_8\text{H}_7\text{N}_2\text{O}_2$: C, 54.23; H, 3.99; N, 23.72. Found: C, 54.35, 54.29; H, 4.20, 4.17; N, 23.47, 23.82, 23.36.

Benzophenone-3,4-diazo-oxide. A suspension of 1.38 g. (0.0057 mole) of 3-nitro-4-hydroxybenzophenone²⁶ in 100 ml. of absolute ethanol was hydrogenated at atmospheric pressure in the presence of 0.40 g. of Adams' Catalyst. The filtered mixture was treated with charcoal and evaporated to a small volume under nitrogen and aspirator vacuum. Dilution with ca. 200 ml. of ether and treatment with hydrogen chloride gas precipitated a nearly colorless granular solid, 1.29 g. (91.5%), m.p. 185–196° dec. This presumed 3-amino-4-hydroxybenzophenone hydrochloride decomposed rapidly on exposure to air, and so was used at once in the next step without recrystallization or analysis.

This procedure gave the best results of the several variations tried. A solution of 0.17 g. (0.0025 mole) of sodium nitrite and 0.10 g. (0.0006 mole) of anhydrous copper sulfate in 10 ml. of water was cooled to 3° and then added all at once with shaking to a solution of 0.48 g. (0.0019 mole) of the foregoing crude amine hydrochloride in 30 ml. of water, cooled to 3°. The fluffy yellow precipitate which formed immediately was collected and dried in the dark; 0.42 g. (95%), m.p. 114° expl. Recrystallization from aqueous ethanol gave stout, lustrous red needles, m.p. 116° expl., infrared absorption at 2170, 1610, and 1580 cm^{-1} .

Anal. Calcd. for $\text{C}_{13}\text{H}_9\text{N}_2\text{O}_2$: C, 69.63; H, 3.60. Found: C, 69.56, 69.91, 69.70; H, 4.01, 3.82, 3.69.

Diphenylmethane-3,4-diazo-oxide (4-Benzylbenzene-2,1-diazo-oxide). 3-Nitro-4-hydroxydiphenylmethane²⁷ was hydrogenated at near atmospheric pressure in suspension in absolute ethanol with Adams' Catalyst. Evaporation of the filtered mixture to a small volume, dilution with ether, and treatment with hydrogen chloride precipitated the presumed 3-amino-4-hydroxydiphenylmethane hydrochloride in essentially theoretical yield. It was used at once.

The conditions used for preparing the benzophenone analog from the amine gave only tar; the following procedure was successful, however. A cold solution of 0.8 g. (0.0116 mole) of sodium nitrite in a little water was added all at once to a solution of 2.0 g. (0.0085 mole) of the foregoing crude amine hydrochloride and 4 ml. of concd. hydrochloric acid in 100 ml. of water chilled to 3°. After 15 min. the excess nitrous acid was destroyed with sulfamic acid and the solution was filtered. The cold filtrate was overlaid with ca. 150 ml. of ether and mechanically stirred rapidly while cold dilute sodium carbonate solution was added until the solution became basic. After 10 min. the ether layer was removed and the aqueous layer was extracted with ca. 100 ml. of ether. The combined ether extracts were washed once with water, dried in the dark over calcium sulfate, and treated with charcoal. The solution was then rapidly evaporated to half its volume in a stream of dry air and ca. 100 ml. of petroleum ether (b.p. 60–70°) was added. Further evaporation in an air stream with periodic addition of small portions of petroleum ether precipitated fragile golden flakes; 1.38 g. (72%), m.p. 72–74° dec., infrared absorption at 2200, 2130, and 1630 cm^{-1} .

Anal. Calcd. for $\text{C}_{13}\text{H}_{10}\text{N}_2\text{O}$: C, 74.27; H, 4.79; N, 13.72. Found: C, 74.36; H, 4.85; N, 13.33.

8-Hydroxy-4,5-dihydro-1-benzazepin-2-(3H)-one (lactam of γ -(o-amino-p-hydroxyphenyl)butyric acid) (II). To a stirred mixture of 1.0 g. (0.0057 mole) of 7-hydroxy-1-tetralone²⁸

(26) W. Blakely, W. I. Jones, and H. A. Scarborough, *J. Chem. Soc.*, 2870 (1927).

(27) E. H. Rennie, *J. Chem. Soc.*, 41, 221 (1882).

(28) E. Mosettig and E. L. May, *J. Org. Chem.*, 5, 533 (1940).

(20) R. J. W. Le Fevre, J. B. Sousa, and R. L. Werner, *J. Chem. Soc.*, 4686 (1954).

(21) Analyses by Spang Microanalytical Laboratory, Ann Arbor, or by Dr. Goji Kodama, or by Mrs. A. Griffin. Melting and boiling points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 21 instrument.

(22) M. Julia and M. Baillarge, *Bull. soc. chim. France*, 639 (1952).

(23) F. C. Brown, *J. Am. Chem. Soc.*, 68, 872 (1946).

(24) P. Friedländer and M. Zeitlin, *Ber.*, 27, 197 (1894).

(25) Farbwerke vorm. Meister Lucius and Bruning, D. R. P. 164,295; *Chem. Zentr.*, 1905 II, 1701.

and 30 ml. of methanesulfonic acid cooled to 8° was added 0.55 g. (0.0085 mole) of sodium azide over 0.5 hr. with constant cooling. After an additional hour, the dark brown mixture was poured onto ice. The light brown solid which collected weighed 0.40 g., m.p. 220–225° dec. The filtrate was neutralized with sodium bicarbonate and extracted with three 20-ml. portions of ethyl acetate. Evaporation of the dried extracts left 0.41 g. of brown solid, m.p. 222–225° dec. (total yield 76%). Recrystallization from aqueous ethanol gave an analytical sample, m.p. 232–234° dec.

Anal. Calcd. for $C_{10}H_{11}NO_2$: C, 67.77; H, 6.26. Found: C, 67.74; H, 6.32.

When the reaction was carried out in anhydrous trifluoroacetic acid at room temperature, erratic yields of up to 69% were obtained.

7-Nitro-8-hydroxy-4,5-dihydro-1-benzazepin-2-(3H)-one (lactam of γ -(2-amino-3-nitro-4-hydroxyphenyl)butyric acid) (III). A solution of 0.5 g. (0.0028 mole) of II in 7 ml. of anhydrous trifluoroacetic acid was cooled to 3° and 2.0 ml. of concd. nitric acid (d. 1.42) was added drop by drop while the temperature was kept between 3 and 5°. After 30 min. standing in an ice bath, the deep red mixture was poured into 50 ml. of an ice water slurry. The light yellow solid that precipitated weighed 0.59 g. (90%); m.p. 231–237° dec. Three recrystallizations from 95% alcohol gave 0.40 g., m.p. 236–238° dec.

Anal. Calcd. for $C_{10}H_{10}N_2O_4$: C, 54.06; H, 4.54. Found: C, 54.16; H, 4.80.

7-Amino-8-hydroxy-4,5-dihydro-1-benzazepin-2-(3H)-one (IV). A solution of 0.50 g. of III in 80 ml. of absolute ethanol in the presence of Adams' Catalyst absorbed the calculated amount of hydrogen in 45 min. at atmospheric pressure. Evaporation of the filtered solution in a nitrogen atmosphere and aspirator vacuum left 0.43 g. (100%) of IV, m.p. 227–228° dec. Rapid recrystallization from aqueous ethanol gave a nearly colorless, granular product, m.p. 229–230° dec., which rapidly darkened in air.

Anal. Calcd. for $C_{10}H_{12}N_2O_2$: C, 62.49; H, 6.30. Found: C, 61.98; H, 6.57.

Attempts to prepare a hydrochloride gave a solid decomposing in the range 180–210°, but it turned to gums upon attempts at further purification.

Diazotization of IV. A cold solution of 0.213 g. (0.0031 mole) of sodium nitrite and 0.13 g. (0.0008 mole) of anhydrous copper sulfate in 12 ml. of water was poured into a solution of 0.60 g. (0.0026 mole) of the crude hydrochloride of IV in 35 ml. of water. The mixture turned intense black and evolved gas vigorously. No diazo oxide could be obtained by chloroform extraction, salting out, or freezing. When the reaction was carried out at 3° in the presence of sufficient hydrochloric acid to give pH ca. 2, darkening and effervescence did not occur, and the diazo oxide (V) was presumably formed in solution; all attempts to isolate it were unsuccessful, however.

7-Hydroxy-8-nitro-1-tetralone (VI). Over a 10-min. period, 0.5 ml. (0.007 mole) of concd. nitric acid (d. 1.42) was added in 5-drop portions to a solution of 1.0 g. (0.0062 mole) of 7-hydroxy-1-tetralone in 20 ml. of trifluoroacetic acid cooled to 1°. After 30 min. the dark brown solution was poured on ice, precipitating a light tan solid, m.p. 205–210° dec., 1.18 g. (93%). An analytical sample was obtained as colorless granules by three recrystallizations from aqueous ethanol; m.p. 231° with vigorous decomposition (bath preheated to 225°).

Anal. Calcd. for $C_{10}H_9NO_3$: C, 57.97; H, 4.38. Found: C, 57.88; H, 4.34.

7-Methoxy-8-nitro-1-tetralone (VIII). A. *from 7-methoxy-1-tetralone.* Over a 10-min. period, 36 drops of concd. nitric acid (d. 1.42) was added with occasional stirring to a solution of 2.5 g. of 7-methoxy-1-tetralone^{28,29} in 30 ml. of trifluoroacetic acid cooled to 0°. After 0.5 hr. at 0°, the mixture was

poured on ice, precipitating a fluffy, yellow solid, m.p. 110–117°, 3.0 g. (98.2%). After four recrystallizations from 95% ethanol there was obtained 1.6 g. (52%) as colorless plates, m.p. 127–128°, unchanged by further recrystallizations from benzene-petroleum ether mixture.

Anal. Calcd. for $C_{11}H_{11}NO_4$: C, 59.72; H, 5.01. Found: C, 59.64; H, 5.12.

B. *From 7-hydroxy-8-nitro-1-tetralone* (VI). An excess of ethereal diazomethane was added to a solution of 20 mg. of VI in 40 ml. of a 1:1 mixture of ether and methanol. After 15 min. at 0–5°, the excess diazomethane was destroyed with acetic acid and the solvents were evaporated. Recrystallization of the brown residue from 95% ethanol gave colorless plates, m.p. 125–127°, undepressed when mixed with VIII prepared from 7-methoxy-1-tetralone; the infrared spectra of the two preparations were superimposable.

Oxidation of VIII to 3-nitro-4-methoxyphthalic acid (IX). A suspension of 3.0 g. of VIII in a solution of 19.5 g. of potassium permanganate and 3 ml. of 20% sodium hydroxide in 360 ml. of water was refluxed for 5 hr. The manganese dioxide was filtered and the yellow filtrate was acidified with hydrochloric acid and extracted with three 50-ml. portions of ethyl acetate. Evaporation of the extracts left a brown mass, ca. 1 g., which was dissolved in warm water. The solution was separated from some gummy material which formed on cooling; slow evaporation gave light yellow plates, m.p. 224–225° dec., after two recrystallizations from water (reported³⁰ m.p. 223–224° dec.).

Anal. Calcd. for $C_8H_7NO_5$: C, 44.82; H, 2.93; N, 5.81. Found: C, 44.85; H, 2.96; N, 5.79.

7-Hydroxy-8-nitro-1-benzazepin-2-(3H)-one (X). To a suspension of 0.68 g. (0.0033 mole) of VI in 50 ml. of technical grade methanesulfonic acid at room temperature was added 0.33 g. (0.005 mole) of sodium azide over a 3-hr. period. The ketone slowly dissolved and the solution had become black after 10 hr. The mixture was poured on cracked ice; small, yellow needles separated slowly on standing. The solid was collected by filtration and the mother liquors were extracted with four portions of ethyl acetate. Evaporation of the washed and dried extracts gave a further quantity of yellow solid; total wt. 0.61 g. (84%) m.p. 198–204°. Recrystallization from aqueous ethanol gave fine yellow needles, m.p. 205–207°, unaltered by further recrystallizations. It reduced Tollens' reagent in aqueous alcoholic solution instantaneously to a black precipitate of silver.

Anal. Calcd. for $C_{11}H_{10}N_2O_4$: C, 54.06; H, 4.54; N, 12.61. Found: C, 54.10, 54.13; H, 4.55, 4.57; N, 12.34, 12.23.

When X was mixed with its isomer (III), the m.p. was 185–227° dec.; the infrared spectra are dissimilar.

7-Hydroxy-8-amino-1-tetralone (VII). A solution of 0.308 g. of VI in absolute alcohol was hydrogenated at 33° and 741 mm. pressure over Adams Catalyst; 116 ml. of hydrogen was absorbed in 25 min. Evaporation of the filtered solution left 0.25 g. (96%) of light brown prisms, m.p. 210–213° dec. Sublimation at reduced pressure gave a light yellow powder, m.p. 215–217°. It reduced Tollens' reagent in aqueous alcoholic solution instantaneously to a black precipitate of silver. Under the same conditions, *o*-aminophenol showed similar behavior, but *m*-aminophenol showed slow reduction only after 10 to 15 min., forming a mirror over a 3-hr. period.

Anal. Calcd. for $C_{10}H_{11}NO_2$: C, 67.78; H, 6.26; N, 7.91. Found: C, 67.83; H, 6.38; N, 7.94.

8-Methoxy-9-nitro-4,5-dihydro-1-benzazepin-2-(3H)-one. To a solution of 1.1 g. (0.05 mole) of VIII in 65 ml. of slightly warm methanesulfonic acid was added 0.5 g. (0.075 mole) of sodium azide in portions over a 4-hr. period. After 15 hr. more at room temperature, the red-brown solution was poured into an ice water slurry, precipitating 0.9 g. of a brown powder, m.p. 166–170°. Four recrystallizations from 95% ethanol gave pale yellow plates, m.p. 177.6–

(29) R. D. Haworth and G. Sheldrick, *J. Chem. Soc.*, 1951 (1934).

(30) H. King, *J. Chem. Soc.*, 1162 (1939).

178.5°, insoluble in 5% sodium bicarbonate solution, but easily soluble in 5% sodium hydroxide.

Anal. Calcd. for $C_{11}H_{12}N_2O_4$: C, 55.92; H, 5.12; N, 11.85. Found: C, 55.85, 56.00; H, 4.94, 4.99; N, 11.89, 11.97.

Attempts to prepare the foregoing product by treating X with ethereal diazomethane led to mixtures which were not further investigated when separation proved difficult.

Schmidt reaction on benzosuberan-5-one. During a 1-hr. period, 1.0 g. (0.015 mole) of sodium azide was added in portions to a solution of 1.6 g. (0.01 mole) of benzosuberan-5-one in 15 g. of trichloroacetic acid heated to 60°. After 4.5 hr. the light yellow mixture was still evolving gas slowly. An additional 0.1 g. of sodium azide was added and the heating continued 1.5 hr. more. The pasty mass was then stirred with ice, causing the separation of a light brown oil which solidified within an hour; 2.37 g. (82%), m.p. 95–101°. Four recrystallizations from petroleum ether (b.p. 60–70°) gave fine white needles of 3,4,5,6-tetrahydro-1-benzazocin-2-one-trichloroacetic acid adduct, m.p. 103.5–104.3°.

Anal. Calcd. for $C_{11}H_{12}NO_4$: C, 46.11; H, 4.17; N, 4.14. Found: C, 46.23; H, 4.21; N, 4.21. Equivalent weight to base calcd.: 338.6. Found (phenolphthalein end point): 343.

When the adduct was shaken with dilute sodium hydroxide it liquefied and rapidly resolidified. Crystallization from benzene-petroleum ether mixture gave 3,4,5,6-tetrahydro-1-benzazocin-2-one, m.p. 153–154.5° (reported¹⁸ m.p. 151.5–153°) with only mechanical losses.

Anal. Calcd. for $C_{11}H_{12}NO$: C, 75.40; H, 7.48; N, 8.00. Found: C, 75.32; H, 7.40; N, 7.92.

8-Nitro-4,5-dihydro-1-benzazepin-2-(3H)-one. To a solution prepared from 1.4 g. (0.008 mole) of 7-nitro-1-tetralone³¹ and 0.9 ml. of concd. sulfuric acid in 12 g. of molten trichloroacetic acid was added 0.8 g. (0.012 mole) of sodium azide at such a rate that the temperature was maintained at 70° without having gas evolution become stormy. After 90 min., the viscous, yellow mixture was poured on ice and then treated with 10 ml. of concd. ammonium hydroxide. The light tan solid that separated weighed 1.05 g. (70%) m.p. 217–219°. It was insoluble in 10% sodium hydroxide. Two recrystallizations from ethanol (charcoal) gave an analytical sample, m.p. 220–222°. When mixed with the 7-nitro isomer obtained by nitration of 4,5-dihydro-1-benzazepin-2-(3H)-one, the melting point was strongly depressed.

Anal. Calcd. for $C_{16}H_{16}N_2O_3$: C, 58.24; H, 4.89. Found: C, 58.17; H, 4.90.

When the reaction was attempted without the use of sulfuric acid, only starting material was recovered.

7-Nitro-4,5-dihydro-1-benzazepin-2-(3H)-one. To a solution of 1.5 g. of 4,5-dihydro-1-benzazepin-2-(3H)-one (homodihydrocarbostyryl³²) in 4 ml. of concd. sulfuric acid cooled to 0° was added 1.5 ml. of concd. nitric acid (d. 1.42) over a 15-min. period while the temperature was kept below 10°. The mixture was poured onto ice, precipitating 1.81 g. (94.5%) of light tan crystals, m.p. 206–218°. Two recrystallizations from ethanol gave an analytical sample, pale yellow plates, m.p. 220–222.5° dec. (von Braun and Rawicz reported¹¹ m.p. 225° for the product of this reaction). The compound is slightly soluble in 10% sodium hydroxide.

Anal. Calcd. for $C_{16}H_{16}N_2O_3$: C, 58.24; H, 4.89. Found: C, 58.50; H, 4.95.

7-Methoxy-3,4-dihydronaphthalene-1-acethydrazide. A solution of 2.7 g. of 7-methoxy-1-tetralone and 2.3 ml. of ethyl bromoacetate in 125 ml. of anhydrous ether was added all at once to 3.1 g. of 30-mesh granulated zinc covered with 125 ml. of benzene. A pinch of iodine was added, and the mixture was stirred and warmed; reaction became evident after 5 to 10 min. Thereafter 1.5 g. of zinc and a crystal of

iodine were added after each of three 45-min. intervals. After 3 hr. further refluxing, the mixture was cooled and treated with 200 ml. of 10% hydrochloric acid. The layers were separated and the aqueous phase extracted with three 50-ml. portions of ether. The combined organic phases were washed with three 50-ml. portions of 2% ammonium hydroxide, then with water, and dried. Distillation of the solvents left a red oil, from which was distilled 2.9 g. of a light yellow oil, b.p. 150–155°/0.1 mm. This was boiled for 2-hr. with 2.0 ml. of 85% hydrazine hydrate in 30 ml. of 95% alcohol. Dilution with water and chilling gave 2.5 g. of lustrous white plates, m.p. 118–119°, unchanged by two recrystallizations from benzene-petroleum ether mixture. The same substance was obtained when the red oil was treated with hydrazine hydrate without prior distillation.

Anal. Calcd. for $C_{15}H_{18}N_2O_2$: C, 67.22; H, 6.95. Found: C, 67.11; H, 6.96.

The *N*-isopropylidene derivative was prepared by refluxing a small portion in acetone for 30 min. The white solid produced was recrystallized from benzene-petroleum ether (b.p. 60–70°) mixture to obtain an analytical sample, m.p. 169–170°.

Anal. Calcd. for $C_{16}H_{20}N_2O_2$: C, 70.56; H, 7.40. Found: C, 70.16; H, 7.87.

Ethyl 7-methoxy-3,4-dihydronaphthalene-1-acetate. The Reformatsky reaction was carried out on 60 g. of 7-methoxy-1-tetralone according to the foregoing procedure, and the crude, oily product was warmed with 130 ml. of 90% formic acid for 20 min. and then allowed to stand for 8 hr. Water (200 ml.) and benzene (200 ml.) were added, the resulting layers were separated, and the aqueous phase was extracted with three 50-ml. portions of benzene. The combined organic layers were washed with dilute sodium bicarbonate solution, then water, dried, and distilled, giving 59 g. (70%) of ethyl 7-methoxy-3,4-dihydronaphthalene-1-acetate as a pale yellow oil, b.p. 140–145°/0.35–0.40 mm.; n_D^{25} 1.5557.

Anal. Calcd. for $C_{15}H_{18}O_3$: C, 73.15; H, 7.37. Found: C, 72.99; H, 7.23.

We were unable to obtain the undehydrated ester reported by Hoch.³³

7-Methoxytetralin-1-acethydrazide. A solution of 22 g. of ethyl 7-methoxy-3,4-dihydronaphthalene-1-acetate in 175 ml. of 95% alcohol in the presence of 0.4 g. of Adams' Catalyst in a Parr apparatus absorbed the theoretical amount of hydrogen in 45 min. The solution was filtered and evaporated and 5.2 ml. of 99% hydrazine hydrate was added to the residue. Enough 95% alcohol was added to give a homogeneous solution, and the mixture was refluxed. After 7 days reaction was essentially complete, as indicated by the formation of a nearly clear solution when a few drops of the mixture was diluted with 5% hydrochloric acid. The entire mixture was then poured into an excess of 10% hydrochloric acid and extracted with two 100-ml. portions of ether. Neutralization of the aqueous layer with aqueous sodium acetate precipitated 12.5 g. (60%) of the hydrazide, m.p. 134–136°. Three recrystallizations from benzene-petroleum ether (b.p. 60–70°) mixture gave an analytical sample, m.p. 135.5–137.5°.

Anal. Calcd. for $C_{15}H_{18}N_2O_3$: C, 66.64; H, 7.74. Found: C, 66.69; H, 7.78.

7-Methoxy-1-aminomethyltetralin hydrochloride. A solution of 5.3 g. (0.023 mole) of 7-methoxytetralin-1-acethydrazide and 5 ml. of 6N hydrochloric acid in 40 ml. of water was covered with 150 ml. of ether, cooled to 0°, and 1.75 g. (0.025 mole) of sodium nitrite dissolved in a little water was added with stirring. After 10 min. of stirring the layers were separated and the aqueous phase was extracted with two 50-ml. portions of ether. The combined ether layers were dried (calcium chloride), and the ether was distilled off while the volume was kept roughly constant by the addition of benzene. Toluene was added until the mixture boiled at about 90°, and refluxing was continued for 3 hr.

(31) J. von Braun and H. Jungmann, *Ann.*, 451, 40 (1926).

(32) P. A. S. Smith, *J. Am. Chem. Soc.*, 70, 320 (1948).

(33) J. Hoch, *Bull. soc. chim.*, 55, 264 (1938).

To the warm solution was added all at once 30 ml. of concd. hydrochloric acid which had been saturated with hydrogen chloride at 0°. The resulting mixture was refluxed for 2 hr. (until gas evolution ceased), the layers were then separated, and the nonaqueous phase was extracted twice with water. The combined aqueous phases were decolorized with charcoal, alkalinized with 10% sodium hydroxide, and extracted with three 100-ml. portions of benzene. The combined extracts were washed with water, dried (calcium sulfate) saturated with anhydrous hydrogen chloride, and diluted with 400 ml. of dry ether. Chilling overnight gave 3.35 g. off white granules, and addition of petroleum ether (b.p. 60–70°) precipitated a further 0.9 g.; total yield, 82.5%, m.p. 167–168°.

Anal. Calcd. for $C_{12}H_{18}NOCl$: C, 63.28; H, 7.97. Found: C, 63.10; H, 7.89.

3-Nitrobenzosuberan-5-one (XII). Following the procedure used by von Braun³¹ for nitrating α -tetralone, 6.0 g. of benzosuberan-5-one³⁴ was slowly dropped into 17.5 ml. of yellow fuming nitric acid (d. 1.49) at 14° over a 10-min. period, and the mixture was then kept between –10 and –5° for 25 min. It was then poured on ice, precipitating 7.4 g. (96.2%) of a nearly white solid, m.p. 67–85°. Four recrystallizations from 95% alcohol gave 6.1 g. (82.5%) of clusters of stout colorless rods, m.p. 92–92.8°.

Anal. Calcd. for $C_{11}H_{11}NO_3$: C, 64.38; H, 5.40. Found: C, 64.19; H, 5.37.

The dinitrophenylhydrazone had m.p. 232–234°.

3-Nitrobenzosuberan-5-ol (XIII). A solution of 5.13 g. (0.025 mole) of XII in 25 ml. of anhydrous isopropyl alcohol was added to a boiling solution of 25.5 g. (0.125 mole) of aluminum isopropoxide in 100 ml. of isopropyl alcohol, following the general procedure of Truett and Moulton.³⁵ The light yellow suspension was refluxed for 2 hr. and then poured while warm into about 750 ml. of water and treated with 100 ml. of 10% sodium hydroxide. The precipitated solid weighed 5.0 g. (98%); m.p. 114–116°. Two recrystallizations from benzene-petroleum ether mixture gave an analytical sample, m.p. 116–116.7°.

Anal. Calcd. for $C_{11}H_{13}NO_3$: C, 63.75; H, 6.32. Found: C, 63.79; H, 6.14.

3-Aminobenzosuberan-5-ol (XIV). A solution of 3.50 g. of XIII in 100 ml. of 95% alcohol was hydrogenated at room temperature for 15 min. in the presence of 0.1 g. of Adams Catalyst. The mixture was then warmed, filtered, and diluted with ca. 75 ml. of water. Storage in the refrigerator precipitated slender, white needles, 2.74 g. (92%), m.p. 163–165°. Recrystallization from benzene-petroleum ether mixture gave an analytical sample, m.p. 163.7–164.4°.

Anal. Calcd. for $C_{11}H_{13}NO$: C, 74.54; H, 8.53. Found: C, 74.79; H, 8.66.

3-Hydroxybenzosuberan-5-ol (XV). A. From XIV. A solution of 2.0 g. of XIV in 200 ml. of 10% sulfuric acid was cooled to 0° and diazotized with 0.03 g. of sodium nitrite dissolved in a little water. After 15 min. sulfamic acid was added to destroy excess nitrous acid, the solution was filtered, overlaid with ca. 150 ml. of benzene, and allowed to stand at room temperature for 18 hr. The benzene layer was then separated and the aqueous phase was extracted with three more small portions of benzene. Evaporation of the combined extracts left 1.8 g. of residue, m.p. 145–160°; recrystallization from benzene-petroleum ether mixture gave 0.66 g. (33%) of XV, m.p. 156–157°, and an insoluble residue, m.p. 250°.

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.20; H, 7.72.

When the diazonium solution was decomposed at 70°, the yield was only 7%; when the benzene overlay was omitted, only 17% was obtained.

(34) C. W. Muth, P. O. Steiniger, and Z. B. Papanastassion, *J. Am. Chem. Soc.*, **77**, 1008 (1955).

(35) W. L. Truett and W. N. Moulton, *J. Am. Chem. Soc.*, **73**, 5913 (1951).

B. From 3-hydroxybenzosuberan-5-one (XX, see below). To a solution of 2.0 g. of XX in 42 ml. of 95% alcohol and 75 ml. of water at room temperature was added 1.0 g. of sodium borohydride all at once. After 35 min., the mixture was acidified with dilute hydrochloric acid and extracted with three portions of ether. The combined extracts were washed with water, dried, treated with charcoal, and evaporated under nitrogen at the water pump to give 1.82 g. (90%) of light tan plates, m.p. 151–155°. Two recrystallizations from benzene (charcoal) gave colorless plates, m.p. 156–157°.

Anal. Found: C, 74.14; H, 7.99.

2-Nitro-3-hydroxybenzosuberan-5-ol (XVI). A solution of 0.25 ml. of concd. nitric acid in 3 ml. of glacial acetic acid was added all at once to a solution of 0.70 g. of XV in 30 ml. of glacial acetic acid cooled to 15°. After standing for 15 min. between 18 and 22°, the solution was poured on ice, precipitating 0.47 g. (53%) of light yellow needles, m.p. 140–143°. Two recrystallizations from benzene-petroleum ether mixture gave an analytical sample, m.p. 141–142.5°.

Anal. Calcd. for $C_{11}H_{13}NO_4$: C, 59.18; H, 5.87; N, 6.28. Found: C, 59.15; H, 5.85; N, 6.31.

2-Amino-3-hydroxybenzosuberan-5-ol (XVII). A solution of 0.503 g. of XVI in 30 ml. of absolute alcohol was hydrogenated over Adams Catalyst for 20 min. at ambient pressure and temperature. The filtered solution was evaporated under nitrogen at the water pump to give 0.400 g. (92.5%) of white powder, m.p. 155–157° with evolution of water and apparent polymerization.

Anal. Calcd. for $C_{11}H_{13}NO_2$: C, 68.37; H, 7.82. Found: C, 68.26; H, 7.76.

Benzosuberan-5-ol-2,3-diazoide (XVIII). A solution of 252 mg. of XVII in 50 ml. of 10% hydrochloric acid was diazotized at 5° with 0.112 g. of sodium nitrite dissolved in a little water. The light yellow diazonium solution was overlaid with ether and alkalinized with cold, dilute sodium carbonate solution. The ether layer was separated after shaking, and the aqueous phase was extracted with three more portions of ether. The extracts were combined, washed with water, dried in the dark, and evaporated under nitrogen at the water pump, leaving about 125 mg. of an explosive, yellow-brown solid, m.p. 92–97° dec., infrared absorption at 2120 and 1620 cm^{-1} .

Anal. Calcd. for $C_{11}H_{12}N_2O_2$: C, 64.69; H, 5.92. Found: C, 64.70; H, 6.12.

3-Aminobenzosuberan-5-one (XIX). A suspension of 15.7 g. of 3-nitrobenzosuberan-5-one (XII) in 150 ml. of 95% alcohol was hydrogenated in a Parr apparatus at ca. 50 p.s.i. and 28° over 0.1 g. of Adams Catalyst. After 15 min. the resulting light yellow solution was filtered from catalyst and evaporated under nitrogen at the water pump, leaving light orange needles, m.p. 96–102°. This residue was taken up in 10% hydrochloric acid, leaving behind 220 mg. (1.2%) of bright orange material, m.p. 150–162° (*vide infra*). The solution was treated with charcoal and neutralized with sodium acetate to precipitate 14 g. of light yellow solid, m.p. 103–105°. Recrystallization from aqueous ethanol gave an analytical sample, m.p. 104–105°.

Anal. Calcd. for $C_{11}H_{13}NO$: C, 75.40; H, 7.48. Found: C, 75.14; H, 7.25.

An acetyl derivative, prepared in the usual manner, formed colorless plates, m.p. 103–104°.

Anal. Calcd. for $C_{13}H_{15}NO_2$: C, 71.87; H, 6.96. Found: C, 72.12; H, 6.87.

The orange by-product of the reduction kept the same long melting range in spite of recrystallizations and chromatography (alumina). Its color was destroyed by either zinc dust and acetic acid or sodium hydrosulfite. Reductive acetylation with zinc dust and acetic anhydride gave 3-acetamidobenzosuberan-5-one, m.p. 99–102°, undepressed by mixture with a sample prepared directly from the amine. The orange material is thus believed to be 3,3'-azobenzosuberan-5-one.

Anal. Calcd. for $C_{22}H_{22}N_2O_5$: C, 76.27; H, 6.40; N, 8.09. Found: C, 76.29, 76.34; H, 6.63; N, 7.93, 7.82.

3-Hydroxybenzosuberan-6-one (XX). A solution of 11.1 g. of XIX in 300 ml. of 10% sulfuric acid was diazotized at 8° with 4.55 g. of sodium nitrite in a little water. Sulfamic acid was added to destroy excess nitrous acid, and the mixture was filtered, poured into 800 ml. of 10% sulfuric acid, overlaid with 300 ml. of benzene, and kept at room temperature for 3 days. The layers were then separated and the aqueous phase extracted with three 150-ml. portions of benzene. The combined extracts were dried and evaporated, leaving 8.5 g. (76%) of hard, yellow needles, m.p. 96–99°. Sublimation at 97° and 0.3 mm. gave a colorless analytical sample, m.p. 99–100°.

Anal. Calcd. for $C_{11}H_{12}O_2$: C, 74.97; H, 6.87. Found: C, 74.97; H, 6.87.

2-Hydroxybenzosuberan (benzosuberan-2-ol) (XXI). A solution of 2.0 g. (0.0114 mole) of XX, 2.0 g. (0.03 mole) of potassium hydroxide and 1.2 ml. of hydrazine hydrate in 30 ml. of diethylene glycol was heated at 155° for 105 min. under a condenser equipped with an alembic take-off adapter, after which distillation was allowed to occur until the temperature had risen to 207°, and refluxing was then continued for 4 hr. The cooled solution was then poured into ca. 250 ml. of water, acidified with dilute hydrochloric acid, and extracted with three portions of ether. The combined extracts were washed with water, dried, treated with charcoal, and evaporated under nitrogen at the water pump, leaving an oil which solidified on standing to a light tan solid, wt. 1.70 g. (92.5%), m.p. 63–69°. Two recrystallizations from petroleum ether (b.p. 60–70°) gave 1.4 g., m.p. 70–72°, and a sample sublimed *in vacuo* had m.p. 71–72° (reported,¹⁶ m.p. 72°).

3-Nitro-2-hydroxybenzosuberan (3-nitrobenzosuberan-2-ol) (XXII). A solution of 1.17 ml. (0.0185 mole) of concd. nitric acid (d. 1.42) in 10 ml. of glacial acetic acid was added over 4 min. to a solution of 3.0 g. (0.0185 mole) of XXI in 30 ml. of glacial acetic acid cooled to 15° and kept below 20° during the addition and 2 min. more. The mixture was then poured into ca. 350 ml. of water, and the resulting suspension was extracted with three portions of ether. The combined extracts were washed with seven portions of water, dried, treated with charcoal, and evaporated under nitrogen at the water pump. The viscous, brown residue was taken up in hot 95% alcohol, from which on cooling there crystallized 1.7 g. (45%) of small, yellow plates, m.p. 83–86°. Two recrystallizations from 95% alcohol raised the m.p. to 85–87°, and vacuum sublimation gave an analytical sample, m.p. 86–86.8°.

Anal. Calcd. for $C_{11}H_{13}NO_3$: C, 63.76; H, 6.32. Found: C, 63.78; H, 6.29.

3-Amino-2-hydroxybenzosuberan (3-nitrobenzosuberan-2-ol) (XXIII). A solution of 0.50 g. of XXII in 50 ml. of ethanol was hydrogenated over Adams Catalyst at ambient temperature and pressure for 45 min. Evaporation of the filtered solution in a stream of nitrogen at the water pump left 0.414 g. (96.5%) of nearly white plates, m.p. 156–160° dec. Vacuum sublimation gave an analytical sample, m.p. 163–165° dec. It reduced Tollens' reagent instantly.

Anal. Calcd. for $C_{11}H_{15}NO$: C, 74.54; H, 8.53. Found: C, 74.54; H, 8.65.

Benzosuberan-3,2-diazoöxide (XXIV). A solution of 0.20 g. (1.13 mmole) of XXIII in 30 ml. of 5% hydrochloric acid was diazotized at 5° by adding all at once 0.09 g. (1.13 mmole) of sodium nitrite in 8 ml. of water. After 10 min., the solution was overlaid with 75 ml. of ether, recooled to 5°, and adjusted to pH 9 by the addition of dilute sodium carbonate solution. The ether layer was separated after shaking, and the aqueous phase was extracted twice more with ether. The combined extracts were washed with water, dried (calcium sulfate) in the dark, treated with charcoal, and evaporated in the dark under nitrogen at the water pump, leaving 0.107 g. (51%) of light brown solid, m.p. 96–98° with vigorous decomposition. When heated in a

flame it explodes with a flash. Infrared absorption: 2150, 2100, 1625 cm^{-1} .

Anal. Calcd. for $C_{11}H_{13}N_2O$: C, 70.18; H, 6.43; N, 14.89. Found: C, 70.14; H, 6.48; N, 14.81.

Irradiation experiments. The various diazoöxides were irradiated in concentrations of $5 \times 10^{-3}M$ and lower in solution in water, hydrochloric acid (concd. and dilute), water containing copper or manganese salts, aqueous acetic acid, aqueous dioxane, aqueous-alcoholic hydrochloric acid, or chloroform containing aniline. Radiation sources used were a 400-watt General Electric AH-1 mercury arc, a 250-watt General Electric RS-1 Sunlamp, a 1500-watt Sylvania tungsten lamp, a 500-watt resonance arc, and sunlight. Solutions were kept at 0–5° during irradiation. Completion was determined by a negative test for diazo coupling with aqueous-ammoniacal phloroglucinol. The time required for completion was roughly proportional to the intensity of the radiation. Deep red to black substances were invariably produced, usually containing little or nothing extractable by aqueous bicarbonate. However, in the case of naphthalene-1,2-diazoöxide we were able to extract indene-1-carboxylic acid in about 35% yields after irradiation by the AH-1 mercury arc, in qualitative confirmation of earlier reports.^{2,4,5}

Irradiation of benzophenone-3,4-diazoöxide. A solution of 2.24 g. (0.01 mole) in 2 l. of 30% acetic acid was irradiated with an RS-1 Sunlamp; completion was reached in 1 hr. A black sludge, 1.9 g., m.p. 200–210°, was collected by filtration. It was dissolved in hot 5% sodium hydroxide, treated with charcoal, and reprecipitated by acid to give an apparently similar reddish-black material. Digestion of a portion with benzene gave a brilliant red solution and left only a small black residue. The extract was chromatographed on Magnesol-Celite (2:1) and eluted with 1% methanol in benzene to give five bands in various shades of red. Another portion of the material was extracted with 5% sodium bicarbonate solution, the extracts treated with charcoal, and acidified. A deep red solid, m.p. 180–184°, was obtained.

Anal. Calcd. for $C_{20}H_{12}N_2O_8$: C, 71.77; H, 4.32; N, 4.29. Found: C, 71.25, 70.64; H, 4.73, 4.86; N, 4.52, 4.43.

The portion insoluble in sodium bicarbonate was taken up in 5% sodium hydroxide solution, treated with charcoal, and reprecipitated with acid. A red solid, m.p. 210–220° dec., was obtained.

Anal. Found: C, 70.95, 70.40; H, 4.34, 4.53; N, 5.75, 6.23.

These substances were not further investigated.

Thermal rearrangement of naphthalene-1,2-diazoöxide. A. *In aniline.* A solution of 1.0 g. of naphthalene-1,2-diazoöxide in 10 ml. of freshly distilled aniline was plunged into an oil bath preheated to 180°. After a ca. 20-second induction period, gas evolution began and continued vigorously for 3 min. After 5 min. the now black mixture was cooled and poured into dilute hydrochloric acid, precipitating a red-brown amorphous mass, 1.1 g. Extraction of 0.5 g. of this for 2 hr. with hot petroleum ether (b.p. 60–70°) gave a pale red solution, which was treated with charcoal and evaporated, giving 0.2 g. (32%) of fine white needles of indene-1-carboxanilide, m.p. 158–159.5° (reported⁸ m.p. 159–160°).

Anal. Calcd. for $C_{16}H_{13}NO$: C, 81.68; H, 5.57. Found: C, 81.78; H, 5.43.

B. *In p-toluidine.* In a similar experiment with 10 ml. of molten *p*-toluidine in place of aniline, 0.95 g. of crude product was obtained, which in turn yielded 34% of indene-1-carbox-*p*-toluidide, m.p. 168–169°.

Anal. Calcd. for $C_{17}H_{15}NO$: C, 81.90; H, 6.07. Found: C, 82.02; H, 6.16.

C. *In phenol.* A similar procedure was followed, with 10 ml. of molten phenol in place of aniline. The reaction mixture was poured into water, precipitating a red oil. The mixture was then extracted with three 100-ml. portions of ether, and the combined extracts were washed with 10% sodium hydroxide, then water, and dried. Evaporation of the ether at the water pump gave 0.51 g. (57%) of phenyl indene-1-

carboxylate as pale orange needles, m.p. 108–111°. Sublimation gave an analytical sample, m.p. 110–111°.

Anal. Calcd. for $C_{15}H_{12}O_2$: C, 81.33; H, 5.12. Found: C, 81.42; H, 5.11.

Reaction of diphenylmethane-3,4-diazooxide with aniline and with benzyl alcohol. A solution of 0.57 g. of diphenylmethane-3,4-diazooxide in 10 ml. of pure aniline was plunged into an oil bath preheated to 180°. When gas evolution ceased (3 min.), the reddish black mixture was poured on ice drenched with hydrochloric acid, precipitating a dark red, amorphous solid, 0.50 g., m.p. 205–215° dec. Attempted crystallization by extraction with aqueous alcohol or petroleum ether was not successful, but a benzene solution deposited a presumably purified material (deep red) when diluted with petroleum ether (b.p. 60–70°) and chilled; m.p. 220–221° dec. (bath preheated to 215°). Its identity was not apparent from its analysis, and no more was done with it.

Anal. Found: C, 77.92; H, 5.38; N, 8.39.

A similar experiment using benzyl alcohol in place of aniline gave only brown to black, intractable tars.

Reactions of benzophenone-3,4-diazooxide with aniline, with benzyl alcohol, and with phenol. A solution of 0.7 g. of benzophenone-3,4-diazooxide in 8 ml. of aniline was heated at 180° for 1.5 min., then cooled and poured on ice drenched with excess hydrochloric acid; a dark red solid, 0.73 g., m.p. 200–245°, was obtained. Hot petroleum ether did not dissolve this material significantly, and extraction with hot alcohol yielded only slimes from the extract. Extraction of 0.23 g. with boiling benzene for 3 hr. gave a bright red solution. Washing with dilute sodium hydroxide removed the color, but acidification then gave only 13 mg. of red solid, not further investigated. Evaporation of the benzene solution left a light solid, 0.20 g., m.p. high and indefinite.

Anal. Found: C, 74.28; H, 5.08; N, 7.57.

Similar experiments using benzyl alcohol or phenol in place of aniline gave intractable tars accompanied by lesser amounts of amorphous, red solids.

Reaction of naphthalene-1,2-diazooxide with silver benzoate triethylamine and methanol. Following the procedure of Newman and Beal,⁷ a solution of 1.0 g. of silver benzoate in 13 ml. of triethylamine was added dropwise to a solution of 0.15 g. of naphthalene-1,2-diazooxide in 10 ml. of dry methanol. The solution darkened appreciably and a silver mirror formed; no gas evolution was observed. After 0.5 hr., the mixture was filtered and concentrated, but only viscous, black tars could be obtained.

Reaction of naphthalene-1,2-diazooxide with benzyl alcohol.
A. Alone. A solution of 1.0 g. of naphthalene-1,2-diazooxide in 10 ml. of benzyl alcohol was plunged into an oil bath preheated to 180°. When gas evolution ceased (3 min.), the mixture was cooled, diluted with 75 ml. of ether, and extracted with three portions of 5% sodium hydroxide, then water, and dried. Acidification of the basic extracts precipitated 0.40 g. (47%) of β -naphthol, m.p. 120–121°, undepressed by mixture with an authentic sample. Treatment of the ethereal solution with 2,4-dinitrophenylhydrazine reagent gave 3.56 g. (212%) of benzaldehyde dinitrophenylhydrazone, m.p. 234–236°, undepressed by mixture with an authentic sample.

B. In the presence of tri-*n*-butylamine. A mixture of 0.5 g. of naphthalene-1,2-diazooxide, 1 ml. of tri-*n*-butylamine and 6 ml. of benzyl alcohol began to evolve gas at room temperature within a minute of mixing. After 30 min., the mixture was worked up as described in part A, to give 0.19 g. (44%) of β -naphthol, and much benzaldehyde (as dinitrophenylhydrazone).

Reaction of naphthalene-1,2-diazooxide with benzylamine
A. With heat. A solution of 1.0 g. of naphthalene-1,2-diazooxide in 11 ml. of dry benzylamine was placed in an oil bath preheated to 184°; gas evolution began after a short induction period and lasted for 3 min. The resulting green mixture was poured into dilute hydrochloric acid, precipitating a red oil. It was extracted with three portions of benzene, and the combined extracts were washed with water and dried. Evaporation at the water pump left a red solid, from which was obtained by three recrystallizations from benzene-petroleum ether mixture, 0.45 g. (53%) of β -naphthol, m.p. 120–122°. In another experiment, the drowned reaction mixture was treated with dinitrophenylhydrazine reagent, precipitating a large quantity of the benzaldehyde derivative (identity confirmed by mixed melting point).

B. At room temperature. A solution of 0.20 g. of naphthalene-1,2-diazooxide in 8 ml. of benzylamine was kept at room temperature for 35 min. Work-up as before yielded 0.083 g. (50%) of β -naphthol.

Effect of benzoyl peroxide on naphthalene-1,2-diazooxide. Two solutions were prepared, each consisting of 0.27 g. of naphthalene-1,2-diazooxide in 7 ml. of benzyl alcohol, and to one was added ca. 50 mg. of benzoyl peroxide. Both solutions were then heated at 83° for 4 hr. Workup as before gave no more than traces of β -naphthol from either solution.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, KANSAS STATE UNIVERSITY]

Reactions of Sodium Methoxide with 2-Alkyl-2,3-dichloroaldehydes.

II. Methacrolein Dichloride

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Received April 4, 1960

Reaction of 2,3-dichloro-2-methylpropanal (methacrolein dichloride) with sodium methoxide in methanol gave 1,1-dimethoxy-2,3-epoxy-2-methylpropane (epoxymethacrolein dimethyl acetal, IIc) in 70–80% yield, whereas in dry ether the product is 3-chloro-2-methoxy-2-methylpropanal. In methanol this aldehyde appears to form a relatively stable hemiacetal, thought to be the intermediate in the formation of IIc. The mechanism of the reaction in ether appears to be of the "borderline S_N2 " type. A third type of reaction, resulting only in substitution of the β -chlorine atom, was observed when the dichloroaldehyde was treated with potassium *t*-butoxide in *t*-butyl alcohol.

It was established recently that α,β -dichloro- α -alkylaldehydes (Ia,b) reacted with two moles of methanolic sodium methoxide to form the corresponding epoxyacetals (IIa,b).¹ These products

had previously been assumed to be either 2,3-di-

(1) S. Searles, Jr., E. K. Ives, and H. M. Kash, *J. Org. Chem.*, **22**, 919 (1957).