gum, the infrared spectrum of which was very similar to that of the benzocyclobutadiene polymer obtained as a by-product in the zinc dehalogenation of the diiodide II and the dibtomide I.² Its weight corresponded to a yield of 40%, calculated as $(C_8H_6)_x$. In place of aged sodium ethoxide, freshly prepared so-

In place of aged sodium ethoxide, freshly prepared sodium ethoxide could be employed in the hydrogenolysis: the yields of benzocyclobutene were, however, consistently lower (20-38%). The use of other bases (pyridine, sodium carbonate, sodium hydroxide) in place of the ethoxide led to yields of benzocyclobutene below 20%. Thermal Stability of Benzocyclobutene.—Refluxing the

Thermal Stability of Benzocyclobutene.—Refluxing the hydrocarbon for one hour under nitrogen at atmospheric pressure produced no change in the boiling point of the liquid or in its infrared spectrum; at room temperature, no change in the refractive index or infrared spectrum of a sample was detected after one year.

Acid Sensitivity of Benzocyclobutene.—(a) Benzocyclobutene (0.50 g.) was dissolved in methanol (58.5 ml.) and concentrated hydrochloric acid (5 ml.) added. The resulting solution (1 N in acid) was allowed to stand for 48 hours, diluted with water (200 ml.) and the hydrocarbon isolated by extraction with petroleum ether ($30-60^{\circ}$). The infrared spectrum of the recovered benzocyclobutene (0.49 g.) was identical with that of the starting material.

(b) Benzocyclobutene (3.0 g.) was added dropwise to liquid hydrogen fluoride (50 ml.) contained in a polyethylene beaker. A milky suspension resulted which was allowed to evaporate at room temperature under the hood. The residue was dissolved in methylene chloride and filtered through alumina. Evaporation of the solvent left a somewhat sticky, transparent glass (3.0 g.). The infrared spectrum exhibited a strong band at 14.2 μ (monosubstituted benzene).⁹

1-Bromobenzocyclobutene (VI).—A mixture of benzocyclobutene (17.0 g.), N-bromosuccinimide (29.2 g.), benzoyl peroxide (0.01 g.) and carbon tetrachloride (75 ml.) was refluxed with stirring for 2.5 hours. Petroleum ether ($30-60^{\circ}$, 30 ml.) was added and the solution decanted onto a column (1 × 10 cm.) of alumina. The column was eluted with petroleum ether ($30-60^{\circ}$, 1000 ml.) and the eluate concentrated carefully to a volume of about 15 ml. Distillation through a spinning band column gave the pure 1-bromobenzocyclobutene (17.4 g., 58%) as a colorless oil, b.p. 90° (10.5 mm.), n²⁶D 1.5907.

Anal. Caled. for C₈H₇Br: C, 52.49; H, 3.86; Br, 43.66. Found: C, 52.67; H, 4.01; Br, 43.49.

Attempted Bromination of 1-Bromobenzocyclobutene.— A mixture of monobromide VI (0.64 g., 0.0035 mole), Nbromosuccinimide (0.7 g., 0.0392 mole), benzoyl peroxide (0.005 g.) and carbon tetrachloride (10 ml.) was refluxed for 2 hours. The mixture was cooled and filtered through alumina, using petroleum ether ($30-60^\circ$) as the eluting agent. Evaporation of the eluate gave a colorless oil (0.62g.), the infrared spectrum and refractive index of which were identical to those of the original monobromide.

Dehydrobromination of 1-Bromobenzocyclobutene.—The monobromide VI (1.00 g.) was added to 12 ml. of a 0.98 molar solution of potassium *t*-butoxide in *t*-butyl alcohol. After refluxing the mixture for 7 hours, water (40 ml.) was added and the hydrocarbon extracted out with two 40-ml. portions of petroleum ether (30-60°). The extract, after filtration through sodium sulfate, was evaporated to dryness and the residue sublimed at 100° (1 mm.) to give 0.475 g. (84%) of benzocyclobutadiene dimer (IX), m.p. 68-74°. After one recrystallization from petroleum ether (30-60°) the melting point (74-74.5°) was not depressed upon admixture with an authentic sample.² In addition, the infrared spectra of both samples were identical.

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[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

Condensed Cyclobutane Aromatic Systems. V. The Synthesis of Some α -Diazoindanones: Ring Contraction in the Indane Series

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A new and convenient method is described for the conversion of cyclic α -diketones to the corresponding α -diazoketones, employing monotosylhydrazones of the diketones as intermediates. By this procedure, a number of cyclic diazoketones, including some diazoindanones, have been prepared. In addition, several diazoindanones have been obtained using the reaction of Forster, *i.e.*, treatment of an α -oximinoketone with chloramine. The Wolff rearrangement of 2-diazo-1-indanone, 4,7-dimethyl-2-diazo-1-indanone and 4-methyl-7-chloro-2-diazo-1-indanone has been effected under the influence of ultraviolet light to give benzocyclobutene-1-carboxylic acid, 3,6-dimethylbenzocyclobutene-1-carboxylic acid and 3-methyl-6chlorobenzocyclobutene-1-carboxylic acid. The structure of the simple benzocyclobutene-1-carboxylic acid was confirmed by an unambiguous synthesis from 1-bromobenzocyclobutene.

Although acyclic α -diazoketones, especially α diazomethyl ketones, usually are prepared readily from acid chlorides and diazoalkanes,² this method of synthesis is intrinsically inapplicable to the synthesis of cyclic α -diazoketones.

Excluding from consideration the special case of the aromatic *o*-diazoöxides, only a very limited number of cyclic α -diazoketones has been reported. Most of these have been prepared by the mercuric oxide oxidation of the monohydrazone of an α -diketone. Examples are found in the preparation of 3diazocamphor (Ic),⁸ diazoöxindole (IIc)⁴ and 7diazo-8-acenaphthenone (IIIc),⁵ the yield in the latter case being very low.



The primary purpose of the investigation reported here was to synthesize the hitherto unknown 2-diazo-1-indanone (Xa) and some substituted analogs of Xa for ring contraction studies. The monohydrazone approach was investigated in some detail in the 4,7-dimethylindane series. 4,7-

- (3) J. Bredt and W. Holz, J. prakt. Chem., [2] 95, 133 (1917).
- (4) T. Curtius and H. Lang, ibid., [2] 44, 551 (1891).
- (5) L. Berend and J. Hermes, *ibid.*, [2] 60, 1 (1899).

 ⁽¹⁾ From the Ph.D. Dissertations of R. L. Litle and D. R. Napier, The Ohio State University, 1957; for a preliminary report of a portion of this work, see: M. P. Cava and R. L. Litle, *Chemistry & Industry*, 367 (1957). The remaining material of this paper was presented before the Division of Organic Chemistry at the 132nd Meeting of the American Chemical Society, New York, N. Y., September, 1957.
 (2) W. E. Bachmann and W. S. Struve, "The Arndt-Eistert Syn-

⁽²⁾ W. E. Bachmann and W. S. Struve, "The Arndt-Eistert Synthesis," Organic Reactions, Vol. 1, John Wiley and Sons, New York, N. Y., 1942, p. 38.

Dimethyl-1-indanone⁶ (VIb) was converted, in good yield, to 4,7-dimethyl-2-oximino-1-indanone (VIIb) by *n*-butyl nitrite and hydrochloric acid; hydrolysis of the oximino ketone by hydrochloric acid in the presence of formaldehyde gave the yellow 4,7-dimethyl-1,2-indanedione (VIIIb). The reaction of this diketone with hydrazine in methanol was capricious, yielding red oils or difficultly purified, colored solids. However, when excess hydrazine was added to a benzene solution of the dione VIIIb an almost instantaneous reaction occurred, yielding the desired monohydrazone IV as white needles in 83% yield. The oxidation of the hydrazone was attempted under conditions used successfully in the standard preparation of azibenzil.⁷ Mercuric oxide alone was without effect on the hydrazone; however, on addition of the recommended basic catalyst⁷ a rapid development of color was observed and it was possible to isolate, after chromatography, a poor yield (3-10%) of crude diazoketone Xb, exhibiting the characteristic diazo absorption band in the infrared at about 4.8 μ .⁸ Variations in reaction time, temperature or physical state of the reactants did not alter the results materially.

Attention was turned then to devising a method for oxidizing the hydrazone function of an α -ketohydrazone by an internal oxidation-reduction reaction, rather than by the use of an external oxidant. A known oxidation-reduction of this type occurs when sulfonyl derivatives of hydrazones (such as tosylhydrazones) are heated with base to an elevated temperature,⁹ when decomposition products of aliphatic diazo compounds are obtained, the original sulfonate residue being reduced to the corresponding sulfinate ion



An older observation even more pertinent to the problem under consideration was that of Borsche and Frank,¹⁰ who found that p-benzoquinone monotosylhydrazone (V) decomposed readily in cold alkaline solution to the same unstable p-diazoöxide which is produced when p-aminophenol is diazotized



The extension of Borsche's observations to α diketone systems was investigated using 4,7-di-

(6) We are indebted to Prof. M. S. Newman of this department for a generous gift of this material.

(7) C. D. Nenitzescu and E. Solomonica, "Organic Syntheses,"
Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 496.
(8) A. K. Bose and P. Yates, THIS JOURNAL, 74, 4703 (1952).

(9) W. R. Bamford and T. S. Stevens, J. Chem. Soc., 4735 (1952).
 (10) W. Borsche and R. Frank, Ann., 450, 75 (1926).

methyl-1,2-indanedione (VIIIb), 1,2-indanedione (VIIIa) and 4-methyl-7-chloro-1,2-indanedione (V-IIIc); the last two diketones were prepared by the same method used for the dimethyl analog, starting from 1-indanone (VIa) and 4-methyl-7-chloro-1-indanone (VIc),⁶ respectively. All three diketones reacted readily with p-toluenesulfonylhydrazine in methanol to give good yields (79-86%) of the corresponding 2-monotosylhydrazones IXa, b, c. These tosylhydrazones were insoluble in water, but dissolved readily in an equivalent quantity of dilute sodium hydroxide to give bright yellow solutions. On standing at room temperature, these solutions slowly deposited neutral material. The neutral products, which were purified readily by chromatography on alumina or by recrystallization, were bright yellow solids, and were shown by analysis and infrared spectra (band at about 4.8 $(\mu)^{8}$ to be the desired α -diazoketones Xa, b, c; the yields of recrystallized products were quite satisfactory (58-90%). The original aqueous filtrates yielded, after acidification, p-toluenesulfinic acid. The location of the diazo group in the 2-position in these diazoindanones was confirmed by hydriodic acid reduction¹¹ of Xa and Xc to the original 1indanones (VIa, VIc).

In view of the success of the tosylhydrazone method in the synthesis of diazoindanones, it was of interest to test its possible extension to a few other readily available α -diketone types. Acenaphthenequinone (IIIa), camphorquinone (Ia) and isatin (IIa) each yielded the corresponding monotosylhydrazones IIIb, Ib, IIb, the sodium salts of which all decomposed smoothly in aqueous solution to the corresponding diazoketones IIIc, Ic, IIc. In the case of 9,10-phenanthrenequinone (XIa) a tosylhydrazone could not be isolated, but decomposition occurred spontaneously to the hitherto unknown 9-diazo-10-phenanthrone (XIc). It is noteworthy that the simple hydrazone approach to 9-diazo-10-phenanthrone is not feasible, since the action of hydrazine itself on phenanthrenequinone leads to reduction rather than to hydrazone formation.12

A little used but very interesting diazoketone synthesis was discovered by Forster,¹³ who found that 3-diazocamphor (Ic) was formed when a cold alkaline solution of 3-oximinocamphor was treated with chloramine. Using a slight modification of Forster's procedure (*i.e.*, generation of the chloramine *in situ*: see Experimental) we have applied this reaction in the indane series as a second good synthesis of 2-diazo-1-indanone (Xa)¹⁴ and 4-methyl-7-chloro-2-diazo-1-indanone (Xc).

An interesting illustration of the complimentary use of the tosylhydrazine and the chloramine diazoketone syntheses is provided by the results obtained in the 3,3-diphenylindane series. 3,3-Diphenyl-1-indanone (XII) was converted *via* 3,3-diphenyl-2-oximino-1-indanone (XIII) to

(11) M. L. Wolfrom and R. L. Brown, THIS JOURNAL, 65, 1516 (1943).

(12) S. Dutt, J. Chem. Soc., 2971 (1925).

(13) M. O. Forster, ibid., 107, 260 (1915).

(14) During the course of our work, an independent report appeared (without experimental details) of the synthesis of 2-diazo-1-indanone by the Forster reaction, and of its photolysis to benzocyclobutene-l-carboxylic acid; see W. Kirmse, Angew. Chem., 69, 106 (1957).



CHART I

3,3-diphenyl-1,2-indanedione (XIV). In the latter diketone, because of the steric hindrance of the 2-carbonyl by the phenyl groups, it is known that the ordinarily less reactive 1-carbonyl of the 1,2-



indanedione system is the one which reacts with the usual carbonyl reagents.¹⁵ The monotosylhydrone of XIV thus would be expected to be the 1-isomer XV. Indeed, decomposition of this tosylhydrazone by base afforded the red-orange 3,3-diphenyl-1-diazo-2-indanone (XXVI); while treatment of the known oximinoketone (XIII) with chloramine gave the isomeric pale yellow 3,3-diphenyl-2-diazo-1-indanone (XVII).



The only route hitherto available for synthetic entry into the benzocyclobutene series has been that employing $\alpha, \alpha, \alpha', \alpha'$ -tetrabromo-o-xylene as

(15) C. F. Koelsch and C. D. LeClaire, J. Org. Chem., 6, 531 (1941).

 $V = V_X$ III I Series a: X = O; series b: X = NNHSO₂C₇H₇; series C: X = N₂

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the starting material.¹⁶ Presumably benzocyclobutenes bearing substituents on the benzene ring could be obtained starting from ring substituted analogs of this tetrabromide. However, no such substitution products have been described and in many instances their synthesis would involve considerable difficulties.

A very different approach to substituted benzocyclobutenes was sought in the ring contraction of diazoindanones.

The Wolff rearrangement of α -diazoketones to acids (via intermediary ketenes) is a reaction of very wide applicability, not only in acyclic cases, but with cyclic diazoketones as well. Particularly worthy of note is the observation¹⁷ that 3-diazocamphor (Ic) upon ultraviolet irradiation

$$\begin{array}{c} R \\ C = 0 \\ \downarrow \\ R \\ C = N_2 \end{array} \xrightarrow{-N_2} \begin{array}{c} R \\ R \\ R \end{array} \xrightarrow{C = C = 0} \begin{array}{c} H_2 0 \\ H_2 0 \\ R \\ R \\ C C O O H \end{array}$$

in aqueous dioxane at 0° gave 1,6,6-trimethyl-(1,1,2)-bicyclohexane-2-carboxylic acid in good yield.

The successful contraction of a cyclopentane to a cyclobutane ring in the above case suggested the possibility of obtaining similar results in the indane series.

Ring contraction experiments were carried out with the following examples: 2-diazo-1-indanone (Xa), 4,7-dimethyl-2-diazo-1-indanone (Xb) and 4-methyl-7-chloro-2-diazo-1-indanone (Xc). In all cases, solutions of the diazoindanones in aqueous tetrahydrofuran were irradiated by ultraviolet light from a quartz discharge tube. Further variations in the conditions were studied using Xc. Except in one experiment in which triethylamine was added, a readily crystallized acid having the expected composition for 3-methyl-6-chlorobenzocyclobutene-1-carboxylic acid (XVIIIc) was obtained over a range of temperatures both in the presence and in the absence of added sodium bicarbonate. Varying the temperature alone had little effect on the yield of acid, but the presence of

(16) M. P. Cava and D. R. Napier, THIS JOURNAL, 79, 1701 (1957).
(17) L. Horner and E. Spietschka, Ber., 88, 934 (1955).

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XI

sodium bicarbonate in the photolysis mixture increased the yield of acid considerably, to a maximum value of 19%.

The neutral photolysis products were red gums which did not crystallize and which were discarded, after showing they contained no unchanged diazoketone (absence of $4.8 \ \mu$ infrared band).

When the diazoketones Xb and Xa were photolyzed, under the conditions found favorable for the chloromethyl analog, the corresponding acids, 3,6dimethylbenzocyclobutene-1-carboxylic acid (XV-IIIb) and benzocyclobutene-1-carboxylic acid (X-VIIIa) were obtained in yields of 22 and 21%, respectively.



The formulation of the acidic rearrangement products as benzocyclobutene derivatives was confirmed by an independent synthesis of the simple benzocyclobutene-1-carboxylic acid (XVIIIa).¹⁴

1-bromobenzocyclobutene The reaction of (XIX)¹⁸ with sodium cyanide proceeded very sluggishly under ordinary conditions: after eleven hours in refluxing methanol most of the bromide was unchanged, but infrared analysis indicated that about 30% of it had been converted to 1cyanobenzocyclobutene (XX). However, when warm dimethyl sulfoxide was employed as the solvent in this reaction, the bromide XIX was converted to the desired nitrile XX in 93% yield after only one hour. Oxidation of this nitrile by alkaline hydrogen peroxide gave in 73% yield benzocyclobutene-1-carboxamide (XXI); alkaline hydrolysis converted the amide in 97.5% yield to benzocyclobutene-1-carboxylic acid (XVIIIa). The acid XV-IIIa prepared by this route was identical in melting point and infrared spectrum with that obtained by the Wolff rearrangement of 2-diazo-1-indanone (Xa).

Experimental¹⁹

4,7-Dimethyl-2-oximino-1-indanone (VIIb).—To a solution of 4,7-dimethyl-1-indanone⁶ (10.0 g.) in a mixture of methyl Cellosolve (150 ml.) and concentrated hydrochloric acid (35 ml.) was added, with stirring, *n*-butyl nitrite (8 ml.). The mixture was allowed to stand at room temperature for 90 minutes, and the resulting crystalline slurry was poured into cold water (800 ml.). The oximinoketone (10.5 g., 90%) was collected, washed with cold water and was obtained as silky white needles after two recrystallizations from ethanol.

Anal. Calcd. for $C_{11}H_{11}NO$: C, 69.83; H, 5.86; N, 7.40. Found: C, 69.78; H, 5.87; N, 7.28.

4,7-Dimethyl-1,2-indanedione (VIIIb).—A suspension of the oximinoketone VIIb (10.0 g.) in a mixture of water (70 ml.), 36% formaldehyde (50 ml.) and concentrated hydrochloric acid (25 ml.) was heated on the steam-bath with occasional shaking for 30 minutes, then cooled to room temperature and diluted with water (1000 ml.). The crude

product was filtered, washed with water until free of formaldehyde, and air-dried. The yellow powder was dissolved in a minimal amount of benzene, and the solution poured with stirring into $30-60^{\circ}$ petroleum ether (500 ml.); the diketone separated as tiny bright yellow crystals (7.0 g.). A second crop (1.2 g.) was obtained by chilling the mother liquor, raising the yield to 89%. Recrystallization from a cyclohexane-ethyl acetate mixture afforded long, golden-yellow needles, m.p. $172-175^{\circ}$. In the infrared, the carbonyl groups absorbed at 5.63 and 5.81 μ .

Anal. Caled. for $C_{11}H_{10}O_2$: C, 75.84; H, 5.79. Found: C, 75.81; H, 5.76.

2-Hydrazone of 4,7-Dimethyl-1,2-indanedione (IV).—To a solution of the diketone VIIIb (2.0 g.) in benzene (20 ml.) was added dropwise anhydrous hydrazine (0.5 ml.). After several minutes, the mixture, which had set to a gellike mass, was diluted with petroleum ether and filtered. After recrystallization from aqueous methanol the hydrazone (1.8 g., 83%) formed long, white needles, m.p. 165– 173° dec. Further recrystallization from the same solvent raised the melting point to 166–175° dec.

Anal. Caled. for C₁₁H₁₂N₂O: C, 70.18; H, 6.43; N, 14.88. Found: C, 70.32; H, 6.48; N, 14.88.

4-Methyl-7-chloro-2-oximino-1-indanone (VIIc).—To a solution of 4-methyl-7-chloro-1-indanone⁶ (20.0 g.) in a mixture of methyl Cellosolve (400 ml.) and concentrated hydrochloric acid (50 ml.) was added, with stirring, *n*-butyl nitrite (16 ml.). After standing for 45 minutes at room temperature the crystalline slurry was poured into cold water (1000 ml.) and the white crystalline precipitate (21.3 g., 92%) filtered, washed with cold water and air-dried. The analytical sample was obtained as fine white needles, m.p. $245-250^{\circ}$ dec., after two recrystallizations from aqueous methanol.

Anal. Caled. for $C_{10}H_8NO_2C1$: C, 57.29; H, 3.85; N, 6.68; Cl, 16.91. Found: C, 57.47; H, 3.97; N, 6.49; Cl, 16.71.

4-Methyl-7-chloro-1,2-indanedione (VIIIc).—A suspension of oximinoketone VIIc (33.0 g.) in a mixture of water (250 ml.), 36% formaldehyde (250 ml.) and concentrated hydrochloric acid (125 ml.) was heated on the steam-bath with occasional shaking for 35 minutes, then cooled to room temperature and diluted with cold water (1000 ml.). The diketone (24.0 g., 78%) separated as a bright yellow powder which was washed well with cold water and air-dried. Recrystallization from 30-60° petroleum ether-ethyl aceate gave the analytical sample as orange needles, m.p. 195–200°. In the infrared, the carbonyl groups absorbed at 5.66 and 5.80 μ .

Anal. Caled. for $C_{10}H_7O_2C1;\ C,\ 61.70;\ H,\ 3.63;\ Cl,\ 18.23.$ Found: C, $61.74;\ H,\ 3.73;\ Cl,\ 18.45.$

2-Oximino-1-indanone (VIIa).—The literature preparations of this compound gave,^{20,21} in our hands, unsatisfactory results and a different procedure was employed: To a solution of 1-indanone (10.0 g.) in methyl Cellosolve (60 ml.) and concentrated hydrochloric acid (20 ml.) was added, with stirring, *n*-butyl nitrite (5 ml.). When solid began to separate (less than one minute), additional *n*-butyl nitrite (5 ml.) was added. After standing for 30 minutes the mixture was poured into cold water (1000 ml.). The crude oxime was filtered, washed well with water, sucked nearly dry and recrystallized from methanol to give long colorless needles (8.7 g., 71%), m.p. 190–215° dec. After a further crystallization from methanol the material sintered at 190–200° and melted with decomposition at 210– 220°, reported²¹ m.p. 210° dec., with some decomposition at 200°.

1,2-Indanedione (VIIIa).—Difficulties were encountered by us in the original preparation procedure²² because of lack of crucial details. The following elaboration was employed: A suspension of finely ground 2-oximino-1-indanone (10 g.) in a mixture of 36° formaldehyde (20 ml.) and concentrated hydrochloric acid (40 ml.) was stirred at room temperature (no external heating!) for 20 minutes and the suspension then diluted with cold water (300 ml.) and filtered. The yellow diketone (5.0 g.) was washed well with cold water

⁽¹⁸⁾ M. P. Cava and D. R. Napier, THIS JOURNAL, 80, 2255 (1958).
(19) Melting points are uncorrected. Analyses carried out by Galbraith Laboratories, Knoxville, Tenn.

⁽²⁰⁾ F. Kipping, J. Chem. Soc., 65, 492 (1894).

⁽²¹⁾ S. Gabriel and R. Stelzner, Ber., 29, 2604 (1896).

⁽²²⁾ W. Perkin, W. Roberts and R. Robinson, J. Chem. Soc., 101, 234 (1912).

and allowed to dry. The filtrate, on standing, deposited crystalline starting material (4.0 g., identity confirmed by mixed melting point). The conversion to diketone was 55%; the yield of diketone, based upon unrecovered VIIa, was 92%. After crystallization from ether, the 1,2-indanedione melted at $95-112^{\circ}$, reported²² $95-115^{\circ}$.

2-Tosylhydrazone of 4,7-Dimethyl-1,2-indanedione (IXb).—To a solution of the diketone VIIIb (3.5 g.) in hot methanol (100 ml.) was added a solution of *p*-toluenesulfonylhydrazine²³ in hot methanol (30 ml.). After two minutes crystals began to separate copiously, and the mixture was allowed to cool to room temperature. After one hour, the white needles (5.46, 79%) were filtered and washed with a little cold methanol. After one recrystallization from absolute ethanol, the tosylhydrazone formed glistening white needles, m.p. 170–171° dec.

Anal. Calcd. for $C_{18}H_{15}N_2O_8S$: C, 63.14; H, 5.30; N, 8.18; S, 9.36. Found: C, 63.38; H, 5.45; N, 8.11; S, 9.35.

2-Tosylhydrazone of 4-Methyl-7-chloro-1,2-indanedione (IXc).—To a solution of the diketone VIIIc (20.0 g.) in methanol (425 ml.) at 50° was added, with stirring, p-toluenesulfonylhydrazine (20.0 g.). After four hours at room temperature, the tiny, pale yellow needles (31.0 g., 83%) were filtered, washed with a little cold methanol and dried; m.p. 176–177° dec. Recrystallization from ethanol gave fine white needles, m.p. 177–178° dec.

Anal. Calcd. for $C_{17}H_{15}N_2O_4ClS$: C, 56.27; H, 4.17; N, 7.72; Cl, 9.77; S, 8.82. Found: C, 56.28; H, 4.15; N, 7.90; Cl, 9.77; S, 9.02.

2-Tosylhydrazone of 1,2-Indanedione (IXa).—A solution of the diketone VIIIa (10.0 g.) and p-toluenesulfonylhydrazine (12.8 g.) in methanol (300 ml.) was prepared at room temperature and allowed to stand overnight. The buff needles (18.3 g., 86%) were filtered, washed with a little cold methanol and dried; m.p. 175–177° dec. Recrystallization from ethanol gave tiny prisms, m.p. 178–179° dec.

Anal. Caled. for $C_{16}H_{14}N_{2}O_{2}S$: C, 61.13; H, 4.49; N, 8.91. Found: C, 61.30; H, 4.56; N, 9.02.

4-Methyl-7-chloro-2-diazo-1-indanone (Xc). A. From the Tosylhydrazone IXc.—The tosylhydrazone IXc (10.9 g., 0.030 mole) was dissolved, at room temperature, in 0.1 N sodium hydroxide solution (305 ml., 0.0305 mole). After standing for 8 hours at room temperature, the tan precipitate of diazoketone (6.0 g., 97%) was filtered, washed well with water and air-dried. Recrystallization from 95% ethanol afforded (in two crops) 5.6 g. (90%) of long, pale yellow needles. After an additional crystallization from 95% ethanol, the analytical sample melted at 170–176° dec. The infrared spectrum (methylene chloride solvent) showed intense bands at 4.82 and 6.00 μ .

Anal. Calcd. for $C_{10}H_7N_2OC1$: C, 58.13; H, 3.42; N, 13.70; Cl, 17.18. Found: C, 57.91; H, 3.56; N, 13.88; Cl, 17.21.

The alkaline aqueous filtrate was extracted with ether, the ether layer discarded and the aqueous phase acidified and extracted with ether. Evaporation of the dried ether phase left a white crystalline residue, identical in melting point and infrared spectrum with authentic p-toluenesulfinic acid.

B. From the Oximinoketone VIIc.—In a one-liter, threenecked flask equipped with a mechanical stirrer, dropping funnel and thermometer, and cooled in an ice-bath was placed a solution of oximinoketone VIIc (6.3 g., 0.03 mole) in a mixture of water (200 ml.) and 1 N sodium hydroxide (30 ml., 0.03 mole). The stirred solution was cooled to 2°, when a portion of the sodium salt of the oxime separated. There was then added 15 N ammonium hydroxide (4 ml., 0.60 mole), followed by 5.25% sodium hypochlorite solution (100 ml., 0.071 mole), added dropwise over a period of 20 minutes. One hour after the completion of the addition of the hypochlorite, the ice-bath was removed, and stirring was continued for an additional 5 hours. The precipitated brown solid was filtered, washed well with water and dissolved in methylene chloride. The resulting deep red solution was treated with charcoal until orange in color, filtered, concentrated and chilled to give fine yellow needles (3.9 g.,63%) of diazoketone, m.p. 173–180° dec. The infrared spectrum of this material was identical to that obtained in procedure A. The reduction of the diazoketone Xc was effected by shaking a solution of it (0.50 g.) in methylene chloride (25 ml.) with 47% hydriodic acid (4 ml.). After the initial copious evolution of nitrogen had ceased, the mixture was allowed to stand for 15 minutes, diluted with water, and the organic layer washed twice with dilute sodium thiosulfate, twice with water, dried and evaporated. The solid residue was sublimed at 115° (4 mm.) to give 0.30 g. (theory requires 0.47 g.) of pale yellow prisms, m.p. $128-129^{\circ}$ alone or admixed with authentic 4-methyl-7-chloro-1-indanone (VIc).^{6,24}

2-Diazo-1-indanone (Xa). A. From the Tosylhydrazone IXa.—A solution of the tosylhydrazone IXa (5 g., 0.016 mole) in 0.162 N sodium hydroxide (100 ml., 0.0162 mole) was mixed with methylene chloride (50 ml.) and the mixture stirred slowly for 2.5 hours. The yellow organic layer was washed with water, dried and evaporated to give 2.0 g. of yellow-brown solid. This solid was taken up in boiling cyclohexane, decanted from a small amount of oil and chilled, to yield yellow needles (1.08 g.). Dilution of the mother liquor with 30-60° petroleum ether and chilling gave a second crop (0.38 g.), raising the total yield of diazo-ketone, m.p. 86-88°, to 1.46 g. (58%). Sublimation at 78° (0.5 mm.) afforded bright yellow prisms, m.p. 87-88° The infrared spectrum (methylene chloride solution) showed strong bands at 4.82 and 6.00 μ .

Anal. Calcd. for C₉H₆N₂O: C, 68.37; H, 3.82; N, 17.71. Found: C, 68.38; H, 3.99; N, 17.60.

B. From the Oximinoketone VIIa.—The chloramine reaction, using a solution of 2-oximino-1-indanone (5.0 g., 0.031 mole) in 0.32 N sodium hydroxide (100 ml., 0.032 mole), was carried out exactly as described above for the chloromethyl analog VIIc. Thirty minutes after completion of the hypochlorite addition the ice-bath was removed and stirring continued for an additional 2 hours. The precipitate was filtered, dissolved in methylene chloride and the dried solution evaporated to yield yellow crystals (2.85 g., 58%) of 2-diazo-1-indanone, identical in melting point and infrared spectrum with the material obtained in procedure A.

The reduction of the diazoketone Xa (0.50 g.) was effected with hydriodic acid exactly as described for the chloromethyl analog Xc, to yield an oil which was converted to a bright red-orange 2,4-dinitrophenylhydrazone (0.92 g.), theory 0.97 g.). The derivative melted at 260° ; the melting point was not depressed by admixture with the 2,4-dinitrophenylhydrazone prepared from authentic 1-indanone.

4,7-Dimethyl-2-diazo-1-indanone (Xb). A. From the Tosylhydrazone (IXb).—A solution of the tosylhydrazone IXb (3.4 g., 0.0099 mole) in 0.1 N sodium hydroxide (100 ml., 0.01 mole) was stirred slowly with methylene chloride (50 ml.) for 2 hours. Evaporation of the dried organic layer left an orange crystalline residue (1.75 g., 93%) of crude diazoketone. After two crystallizations from cyclohexane an analytical sample, m.p. 120–122°, was obtained. The infrared spectrum (methylene chloride solution) showed strong bands at 4.79 and 6.00 μ .

Anal. Caled. for $C_{11}H_{10}N_2O$: C, 70.95; H, 5.41; N, 15.05. Found: C, 70.81; H, 5.50; N, 15.09.

B. By Mercuric Oxide Oxidation of the Hydrazone IV.— An intimately ground mixture of hydrazone IV (1.90 g.), freshly prepared yellow mercuric oxide (4.5 g.) and anhydrous sodium sulfate (2.0 g.) was shaken with dry ether (100ml.). After 5 minutes no apparent change had occurred. A few drops of 10% ethanolic potassium hydroxide was added and the shaking was continued, when the ether became successively orange, green and purple. After 25 minutes the mixture was filtered, the solids being washed with ether until the washings were colorless. Evaporation of the filtrate left a purple residue, which was dissolved in methylene chloride, and placed on a column of neutral alumina. Elution of the column with methylene chloride gave an orange eluate, which on evaporation left small brown-yellow needles (0.056 g., 3%) of crude diazoketone, m.p. $110-113^{\circ}$. The infrared spectrum confirmed the identity of this material with that obtained in preparation A. Varying the oxidation time of the hydrazone from 15 to 45 minutes did not appreciably affect the yield of diazoketone, or improve its quality.

⁽²³⁾ K. Freudenberg and F. Blummel, Ann., 440, 51 (1924).

⁽²⁴⁾ L. F. Fieser and A. M. Seligman, This Journal. 58, 2482 (1936), report m.p. 128° .

Monotosylhydrazone of Acenaphthenequinone (IIIb).— To a suspension of acenaphthenequinone (5.0 g.) in boiling methanol (50 ml.) was added p-toluenesulfonylhydrazine (5.5 g.). The mixture was refluxed on the steam-bath until all of the solid had dissolved, allowed to cool to room temperature, and the fine yellow needles (8.5 g., 89%) filtered and washed with a little cold methanol. Recrystallization from isopropyl alcohol-methanol gave yellow needles, m.p. 179° dec.

Anal. Calcd. for $C_{19}H_{14}N_2O_3S$: N, 8.00. Found: N, 8.06.

7-Diazo-8-acenaphthenone (IIIc).—A solution of the tosylhydrazone IIIb (7.0 g.) in methylene chloride (100 ml.) was stirred mechanically with 0.1 N sodium hydroxide (200 ml.) for 3 hours. The organic layer was separated, washed with water, dried over sodium sulfate, concentrated to 20 ml. and placed on a column of alumina. Elution of the column with a 1:1 mixture (by volume) of methylene chloride and 30-60° petroleum ether, and evaporation of the eluate left an orange solid which crystallized from petroleum ether as bright orange needles (2.9 g., 73%), m.p. 94° (reported 29 29-94°). A methylene chloride solution absorbed strongly in the infrared at 4.83 and 6.00 μ .

3-Tosylhydrazone of Camphorquinone (Ib).—A solution of camphorquinone (5.3 g.) and p-toluenesulfonylhydrazine (6.0 g.) in methanol (50 ml.) was refluxed for one hour. The solution was cooled, diluted with water, and the thick yellow oil which separated was taken up in methylene chloride. The organic layer was washed with water, dried and concentrated to a small volume. Upon gradual addition of petroleum ether powdery, faintly yellow crystals (6.0 g., 56%) were obtained, which were washed with petroleum ether and dried; the crystals melted at 110–113°.

Anal. Calcd. for $C_{17}H_{22}N_2O_3S\colon$ N, 8.38. Found: N, 8.28.

3-Diazocamphor (Ic).—A solution of the tosylhydrazone Ib (3.3 g.) in 0.1 N sodium hydroxide (100 ml.) was covered with 30–60° petroleum ether (50 ml.) and the mixture stirred mechanically at room temperature for 2 hours. Evaporation of the dried organic phase (reduced pressure) gave bright yellow crystals (1.03 g.). Stirring the aqueous layer with petroleum ether for an additional 12 hours gave a further quantity (0.33 g.) of diazocamphor. The total yield of yellow prisms, m.p. $70-74^\circ$, was 1.36 g. (76%). Sublimation of a small sample at 50° (2 mm.) raised the melting point to 75° (reported²⁶ 75°).

3-Tosylhydrazone of İsatin (IIb).—To a solution of isatin (10.0 g.) in warm methanol (250 ml.) was added *p*-toluenesulfonylhydrazine (12.8 g.). After all of the latter had dissolved, the solution was allowed to stand (room temperature) for 2 hours. The golden platelets (19.4 g., 91%) were filtered and washed with a little cold methanol. Recrystallization from methanol gave small yellow prisms, m.p. 190-200° dec.

Anal. Calcd. for $C_{1\delta}H_{1\delta}N_{\delta}O_{\delta}S;$ N, 13.33. Found: N, 13.17.

3-Diazoöxindole (IIc).—A solution of the tosylhydrazone IIb (6.3 g., 0.02 mole) in 0.2 N sodium hydroxide (200 ml., 0.04 mole) was allowed to stand overnight. The deep red solution was saturated with carbon dioxide and the precipitated orange powder (3.0 g., 94%) was washed well with cold water and dried. Recrystallization from benzene gave hard blood-red crystals, m.p. 168° dec., reported⁴ 168° dec. A methylene chloride solution showed strong infrared bands at 4.78 and 5.87 μ .

4.78 and 5.87 μ . 9-Diazo-10-phenanthrone (XIc).—A mixture of 9,10phenanthrenequinone (2.08 g.), p-toluenesulfonylhydrazine (1.80 g.) and 95% ethanol (20 ml.) was refluxed until all of the quinone dissolved (about 10 minutes). The cooled solution, which deposited a thick slurry of yellow crystals, was diluted with cold water (100 ml.). The acidic yellow suspension was made slightly basic by the addition of dilute potassium hydroxide (bright green color at end point), the solid filtered and dissolved in a little methylene chloride. The organic solution was dried (sodium sulfate) and passed through a column of alumina, which was eluted with methylene chloride. The yellow-orange eluate was evaporated rated and the residue crystallized from benzene by the slow addition of 30-60° petroleum ether to give (in two crops) yellow-orange needles, m.p. $104-108^{\circ}$ (1.36 g., 62%). Recrystallization from cyclohexane-petroleum ether raised the melting point to $107-109^{\circ}$. A methylene chloride solution showed strong infrared bands at 4.84 and 6.13 μ .

Anal. Caled. for $C_{14}H_8N_2O$: N, 12.72. Found: N, 12.58.

In a similar experiment using the same quantities of starting materials the formation of the diazoketone during the original refluxing period was confirmed by cooling the hot ethanol and removing the crude yellow crystals (1.36 g.) which separated. These were shown by their infrared spectrum to be diazoketone.

1-Tosylhydrazone of 3,3-Diphenyl-1,2-indanedione (XV). —To a solution of 3,3-diphenyl-1,2-indanedione¹⁵ (3.0 g.) in boiling methanol (150 ml.) was added *p*-tolucnesulfonylhydrazine (1.90 g.). Without further heating, the clear solution was allowed to stand overnight (room temperature), and the large yellow prisms (2.80 g.) filtered. Concentration of the filtrate gave a further 0.60 g., bringing the total yield to 3.4 g. (72%). Recrystallization from absolute ethanol gave fine yellow prisms, m.p. 188–190° dec.

Anal. Caled. for $C_{23}H_{22}N_2O_3S$: C, 72.08; H, 4.75; N, 6.01. Found: C, 72.03; H, 4.93; N, 6.11.

3.3-Diphenyl-1-diazo-2-indanone (**XVI**).—A solution of the tosylhydrazone (1.50 g.) in methylene chloride (30 ml.) was stirred with 0.1 N sodium hydroxide (45 ml.) for 4 hours. The orange organic layer was washed with water, dried and placed on a column of alumina. Elution of the column with a 1:1 mixture (by volume) of 30–60° petroleum ether and methylene chloride and evaporation of the eluate left 0.65 g. (65%) of tiny orange prisms. Recrystallization from cyclohexane gave red rods, m.p. 162-164° dec. A methylene chloride solution showed strong infrared bands at 4.81 and 5.92μ .

Anal. Caled. for $C_{21}H_{14}N_2O;\ C,\ 81.27;\ H,\ 4.55;\ N,\ 9.03.$ Found: C, 81.46; H, 4.57; N, 8.89.

3.3-Diphenyl-2-diazo-1-indanone (**XVII**).—A solution of 3,3-diphenyl-2-oximino-1-indanone¹⁵ (1.60 g.) in 1.2 N sodium hydroxide (5.0 ml.) and water (150 ml.) was cooled to 4° and 15 N ammonium hydroxide (1.5 ml.) added, followed by 5.25% sodium hypochlorite (20 ml.), added dropwise with stirring over a 10-minute period. After an additional 3 hours of stirring (cooling bath removed) the yellow product was taken up in methylene chloride, and the extract washed with water and dried. Removal of the solvent left a yellow oil which soon crystallized. After trituration with ligroin small pale yellow crystals (1.0 g., 65%) were obtained. Recrystallization from ethyl acetate-petroleum ether afforded yellow platelets, m.p. 179-180°. A methylene chloride solution showed strong infrared bands at 4.81 and 6.00 μ .

Anal. Caled. for $C_{2i}H_{14}N_2O;\ C,\ 81.27;\ H,\ 4.55;\ N,\ 9.03.$ Found: C, 80.65; H, 4.48; N, 9.16.

The photolysis apparatus employed in the irradiation experiments consisted of a Pyrex tube $(2'' \times 14'')$ bearing a 45/50 female standard taper joint into which fit the U-shaped quartz ultraviolet source. Below the joint was attached a side-arm connected via 24/40 joints to a Friedrichs condenser and thence to a water reservoir from which water was displaced by the evolved gas during the photolysis. The ultraviolet source was a low-pressure argon-filled mercury discharge tube, operated with voltage supplied from the secondary of a commercial neon sign transformer (500:1 step-up). The primary voltage (60 v.) was regulated by a variable transformer. The reaction vessel could be cooled in a Dewar flask or heated in a water-bath; with no external heat control the internal heating from the source tube brought the irradiated solutions to an equilibrium temperature of 50 $\pm 2^{\circ}$.

3-Methyl-6-chlorobenzocyclobutene-1-carboxylic Acid (**XVIIIc**).—A solution of 4-methyl-7-chloro-2-diazo-1-indanone (Xc) (2.00 g., 0.0097 mole) in tetrahydrofuran (170 ml.) and water (30 ml.) containing suspended sodium bicarbonate (2 g.) was irradiated at 50° until gas evolution ceased (9 hours). The orange solution was diluted with water (50 ml.) and the tetrahydrofuran was distilled. The aqueous residue was extracted repeatedly with methylene chloride to remove insoluble tars. Acidification of the cold aqueous layer yielded the crude acid (0.42 g.), which was filtered and taken up in boiling water (100 ml.). The hot solution was filtered from a trace of tar; on cooling, it de-

⁽²⁵⁾ H. Staudinger, Ber., 49, 1970 (1916).

⁽²⁶⁾ A. Angeli, Gazz. chim. ital., 24, 11, 44, 317 (1894).

posited white needles of XIIc (0.36 g., 19%), m.p. 144-145°. An analytical sample was obtained as fine white needles, m.p. 143-144°, by sublimation at 95° (0.5 mm.).

Anal. Caled. for $C_{10}H_9O_2Cl$: C, 61.11; H, 4.62; Cl, 18.05. Found: C, 61.38; H, 4.87; Cl, 17.84.

3,6-Dimethylbenzocyclobutene-1-carboxylic Acid (XVIIIb). —A solution of 4,7-dimethyl-2-diazo-1-indanone (Xb) (1.00 g., 0.0054 mole) in tetrahydrofuran (170 ml.) and water (30 ml.) containing suspended sodium bicarbonate (1 g.) was irradiated at 50° for 16 hours. The solution was distilled until free of tetrahydrofuran and the tarry aqueous layer extracted with methylene chloride. The aqueous layer was acidified, extracted with ether, and the ether layer dried and evaporated. The residual yellow solid was sub-limed at 78° (0.5 mm.) to give the acid XIIb as tiny white prisms (0.21 g., 22%), m.p. 107–109°.

Anal. Calcd. for $C_{11}H_{12}$, O_2 : C, 75.02; H, 6.87. Found: C, 75.12; H, 6.97.

1-Cyanobenzocyclobutene (XX). (a).—Monobromide XIX (5.00 g., 0.0273 mole) and sodium cyanide (2.0 g., 0.041 mole) were dissolved in dimethyl sulfoxide (30 ml.), heated at 50° for 30 minutes and finally at 95° for another 30 minutes. Water (150 ml.) was added and the solution was then extracted with 8:1 ether-petroleum ether (150 ml.). The ether solution was washed several times with water and then passed through anhydrous sodium sulfate. The solvent was evaporated and the residue distilled under reduced pressure. Three fractions, b.p. 88° (1.3 mm.), were obtained: (1) 0.615 g., n^{25} D 1.5657; (2) 1.462 g. n^{25} D 1.5492; (3) 1.204 g., n^{25} D 1.5450; yield 3.28 g. (93%). Fraction 2 was analyzed.

Anal. Caled. for C₃H₇N: C, 83.69; H, 5.46; N, 10.85. Found: C, 83.74; H, 5.48; N, 10.87.

(b).—A solution of monobromide XIX and sodium cyanide (excess) in methanol was refluxed for 11 hours and the reaction mixture worked up in the manner described above. A comparison of the infrared spectra of the product with those of the monobromide and nitrile indicated that only a 25-30% conversion to 1-cyanobenzocyclobutene took place under these conditions.

Hydrogen Peroxide Oxidation of 1-Cyanobenzocyclobutene (XX).—A mixture of the nitrile (1.00 g., 0.0078 mole), 30% hydrogen peroxide (2 ml., 0.017 mole) and 20% sodium hydroxide (2 ml.) reacted exothermically with evolution of oxygen. After 15 minutes of shaking, methanol was added carefully to sustain the reaction. If the temperature of the reaction mixture was allowed to increase above 60° , hydrolysis of the amide occurred as was evidenced by the evolution of ammonia. In all, 8–10 ml. of methanol was added; the use of less methanol led to incomplete reaction. When the addition of more methanol failed to increase the rate of evolution of oxygen, the mixture was warmed at 60° for 15 minutes longer. The reaction mixture was then transferred to a separatory funnel, diluted with water and extracted with methylene chloride (50 ml.). The methylene chloride solution, after filtration through anhydrous sodium sulfate, was diluted slowly with 30–60° petroleum ether, when benzocyclobutene-1-carboxamide (XXI) (0.835 g., 73%) precipitated in fine white needles, m.p. 158.5–159°. Recrystallization from methylene chloride–30–60° petroleum ether raised the melting point to a constant value of 159.5°.

Anal. Caled. for C_9H_9NO : C, 73.45; H, 6.16; N, 9.52. Found: C, 73.44; H, 6.31; N, 9.34.

Benzocyclobutene-1-carboxylic Acid (XVIIIa). (a).— The amide XXI (1.00 g.) was dissolved in hot 20% aqueous sodium hydroxide (15 ml.) and heated for 5 hours on the steam-bath. The solution was then cooled, made strongly acid with concentrated hydrochloric acid and extracted twice with 100-ml. portions of a 5:1 mixture of petroleum ether (30-60°) and ether. The organic extract was filtered through sodium sulfate, evaporated to dryness, and the residue dissolved in a small amount of petroleum ether (30-60°). On cooling the solution to -5° there was obtained, in two crops, benzocyclobutene-1-carboxylic acid (0.975 g., 97.5%), m.p. 74.5-76°. Several recrystallizations from petroleum ether (30-60°) raised the melting point to 76.5°.

Anal. Calcd. for C₉H₈O₂: C, 72.96; H, 5.44; neut. equiv., 148. Found: C, 72.60; H, 5.58; neut. equiv., 148.

(b).—A solution of 2-diazo-1-indanone (Xa) (2.0 g., 0.0126 mole) in tetrahydrofuran (200 ml.) and water (100 ml.) containing sodium bicarbonate (2.0 g.) was irradiated at the boiling point of the solution for 10 hours. Removal of the tetrahydrofuran by distillation left a tarry aqueous residue which, after extraction with methylene chloride, was acidified and extracted with ether. The ether layer was washed with water, dried over sodium sulfate and evaporated. The tan solid residue was sublimed at 90° (2 mm.) to yield small white prisms of benzocyclobutene-1-carboxylic acid (0.400 g., 21%), m.p. 71-74°. Recrystallization from petroleum ether gave white needles, m.p. 74-75°. The melting point of this material was not depressed upon admixture with a sample prepared by method a; in addition, the infrared spectra of both samples were identical.

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[CONTRIBUTION FROM THE INSTITUTO DE QUÍMICA AGRÍCOLA, MINISTÉRIO DA AGRICULTURA]

The Chemistry of Rosewood. II. Isolation and Identification of Cotoin and Pinocembrin

BY OTTO RICHARD GOTTLIEB AND WALTER B. MORS

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Two additional compounds—2,6-dihydroxy-4-methoxybenzophenone (cotoin) and 5,7-dihydroxy-flavanone (pinocembrin)—have now been isolated each from one of the commercially exploited species of South American rosewood trees (genus *Aniba*). Attention is again called to the chemical relationship between species in this plant genus.

The preceding article¹ described the isolation of two previously unknown substances from two species of South American rosewood trees: anibine (I) and 4-methoxy-paracotoin (II), found to be present in the wood of *Aniba rosaeodora* Ducke and *A. Duckei* Kostermans (family *Lauraceae*). Attention was called to the structural similarity of these two compounds with phenylcoumalin (III) and paracotoin (IV), which occur, respectively, in the barks of *Aniba coto* (Rusby) Kostermans and *A*.

(1) Walter B. Mors, Otto Richard Gottlieb and Carl Djerassi, This Journal, **79**, 4507 (1957). *pseudo-coto* (Rusby) Kostermans.² All these substances can be represented by substituted α -pyrones, with one aromatic substituent attached at position 6. Attention has now been directed to the acidic fraction of the original benzene extracts.

I,
$$Ar = 3$$
-pyridyl
 $R = OCH_3$
II, $Ar = piperonyl$
 $R = OCH_3$
 $R = OCH_3$
 $Ar = piperonyl$
 $Ar = H$
 $IV, Ar = piperonyl$
 $R = H$

⁽²⁾ For historical and botanical background see ref. 1.