[CONTRIBUTION FROM THE INSTITUTE OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF SZEGED]

ADDITION OF MALEIC ANHYDRIDE TO ANETHOLE. I.[1]

V. BRUCKNER AND J. KOVÁCS

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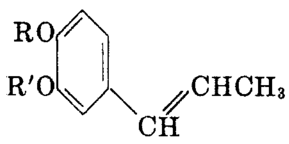
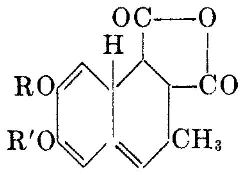
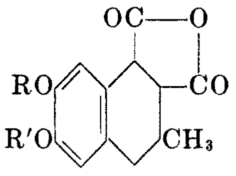
In a previous communication (1) it was proved in agreement with the statements of Hudson and Robinson (2) that O-methylisoeugenol (Ia) and isosafrole (Ib) produce with maleic anhydride tetrahydronaphthalene derivatives of type III, which must be formed from unstable intermediates of type II. Besides this, one of us (1) found that anethole (Ic) with maleic anhydride gives a crystalline product which contains for 1 mole of anethole 2 moles of maleic anhydride. The formation of this "bis-adduct" was explained in the following manner: the unstable intermediate (IIc) was not stabilized by an aromatic rearrangement but reacted immediately as a conjugated diene; in the sense of the rule of Bredt-Windaus (3), it ought then to give the end product of formula IV.



I

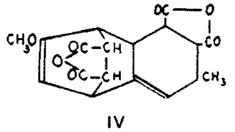


II

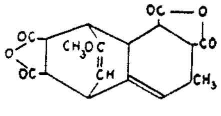


III

a. $R = R' = CH_3$
b. $R + R' = CH_2$
c. $R = CH_3,\ R'O = H$



IV



IVA

In the reaction of anethole with maleic anhydride, Hudson and Robinson (2) observed only the formation of a heteropolymer product (4). Tamayo and Ayestarán (5) isolated, to judge from all signs, the same product; however, they made the mistake of thinking that they had obtained a regular 1:1-adduct. Nevertheless, the formation of this heteropolymer product dominates this reaction, so that previously (1) it was possible to obtain the bis-adduct in only an 8% yield. Now we have found that different inhibitors can entirely repress the formation of the heteropolymer product in favor of the bis-adduct. If the components are melted with a small amount of dimethylaniline at 80°, a 60% yield of the bis-adduct is obtained.

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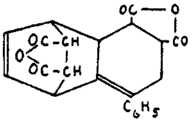
[1] Preliminary report: *Nature*, 1948, in press.

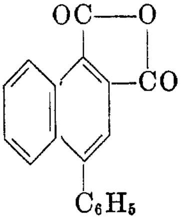
We have reexamined the correctness of formula IV, which was especially indicated by the following two considerations:

A. So far no one has yet exactly proved that it is possible to disturb permanently through a diene synthesis the aromatic character of a mononuclear system. Although Wagner-Jauregg (6) had observed the formation of a bis-adduct in the reaction between 1,1-diphenylethylene and maleic anhydride, and set up first the formula V, later, however, he repudiated (7) the possibility of this formula, without advancing another one. In spite of this, Bergmann *et al.* (8) accepted the correctness of this formula (V), as heating the compound with sulfur gave the naphthalene derivative VI. They also succeeded in converting numerous other 1,1-diarylethylenes in this manner; however, they did not prove conclusively the formulas of the bis-adducts.



V

B. Hudson and Robinson (2) were of the opinion that naphthalene derivatives are obtained only by a Diels-Alder reaction of styrene derivatives when there is an alkoxyl group in the *m*-position to the side chain. The formation of IV through the intermediate IIc is in disagreement with this view.

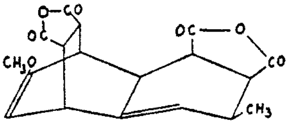


VI

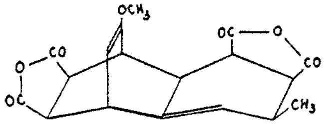
The proof of the correctness of formula IV must first take into account the spatial arrangement. If we assume an *endo-cis* type addition, which has often been proved in Diels-Alder reactions (9), and starting from anethole, which may be supposed to be a *trans*-anethole (10), then we must still take into account the formation of four individual stereomers, *i.e.*, two pairs of antipodes. Formulas VII and VIII show arbitrarily-chosen members of each of the two possible racemates. We obtained a homogeneous bis-adduct, which behaves, as shown below, rather in agreement with formula VIII (and naturally also with its mirror image). Therefore we propose as a simpler manner of design, formula IVa instead of the previously used formula IV.

The naphthalene skeleton. On distilling the bis-adduct *in vacuo*, it decomposed into its components: anethole and maleic anhydride. If it was, however, heated in the presence of sulfur, it gave 7-methoxynaphthalene-1,2-dicarboxylic acid anhydride (11). So at higher temperature the diene synthesis becomes reversible in both its phases, but in the presence of sulfur acting as a dehydrogenating agent, IIc becomes stabilized as a naphthalene derivative without decomposition.

The enol ether character of the methoxyl group. With the calculated amount of 5 *N* sodium hydroxide, the bis-adduct could be quickly saponified even at room temperature; on acidification, an acid was obtained containing a methoxyl group ("A-acid"; m.p. 270–273°), which crystallized as trihydrate and was rather sparingly soluble in hot water. This substance could be converted by treatment with acetic anhydride into the bis-adduct. If the saponification was carried out by boiling with a small excess of alkali, two acids were obtained on acidification; the one which appeared in lesser amount was the A-acid, whereas the other one contained no methoxyl, and was more easily soluble in hot water. The latter ("B-acid"; m.p. 265–270°) crystallized as a tetrahydrate and gave on treatment with acetic anhydride, or by heating, the same anhydride (anhydride of IXb; m.p. 288°), which also could be obtained by treatment of the bis-adduct for a short time with boiling formic acid, and did not contain a methoxyl group. Boiling an aqueous solution of the A-acid leads, in consequence of the easy splitting of the methoxyl group, to the B-acid. Finally, the easy splitting of this group was also proved by the fact that the bis-adduct could be converted with boiling aniline to the same bis-phenylimide (bis-phenylimide of IXb; m.p. 280–285°) which also could be obtained by a similar treatment of the anhydride, the methoxyl group of which was previously split by boiling with formic acid.



VII

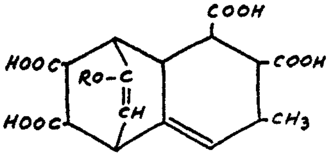


VIII

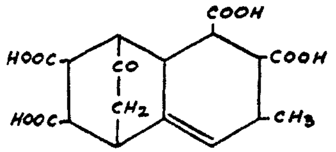
The position of the enol ether methoxyl group. Both acids A and B mentioned above could be sharply titrated with 0.05 *N* sodium hydroxide whereby, however, they showed the presence of only 3 carboxyl groups; the fourth of these groups appeared only during a lactone titration; however, it is possible to split the lactone ring at room temperature. Consequently the acids IXa and IXb (in the latter we can naturally expect a change into the tautomeric keto acid) which are to be derived from formula VIII must contain one of their carboxyl groups in a lactone bond. As the possibility of a lactonization is offered by γ- as well as by δ-unsaturated carboxylic acids (12), also by γ- or δ-oxo acids (13), it is possible to set up different formulas for the lactonized acids. For spatial reasons, some of these formulas are to be preferred, so that as strainless systems there remain only the two types X and XI.

a. R = CH_3
b. R = H

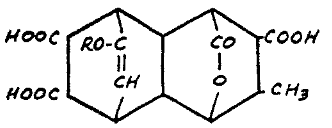
The results of our further investigations seem to support formula XI. Namely, both acids could be esterified with diazomethane, whereby the A-acid (XIa), through consumption of 3 moles of diazomethane formed a lactone methyl ether trimethyl ester (XII; m.p. 178–179°), whereas the B-acid (XIb), through consumption of 4 moles of the reagent, gave a keto acid tetramethyl ester (XIII, m.p. 208–210°). As these esters are isomeric but not identical, we must assume that by the action of diazomethane, the lactone ring of the B-acid (XIb) was opened.



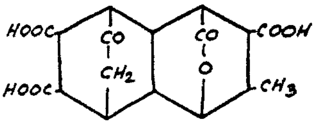
IX



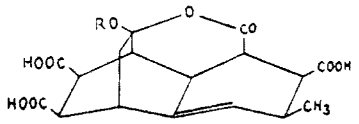
IXb



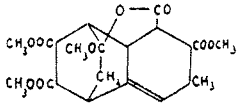
X



Xb



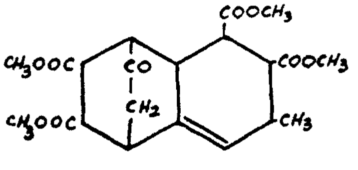
XI



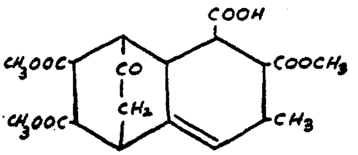
XII

The following experimental facts also support the correctness of this conclusion: (a) ester XIII could also be obtained directly from the bis-adduct (VIII) by boiling it with methanol containing concentrated sulfuric acid; (b) on boiling with formic acid, XII gave by loss of one of its methyl groups a trimethyl ester (m.p. 230–232°) for which we must assume formula XIV, as it shows in alcoholic-aqueous solution, acid reaction, and forms with diazomethane the ester XIII. These reactions, especially the splitting of the lactone ring by diazomethane, agree only with formula XI, and exclude formula X.

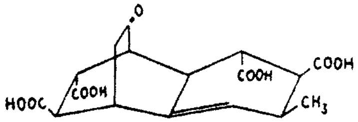
In further support of formula XI may be advanced the following evidence: on boiling VIII, XIa, XIb, or XIII for 10–12 hours with 5 *N* hydrochloric acid, an acid (m.p. 260–262°) was formed, which did not contain a methoxyl group. It was isomeric with XIb, and on titration with 0.05 *N* sodium hydroxide showed sharply 4 carboxyl groups. Obviously we must expect here, just as in the similar treatment of *cis*-hexahydro-*o*-phthalic acid (14), the formation of a *trans* acid, for which we set up formula XV, as it did not form a lactone, and did not give an anhydride when treated with boiling acetic anhydride, but remained unchanged. This *trans* acid produced with diazomethane a tetramethyl ester (m.p. 154°) and gave with hydroxylamine a regular oxime (m.p. 224–225°) containing 4 carboxyl groups. In consequence of their structures, the *trans* acid



XIII



XIV



XV

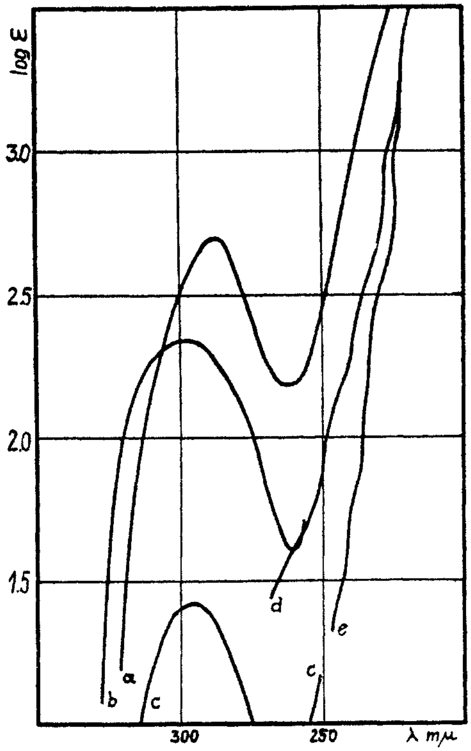
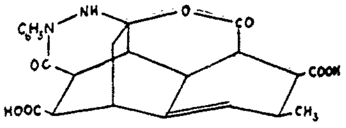


FIG. 1. Ultraviolet spectra of dilute aqueous solutions of XV, curve a; XIa, curve e; XIb, curve d; of dilute chloroform solutions of XV-tetramethyl ester, curve b; XIII, curve c.

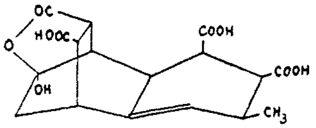
as well as its ester show an ultraviolet absorption spectrum containing the band of the ketone group, which is somewhat displaced towards the long-wave region; the ketone band is also shown by the ester XIII. In accordance with their different structures, the acids XIa and XIb do not show this band (*cf.* Fig. 1).

Decision between the possibilities for the formulas VII and VIII. The experimental facts which have been hitherto stated would also agree with formula VII for the bis-adduct. However, the conversion of the B-acid with phenylhydrazine gave a result which was in better agreement with formula VIII; namely, the B-acid did not form a regular phenylhydrazone but led to a bis-condensed product ($C_{23}H_{26}N_2O_7$; m.p. 180°) which, though it could not be sharply titrated as a dicarboxylic acid, can only contain two carboxyl groups, since it forms with diazomethane a dimethyl ester (m.p. 295–300°).[2]

We can therefore state confidently, that in the reaction of the B-acid with phenylhydrazine a double condensation took place, whereby also one of the carboxyl groups disappeared.[3] So we come to the conclusion that the product of this condensation must be a dihydropyridazinone derivative (15) of formula



XVI



XVII

XVI. If we accept this formula, we can come to a decision between the two formula possibilities VII and VIII. Namely, the hydroxylactone carboxylic acid (XVII), derived from formula VII, contains a hydroxyl group which can react in *trans* position to each of the 3 carboxyl groups and, therefore, a double condensation can not take place. Because of this we decided in favor of formula VIII, in which only the presence and position of that double link which does not belong to the enol ether group remains to be proved. Investigations concerning this question will be reported later.

EXPERIMENTAL

Action of maleic anhydride on anethole in the presence of dimethylaniline (*VIII*). A stirred mixture of maleic anhydride (500 g.), anethole (300 g.), and dimethylaniline (8 g.)

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[2] At the moment we are not able to explain the conspicuously high m.p. of this ester in relation to the m.p. of the free acid.

[3] The B-acid gives with hydroxylamine hydrochloride in acid medium a condensation product which shows the empirical formula of a regular oxime but behaves as a dibasic acid. By treatment with diazomethane or dimethyl sulfate, this acid forms a compound of much higher nitrogen value than calculated for a regular ester. On melting the condensation product, loss of an additional two moles of water takes place and a dibasic acid is again formed. The structure of all these products must be proved by further investigations.

was heated on a bath at 80° for four hours. From the homogeneous liquid, which became viscous and dark brown, a large amount of crystals separated during the heating. After cooling, the crystalline product was filtered, washed with ethyl acetate until colorless, and dried at 100° *in vacuo*; yield 310 g. (44.5%). It crystallized from ethyl acetate in large colorless prisms containing 0.5 mole of solvent of crystallization, which was lost on heating at 100° *in vacuo* for ten hours; m.p. 241° (dec., beginning at 230°); the same m.p. was observed after many recrystallizations, also with change of solvent.

Anal. Calc'd for $C_{18}H_{16}O_7$: C, 62.8; H, 4.7.
Found: C, 62.7; H, 4.9.

After removal of solvent from the filtrate of the reaction mixture, a dark brown viscous oily residue was obtained (383 g.), which on steam distillation gave 17 g. of anethole. The remaining aqueous solution was concentrated to 500 ml., well cooled, acidified, the crystals washed with 250 ml. of cold water, and dried *in vacuo* at 100°. This procedure led to 132 g. (16.5%) of the B-acid (see below), total yield of the addition, 61%.

A-acid (*XIa*). Six and nine-tenths grams of the powdered bis-adduct (VIII) was shaken with 16 ml. of 5 *N* sodium hydroxide for five minutes, cooled, acidified with 2 *N* hydrochloric acid, the crystals washed with 80 ml. of ice-cold water, and dried in air; colorless needles, yield 6 g. The substance is sparingly soluble in hot water (1:100), but on cooling, only one-tenth crystallizes, as the main part has been turned into the readily-soluble B-acid (see below). It forms a trihydrate (*a*), the crystal water of which is completely lost by drying *in vacuo* at 100° (*b*); m.p. 270–273° (dec.).

Anal. Calc'd for $C_{18}H_{20}O_9 + 3H_2O$: C, 49.8; H, 6.0; CH_3O, 7.1; for $C_{18}H_{20}O_9$: C, 56.8; H, 5.3.
Found: (*a*) C, 49.8; H, 6.1; CH_3O, 6.9.
(*b*) C, 56.8; H, 5.4.

Titration[4] of (*a*). Calc'd for 3 COOH groups: COOH, 31.1.
Found: COOH, 31.9.

Lactone titration[5] of (*a*) Calc'd for 4 COOH groups: COOH, 41.1.
Found: COOH, 39.8.

Conversion of the A-acid into its anhydride (*VIII*) was carried out by dissolving it in four parts of boiling acetic anhydride and diluting the cooled solution with dry ether. The crystals, after recrystallization from ethyl acetate, show alone and mixed with the bis-adduct (VIII) obtained directly, the m.p. 241° (dec.).

Anal. Calc'd for $C_{18}H_{16}O_7$: C, 62.8; H, 4.7.
Found: C, 63.0; H, 4.8.

B-Acid (*XIb*). 1. A solution of 6.9 g. of VIII in 20 ml. of 5 *N* sodium hydroxide was boiled for ten minutes, and after acidifying with 10 ml. of 10 *N* hydrochloric acid, cleared with charcoal. On cooling, there separated a mixture of the crystals of both the acids A and B (6 g.), 5 g. of which in 20 ml. of boiling water could be redissolved; the insoluble remainder was the A-acid. The tetrahydrate of the B-acid crystallized from the aqueous solution in colorless large prisms (2.8 g.); they lost their hydrate water by drying *in vacuo* at 100° for three hours; readily soluble in hot water (1:1.8); methoxyl analysis negative; m.p. 265–270° (dec., beginning at 250°).

2. If VIII was boiled with water for a few hours, the B-acid was formed in quantitative yield. For analysis a sample was recrystallized from water and dried (*a*) in open air until the weight became constant; (*b*) *in vacuo* at 100° for three hours.

Anal. Calc'd for $C_{17}H_{18}O_9 + 4H_2O$: C, 46.6; H, 6.0; for $C_{17}H_{18}O_9$: C, 55.7; H, 5.0.
Found: (*a*) C, 46.7; H, 6.2.
(*b*) C, 55.4; H, 5.2.

Titration of (*a*). Calc'd for 3 COOH groups: COOH, 30.8.
Found: COOH, 31.1.

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[4] All carboxyl estimations were made by direct titration of hot alcoholic-aqueous solution of 30–50-mg. samples using 0.05 *N* sodium hydroxide and phenolphthalein.

[5] All lactone titrations were carried out in the customary manner using a solution of 200–350-mg. samples in 10 ml. of *N* sodium hydroxide.

Lactone titration of (*a*). Calc'd for 4 COOH groups: COOH, 41.1.
Found: COOH, 41.0, 40.9.

Conversion of the B-acid into its anhydride. Bis-anhydride of IXb. 1. A suspension of 2 g. of the B-acid (XIb) in 30 ml. of acetic anhydride was refluxed for a few minutes, and the product after filtering washed with ether. The colorless crystals were recrystallized from nitrobenzene; m.p. 288° (dec. beginning at 275°).

2. On boiling 2 g. of the bis-adduct (VIII) with 20 ml. of formic acid, solution took place at first, but after a few seconds the solution deposited crystals (1.1 g.) which did not contain methoxyl; m.p. alone and mixed with a sample obtained *via* 1., 286° (dec. from 275°).

3. On heating the B-acid (XIb) near its m.p., the same anhydride was obtained as by 1. or 2. Hydrolysis of the substance leads to the B-acid.

Anal. Calc'd for $C_{17}H_{14}O_7$: C, 61.8; H, 4.3.
Found: 1. C, 62.0; H, 4.4.
2. C, 61.9; H, 4.5.

Trimethyl ester of the A-acid (XII). Eight-tenths gram of the A-acid (XIa) was dissolved in 50 ml. of boiling methanol, the solution quickly cooled, and treated with an ethereal solution of diazomethane. Concentrated to 5 ml., the solution deposited colorless prisms which were twice recrystallized from methanol. The product can be distilled *in vacuo* (14 mm.) without decomposition; m.p. 178–179°.

Anal. Calc'd for $C_{21}H_{26}O_9$: C, 59.7; H, 6.2; CH_3O, 29.4.
Found: C, 59.8, 59.8; H, 6.2, 6.3; CH_3O, 28.7.

Tetramethyl ester (XIII). 1. A solution of 3 g. of the B-acid (XIb) in 60 ml. of methanol was treated with diazomethane, and the crystals (2.5 g.) recrystallized from methanol; long needles, m.p. 208–210°. The substance can be distilled *in vacuo* (14 mm.) without decomposition.

2. On boiling a mixture of the bis-adduct (VIII, 20 g.), methanol (340 ml.), and concentrated sulfuric acid (40 ml.), for four hours, crystals of ester XIII separated (20.5 g.). After recrystallization from methanol, they showed alone and mixed with a sample obtained *via* 1. the m.p. 208–210°.

3. A sample of the ester XIV (see below) was treated with diazomethane; long needles; m.p. alone and mixed with specimens obtained by 1. and 2., 208–210°.

Anal. Calc'd for $C_{21}H_{26}O_9$: C, 59.7; H, 6.2; CH_3O, 29.4.
Found: 1. C, 59.5, 59.7; H, 6.3, 6.4; CH_3O, 29.8.
2. C, 59.8, 59.7; H, 6.2, 6.2.

Trimethyl ester (XIV). A solution of 0.3 g. of the ester XII in 1 ml. of 98% formic acid was boiled a few minutes; on cooling, crystals separated, which were recrystallized from methanol. The substance dissolves in aqueous alkali instantaneously. It gives with diazomethane, ester XIII (see above), m.p. 230–232°.

Anal. Calc'd for $C_{20}H_{24}O_9$: C, 58.8; H, 5.9; CH_3O, 22.8.
Found: C, 58.9; H, 5.8; CH_3O, 23.4.

trans-Keto acid (XV). 1. On boiling 5 g. of the bis-adduct (VIII) with 100 ml. of 5 *N* hydrochloric acid, slow solution took place. The solution was concentrated at reduced pressure to 20 ml. The crystals were washed with water, recrystallized from water, and dried *in vacuo* at 100°; yield 2.4 g., colorless needles, m.p. 260–262° (dec.).

2. One and seven-tenths grams of the ester XIII was refluxed with 60 ml. of 5 *N* hydrochloric acid for twelve hours, and the solution was worked up as described in 1.; colorless needles, m.p. alone and mixed with a sample obtained *via* 1., 260–262° (dec.).

3. A solution of 5 g. of the B-acid (XIb) in 50 ml. of hot 5 *N* hydrochloric acid was refluxed for twelve hours and then worked up as above; m.p. alone and mixed with specimens obtained by 1. and 2., 260–262° (dec.). In mixture with the B-acid (m.p. 265–267°) there was no noteworthy depression of the m.p. to be observed; however, in contrast to the B-acid, the *trans*-keto acid (XV) crystallized unchanged from its solution in acetic anhydride, even when this solution was boiled for a long time.

Anal. Calc'd for $C_{17}H_{18}O_9$: C, 55.7; H, 5.0.
Found: C, 55.4; H, 5.2.

Titration. Calc'd for 4 COOH groups: COOH, 49.2.
Found: COOH, 47.5.

Methyl ester of the trans-keto acid (XV). It was prepared in the customary manner with diazomethane; colorless crystals from methanol, m.p. 154–155°.

Anal. Calc'd for $C_{21}H_{26}O_9$: C, 59.7; H, 6.2.
Found: C, 59.6, 59.5; H, 6.4, 6.5.

Bis-phenylimide of the keto-tetracarboxylic acid (IXb). 1. Three and six-tenths grams of the bis-adduct (VIII) was slowly heated with 8 ml. of freshly-distilled aniline. As the substance dissolved, the reaction became exothermic, and soon crystals began to separate. They were washed with hot ethyl acetate and recrystallized from acetic acid or nitrobenzene; colorless small prisms, which gave negative methoxyl analysis, m.p. 280–285° (dec.).

2. From the anhydride which was prepared by treatment of the B-acid (XIb) with acetic anhydride the same bis-phenylimide was obtained by reaction with aniline.

Anal. Calc'd for $C_{29}H_{24}N_2O_5$: C, 72.5; H, 5.0; N, 5.8.
Found: C, 72.2; H, 5.3; N, 5.8.

Hydropyridazinone derivative (XVI). A solution of 3.7 g. of the B-acid (XIb) and 0.5 g. of phenylhydrazine hydrochloride in 12 ml. of hot water was boiled for five minutes, whereby crystals separated. The product was washed with water, recrystallized from water, and dried *in vacuo* at 100°; colorless needles, m.p. 180°.

Anal. Calc'd for $C_{23}H_{22}N_2O_7$: C, 63.0; H, 5.1; N, 6.4.
Found: C, 62.9, 63.1; H, 5.0, 5.3; N, 6.2.

Titration. Calc'd for one COOH group: COOH, 10.3.
Found: COOH, 11.7.

Action of diazomethane on the pyridazinone derivative (XIV). A suspension of 0.1 g. of XVI in 25 ml. of dry methanol was treated with an ethereal solution of diazomethane; colorless needles from xylene, m.p. 295–300° (dec.).

Anal. Calc'd for $C_{25}H_{26}N_2O_7$: C, 64.4; H, 5.6; N, 6.0; CH_3O, 13.3.
Found: C, 64.6, 64.4; H, 5.8, 5.8; N, 6.0; CH_3O, 13.2.

Action of hydroxylamine on the B-acid. An aqueous solution of 2 g. of the B-acid (XIb) and 2 g. of hydroxylamine hydrochloride in 5 ml. of hot water was heated on a steam-bath for one hour, whereby crystallization took place. On recrystallization from water, colorless needles were obtained, which were dried in air to constant weight. A tetrahydrate (*a*) was formed, the crystal water of which was lost by drying *in vacuo* over P_2O_5 at 100° for ten hours; the latter (*b*), which is sensitive towards moisture, also was obtained by recrystallization of the tetrahydrate from methanol; m.p. 210–211° (dec.).

Anal. Calc'd for $C_{17}H_{19}NO_9 + 4H_2O$: C, 45.4; H, 6.0; for $C_{17}H_{19}NO_9$: C, 53.5; H, 5.0; N, 3.7.

Found: (*a*) C, 45.4; H, 6.0.
(*b*) C, 53.4; H, 5.1; N, 3.7.

Titration of (*a*). Calc'd for 2 COOH groups: COOH, 24.4.
Found: COOH, 23.6.

Derivatives of the condensation product described above. 1. By treatment with boiling acetic anhydride, colorless prisms were obtained, m.p. 270–272° (dec.). The substance was neutral and did not liberate CO_2 from a concentrated solution of sodium carbonate. It is probably the acetylated oxime of the bis-anhydride of IXb.

Anal. Calc'd for $C_{19}H_{17}NO_8$: C, 58.9; H, 4.4; N, 3.6.
Found: C, 58.6, 58.5; H, 4.5, 4.8; N, 3.4.

2. Melting led to a resin, which on treatment with acetone gave colorless needles, m.p. 274–275° (dec.).

Anal. Calc'd for $C_{17}H_{15}NO_7$: C, 59.1; H, 4.4; N, 4.1.
Found: C, 58.8, 58.8; H, 4.6, 4.6; N, 4.2, 4.2.

Titration (in acetone solution). Calc'd for 2 COOH groups: COOH, 28.9.
Found: COOH, 26.7.

3. On treatment with diazomethane, colorless prisms were obtained, m.p. 206–208°.

Anal. Found: C, 58.9, 58.8; H, 5.9, 5.6; N, 5.0; CH_3O, 24.1.

4. Esterification with dimethyl sulfate led to colorless prisms, m.p. 195°.

Anal. Found: C, 59.3; H, 5.8; N, 5.2, 5.3.

Decomposition of the bis-adduct (VIII) by heating. Four grams of the bis-adduct was placed in a distilling flask and cautiously heated *in vacuo* until distillation began. The oily distillate (3.3 g.) was a mixture containing maleic anhydride and anethole. After the former had crystallized from the oily distillate, it was recrystallized from ethyl acetate, then from benzene; m.p. alone and mixed with an authentic specimen, 54–55°. The oily part of the distillate gave on steam distillation anethole; m.p. alone and mixed with an authentic specimen 21–22°.

3-Methyl-7-methoxynaphthalene-1,2-dicarboxylic acid anhydride. A mixture of 0.35 g. of sulfur and one g. of the bis-adduct (VIII) was heated for fifteen minutes at 230–235° in a metal-bath. After the evolution of hydrogen sulfide stopped, the remainder was extracted with hot ethyl acetate, the solution treated with charcoal, and concentrated to 3 ml. On cooling, red prisms were obtained which gave after two recrystallizations from ethyl acetate yellow needles, the solution of which showed a greenish fluorescence; m.p. 214–217°. The substance was identical with the naphthalene derivative which was obtained by heating a mixture of maleic anhydride and anethole in the manner described in a previous communication (1).

Anal. Calc'd for $C_{14}H_{10}O_4$: C, 69.4; H, 4.2.
Found: C, 69.3; H, 4.3.

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SUMMARY

1. By the action of maleic anhydride on anethole, only a small amount of a crystalline bis-adduct (2:1) could be obtained, the main bulk of the reaction product being a heteropolymer. However, if a small amount of dimethylaniline was added, the formation of the heteropolymer product was prevented, and the yield of the crystalline adduct was high.

2. The correctness of formula IV given earlier for the bis-adduct has been reexamined.

3. If we assume an *endo-cis* type addition, and starting from *trans*-anethole, then the formation of 4 possible stereomers (*i.e.*, 2 racemates) could be expected. All properties of the bis-adduct agree with those expected from VIII (and its mirror image). Therefore we propose as a simpler manner of representation formula IVa instead of the previously used formula IV.

4. The presence and position of the double bond in the condensed ring remains to be established.

SZEGED, HUNGARY

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