[Contribution from the Institute of Organic Chemistry of the University of Budapest]

ON THE STRUCTURE OF THE BIS-ADDUCTS FORMED BY ADDITION OF MALEIC ANHYDRIDE TO 1,2-DIARYLETHYLENES

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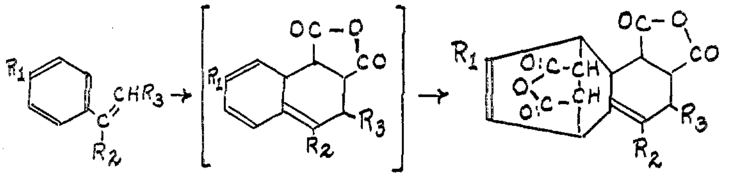
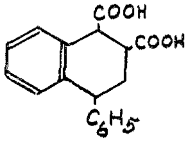
The formation of an addition product between *as*-diphenylethylene (Ia) and maleic anhydride in the mole ratio 1:2 (bis-adduct) was first observed by Wagner-Jauregg (1). The product was suggested to be formed by double addition of the philodiene to Ia through the intermediate IIa, and to possess in consequence structure IIIa.



I II III

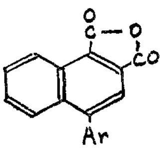


IV

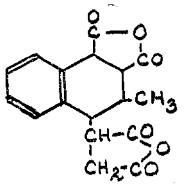
(a) $R_1 = R_3 = H$; $R_2 = C_6H_5$
(b) $R_1 = CH_3O$; $R_2 = H$; $R_3 = CH_3$
(c) $R_1 = CH_3O$; $R_2 = C_6H_5$; $R_3 = H$

Later Wagner-Jauregg (2) revised his opinion, having found that (a) the bis-adduct possesses no C═C bonds, as it was resistant toward catalytic hydrogenation, and reacted with bromine by substitution rather than addition; (b) the bis-adduct loses readily one mole of maleic anhydride in the presence of a glacial acetic acid solution of hydrobromic or hydriodic acid and forms the tetralin derivative IV, while the endoethylene bridge of the anthracene-maleic anhydride adduct (3) is known to be stable under such conditions (2).

Later, Bergmann and co-workers (4) prepared bis-adducts from a number of 1,1-diarylethylenes and maleic anhydrides, converting the products by heating with sulfur to the corresponding 4-arylnaphthalene-1,2-dicarboxylic anhydrides (V). They did not investigate the structure of the bis-adducts more closely, these representing in their opinion probably structures corresponding to III, while Wagner-Jauregg (2)—as shown above—did not believe that the second step of the reaction between *as*-diphenylethylene and maleic anhydride is a diene synthesis, this view being shared also by Hudson and Robinson (5).



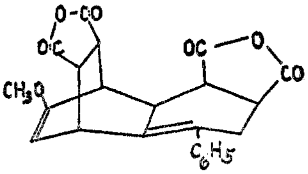
V



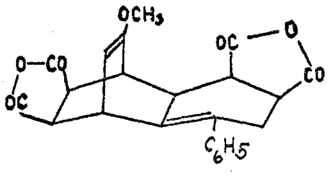
VI

One of us (V. B.) (6) observed the formation of a bis-adduct from anethole (Ib) and maleic anhydride. Extensive study (7) of the product established its IIIb structure, which appears to be closely analogous to the structure IIIa first proposed by Wagner-Jauregg for the 1,1-diphenylethylene-maleic anhydride bis-adduct. The study of the reaction between anethole and maleic anhydride has shown that this reaction is a real diene synthesis proceeding through the steps Ib → IIb → IIIb, and conclusive evidence was also obtained concerning the spatial structure of product IIIb. The probability of a complete analogy between the reaction of anethole and of the 1,1-diarylethylenes with maleic anhydride aroused our interest in the unsettled question of the structure of the 1,1-diarylethylene-maleic anhydride bis-adducts, and this interest was further stimulated by the theoretical aspects of the apparent disturbance of the aromatic character of mononuclear systems in these reactions, although such a possibility was recently refuted by Lora Tamayo (8).

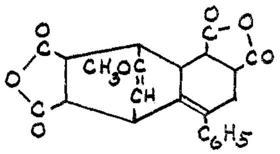
For particular study we chose the bis-adduct formed from 1-phenyl-1-*p*-anisylethylene (Ic) and maleic anhydride (4), since the presence of a methoxyl group promised to be of methodical advantage. A structure IIIc of this bis-adduct would represent a number of stereoisomerides; however, in diene syntheses the endo-cis type of addition is usual (9), and limits the number of the probable stereoisomerides to two (VII and VIII) each representing one of the two stereoisomeric forms of the two probable structures. We now are able to present evidence that the structure of the 1-phenyl-1-*p*-anisylethylene-maleic anhydride bis-adduct corresponds to structure VIII (which is more simply expressed by IX), and is actually analogous with the structure of the bis-adduct of anethole and maleic anhydride (IIIb).



VII



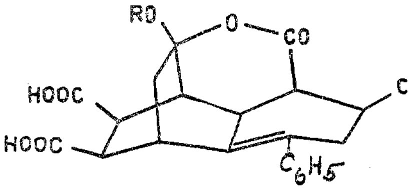
VIII



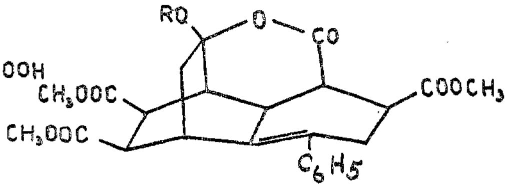
IX

The bis-adduct of 1-phenyl-1-*p*-anisylethylene and maleic anhydride, when heated under diminished pressure, decomposes into its components. This, while fully consistent with the frequently observed reversibility of diene syntheses, proves rather conclusively that the usual formation of the bis-adduct is not followed by any fundamental change in the carbon skeleton of the product. Heating the bis-adduct in the presence of sulfur and concomitant dehydrogenation to the corresponding naphthalene derivative (IVc), studied by Bergmann and coworkers (4), might be considered as proving that also thermal dissociation proceeds in two distinct steps (IIIc—IIc—Ic), in the presence of sulfur, the second step (IIc—Ic) being precluded by instantaneous dehydrogenation of the intermediate IIc.

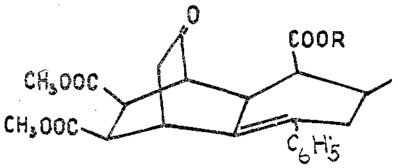
Hydrolysis of the bis-adduct has shown that the methoxyl group in this substance is of enol ether character, and there is one olefinic C,C bond present. Under mild conditions, an acid was obtained (Acid A) in which but three carboxyls are directly titratable, the fourth appearing only during lactone titration. This, together with the observation that acetic anhydride reconverts the acid to the bis-adduct, indicates structure Xa for Acid A. More energetic hydrolysis of the bis-adduct gives rise to another acid (Acid B) which contains no methoxyl group, and yields on treatment with acetic anhydride no longer the starting material, but a bis-anhydride, which forms also directly from the bis-adduct with hot conc'd formic acid. The neutralization equivalent of Acid B falls between the values calculated for a tri- and a tetra- basic acid, indicating structure Xb. Our reaons for assigning to acids A and B the hydroxylactone structures Xa and Xb are identical with those found valid in the analogous hydrolysis of the anethole-maleic anhydride bis-adduct (7).



X

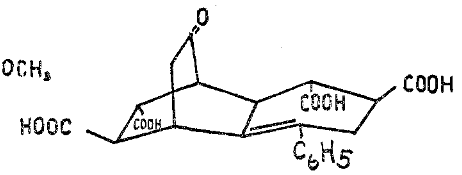


XI



XII

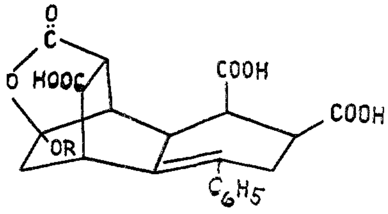
a, R = CH3
b, R = H



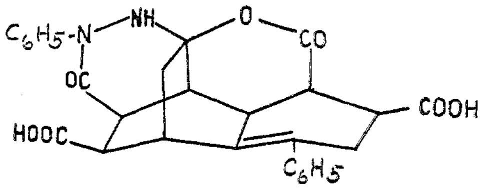
XIII

These structures appear to be fully consistent with the behavior of the two acids in methylation with diazomethane. Acid A (Xa) yields a trimethyl ester XIa, from which—because of the exceptional position of one of the four O-methyl groups—an acidic trimethyl ester (XIIb) was obtained with boiling formic acid. The structure of the acidic ester can not be XIb because the substance (a) liberates carbon dioxide from, and is readily soluble in, dilute cold sodium carbonate solution; (b) is sharply titratable with 0.05 *N* sodium hydroxide as a monobasic acid.

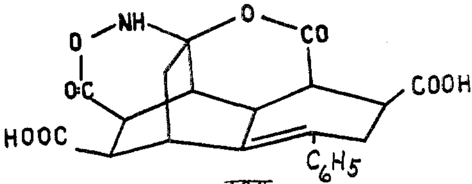
Boiling conc'd hydrochloric acid converts Acid A (Xa) and Acid B (Xb), and aso bis-adduct VIII, to a tetracarboxylic acid, which seems to be—in analogy with the parallel conversion of hexa-hydro-*cis-o*-phthalic acid (10)—to be *trans* acid, titration indicating sharply the presence of four carboxyl groups, and hence, the absence of a lactone grouping. Since boiling acetic anhydride does not convert the acid into an anhydride, both pairs of the carboxyls must be attached to rings in *trans* position. Therefore, we assign to this acid structure XIII, which was further confirmed by the observed ready formation of an oxime.



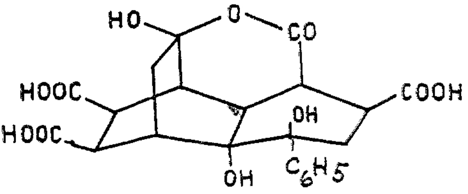
XIV



XV



XVI

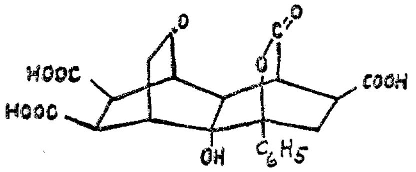


XVII

Although the interpretation of the above reactions by structure VIII of the bis-adduct meets no difficulties, the formation of Acid A or Acid B, and also of their esters, does not exclude the possibility that the bis-adduct may have structure VII, the acids remaining formulable also by XIVa and XIVb, respectively. This possibility was, however, definitely excluded by the observation that Acid B yields with phenylhydrazine a dibasic acid according to the equation $C_{22}H_{20}O_9 + C_6H_8N_2 = 2H_2O + C_{28}H_{24}N_2O_7$. The reaction appears to be of the type of the known double condensations of γ-keto acids with phenylhydrazine, and to be therefore fully consistent with a structure Xb, and by inference also with structure VIII of the bis-adduct, while no such reaction seems to be likely with an acid of structure XIVb. We assign therefore to the phenylhydrazine bis-condensation product the pyridazinone structure XV.

Acid B forms also with hydroxylamine a condensation product. Analysis gave low values by the Dumas method; however, analysis of the dimethyl ester of the product leaves but little doubt that the reaction of Acid B with hydroxylamine is likewise a double condensation. However, the formulation of the substance as a hydro-orthoxazinone derivative XVI remains uncertain, since structure XVI is inconsistent with the observation that the substance was found by titration and by esterification with diazomethane to be a tribasic acid. Although this may find a possible interpretation by scission of the lactone bridge during bis-condensation, which would lead to a —N=C= grouping or to an olefinic bond in the ethylene bridge, the question can not be definitely settled without further investigation.

While all of these reactions prove the presence and the position of one olefinic bond in the ethylenic bridge of bis-adduct VIII beyond reasonable doubt, the other C=C bond remains less easy to detect. This bond shows a striking resistance toward catalytic hydrogenation, even at higher temperatures and pressures. The products obtained with bromine are not homogeneous and are difficult to purify and identify, as the reaction takes place with evolution of hydrogen bromide. At present only the reaction of Acid B (Xb) with hydrogen peroxide can be offered as some evidence that adduct VIII possesses also a second olefinic bond. The reaction, which takes place in glacial acetic acid, produced a tribasic hydroxylactone. Diazomethane does not cleave the lactone ring of this substance, which is therefore believed to belong to a type different from that of the δ-hydroxy-δ-lactone structure present in Xb. It is assumed that the new hydroxylactone arises from Acid B by way of a trans addition of two hydroxyl groups to form intermediate XVII followed by a rearrangement—indicated in XVII and XVIII—and then anhydridization to the hydroxyketolactone tricarboxylic acid XVIII.



XVIII

In our opinion, these results prove the structure IIIc and the spatial configuration VIII of the bis-adduct, and offer all necessary evidence that the reaction between 1-phenyl-1-*p*-anisylethylene and maleic anhydride is a real diene synthesis proceeding with disturbance of the aromatic bond system of the substituted ring. Certain details, however, remain reserved for further investigation, as, *e.g.*, the behavior of δ-hydroxy-δ-lactones in the presence of diazomethane and with carbonyl reactants, which requires separate examination on more simple models.

EXPERIMENTAL

1-Phenyl-1-(p-methoxyphenyl)ethylene; maleic anhydride 1:2-adduct (IIIc, VIII, IX). A mixture of 21 g. (0.1 mole) of 1-phenyl-1-(*p*-methoxyphenyl)ethylene (Ic), 19.6 g. (0.2 mole) of maleic anhydride and 0.4 g. of dimethylaniline was heated with shaking on the water-bath until the mobile melt solidified to a red-brown resin (1–2 hours). Care was taken that the melt formed a thin layer. To the cooled product 50 ml. of acetic anhydride was added. After twenty-four hours at room temperature, the product formed a crystalline mass. This was filtered and washed twice with 15 ml. of acetic anhydride, twice with 15 ml. of alcohol, and twice with 15 ml. of ether; 27.4 g. of colorless substance was obtained, sufficiently pure for the following experiments. It could be recrystallized with about 30% loss from twice its weight of acetic anhydride, as colorless thin plates. For analysis it was once again recrystallized from ethyl acetate and dried *in vacuo* at 100° for three hours; m.p. 232–234°, decomp. The product was identical with that prepared by another method (4).

Anal. Calc'd for $C_{28}H_{18}O_7$: C, 68.0; H, 4.5; OCH_3, 7.6.
Found: C, 67.8; H, 4.7; OCH_3, 7.1.

The residue obtained by evaporation of the combined mother liquors dissolved when refluxed with 200–250 ml. of water. The solution was treated with charcoal and concentrated, giving crystals of Acid B. Total conversion of Ic proceeds with a yield of 76%.

Acid A (Xa). In ice-cooled 2 *N* sodium hydroxide (25 ml.), 5 g. of finely-powdered bis-adduct IIIc was dissolved by shaking, and the solution was diluted with 225 ml. of ice-water, treated with charcoal, acidified under cooling with 260 ml. of 0.2 *N* hydrochloric acid, and allowed to stand in the ice-box for 12 hours. The crystalline precipitate was washed repeatedly with cold water and dried *in vacuo* at 100° over phosphorus pentoxide; yield 3.8 g. of pure substance, m.p. 210–212°. For recrystallization from water, quick solution and rapid cooling seemed to be essential, the instantly separating product being then not contaminated with later-crystallizing Acid B. Water of crystallization remained even after three hours of drying.

Anal. Calc'd for $C_{23}H_{22}O_9$: C, 62.4; H, 5.0; OCH_3, 7.0.
for $C_{23}H_{22}O_9 + \frac{1}{2} H_2O$: C, 61.2; H, 5.1; OCH_3, 6.9.
Calc'd neutr. equiv. for 3 COOH; 147.4, 150.4.
for 4 COOH: 112.8.
Found: C, 61.5; H, 5.3; OCH_3, 6.9; neutr. equiv., 149.2 (direct titr.), 118.0 (lactone titr.).

Dissolved in an equal weight of warm acetic anhydride, the bis-adduct (IIIc) separates, m.p. 232–233°, alone or mixed with original sample.

Trimethyl ester (XIa). A solution of 3.5 g. of Acid A was mixed with an ethereal solution of diazomethane to permanent yellow coloration. Concentration gave 2.2 g. of crystalline solid; colorless prisms from methyl alcohol, m.p. 204°.

Anal. Calc'd for $C_{26}H_{28}O_9$: C, 64.4; H, 5.8; OCH_3, 25.6.
Found: C, 64.2; H, 5.9; OCH_3, 25.1.

Acid B (Xb). (*a*) *From VIII by aqueous hydrolysis.* Refluxing a mixture of 37 g. of VIII and 400 ml. of water gave in 3–4 hours a clear solution which was heated for another two hours. It was filtered (charcoal) and the product was recrystallized from 400 ml. of hot water. The cotton-like long needles were dried at room temperature in a vacuum desiccator over phosphorus pentoxide for twenty-four hours, 33.7 g. (79%). For analysis it was twice recrystallized from water, and dried over phosphorus pentoxide at 5 mm. for forty-eight hours; m.p. 181–182°, gas evolution; methoxyl test, negative.

Anal. Calc'd for $C_{22}H_{29}O_9 + 2H_2O$: C, 56.8; H, 5.4; neutr. equiv. for 3 COOH, 116.1, for 4 COOH, 154.8.
Found: C, 56.9, 57.0; H, 5.4, 5.2; neutr. equiv., 131.0.

(*b*) *From VIII with formic acid.* In 30 ml. of 80% formic acid 10 g. of VIII was dissolved by boiling, and the solution was refluxed for 30 minutes. Adding 70 ml. of water, the hot solution was filtered, giving 8.2 g. (72%) of Acid B. Recrystallization from 100 ml. of water gave analytically pure material of m.p. 181–182°, alone or mixed with a sample prepared by method (a).

(*c*) *From VIII by alkaline hydrolysis.* A solution of 2 g. of VIII in 28 ml. of 2 *N* sodium hydroxide was boiled for fifteen minutes, cooled, and after acidification with 30 ml. of 2 *N* hydrochloric acid, left in the ice-box. A 1:1 mixture of Acid A and Acid B separated (as seen from the methoxyl number), from which pure Acid B was obtained by prolonged boiling of the aqueous solution of the mixture and subsequent crystallization in the ice-box.

(*d*) *From the anhydride of Acid B by hydrolysis.* See below, under Anhydride of Acid B.

The anhydride of Acid B. (*a*) *From Xb by anhydridization.* Acid B (10 g.), when boiled with 30 ml. of acetic anhydride, rapidly dissolved under exothermic reaction and crystals of the anhydride separated. After the reaction subsided, heating was continued for 1–2 minutes, and the mixture was allowed to stand before collecting the product. This was washed with some acetic anhydride and with alcohol; from acetic anhydride, m.p. 298–300°, alone or mixed with a sample prepared by method (b).

(*b*) *From IIIc with formic acid.* A mixture of 1 g. of the bis-adduct VIII and 3 ml. of 98% formic acid was boiled for 15 minutes, and allowed to stand in the ice-box for 24 hours, protected from moisture. The crystalline product was washed with 2 ml. of abs. formic acid, twice with 2 ml. of alcohol, and finally with ether, and dried *in vacuo* at 100° over sodium hydroxide for three hours; m.p. 298–300°. The methoxyl test was negative.

Anal. Calc'd for $C_{22}H_{18}O_7$: C, 67.3; H, 4.1.

Found: C, 67.3, 67.5; H, 4.7, 4.6.

The anhydride is readily soluble in 2 *N* sodium hydroxide, the solution yielding on acidification crystalline Acid B. Prolonged boiling of the anhydride with water had the same effect; this method is the most convenient way of preparing this acid.

Trimethyl ketotetracarboxylate, XIIb. A solution of 0.8 g. of XIa in 3 ml. of 98% formic acid was refluxed for two hours, and 5 ml. of methyl alcohol, and water (about 15 ml.) were added until incipient turbidity. After twenty-four hours the crystals were washed twice with 3 ml. of 60% methyl alcohol and recrystallized from 10 ml. of 60% methyl alcohol, yielding 0.2 g. of colorless needles, m.p. 148–149°.

The product is readily soluble in dilute alkali and liberates carbon dioxide from ice-cold sodium carbonate solution. It is sharply titratable with 0.05 *N* sodium hydroxide; neutr. equiv., 454.0 (calc'd for $C_{25}H_{26}O_9$ and one COOH, 470.5). Analytical characterization was on XIIa, m.p. 172–173°, prepared from XIb with diazomethane.

Tetramethyl ketotetracarboxylate XIIa. (*a*) *Methanolysis of VIII.* To a mixture of 3 g. of finely powdered VIII and 45 ml. of absolute methyl alcohol, 6 ml. of conc'd sulfuric acid in 6 ml. of methyl alcohol was added. With spontaneous warming, partial solution occurred, and was completed by refluxing for two hours. After eight hours in the ice-box the product was collected, the filtrate was diluted with water, and the oily substance separated crystalline in a vacuum desiccator, completing the yield to 2.1 g. For analysis the product was thrice recrystallized from methyl alcohol and dried at 100° *in vacuo* over calcium chloride; m.p. 172–173°.

Anal. Calc'd for $C_{26}H_{28}O_9$: C, 64.4; H, 5.8; OCH_3, 25.6.

Found: C, 64.1, 64.3; H, 5.9, 5.9; OCH_3, 25.1.

(*b*) *Treatment of Acid B (Xb) with diazomethane.* A solution of 1.2 g. of Xb in 20 ml. of abs. methyl alcohol was mixed with ethereal diazomethane. The resulting solution yielded, after being concentrated to 15 ml., treated with charcoal, and then kept in the ice-box, 0.9 g. of colorless prisms. This was recrystallized from methyl alcohol and dried *in vacuo* at 100° over calcium chloride, m.p. 172–173°, alone or mixed with a specimen prepared according to (a).

Anal. Calc'd for $C_{26}H_{28}O_9$: C, 64.4; H, 5.8.

Found: C, 64.4, 64.3; H, 5.6, 6.1.

(*c*) *From XIIb with diazomethane.* The procedure is the same as with Xb under (b). The product was recrystallized once from methyl alcohol, m.p. 172–173°, alone or mixed with samples prepared by (a) and (b), respectively.

Keto-trans-tetracarboxylic acid XIII. Refluxing 10 g. of bis-adduct VIII in 120 ml. of conc'd hydrochloric acid for ten hours gave after fifteen minutes a clear solution which acquired gradually yellow color. This was treated with charcoal, evaporated to incipient crystallization, and kept in the ice-box for three days. The crystalline product (2.1 g.) was washed with cold water and dried *in vacuo* at room temperature over phosphorus pentoxide. For analysis it was twice recrystallized from water and dried as above for three days; m.p. 272°; methoxyl test, negative.

Anal. Calc'd for $C_{22}H_{20}O_9 + 3H_2O$: C, 54.8; H, 5.4; neutr. equiv., 120.8.

Found: C, 54.7; H, 5.3; neutr. equiv. for 4 COOH, 118.5.

The same product was obtained by similar treatment of Acid A (Xa), Acid B (Xb) or the anhydride of Acid B.

XIII forms no anhydride under conditions which convert Acid B to bis-anhydride. A mixture of 0.5 g. of XIII and 1 ml. of acetic anhydride, boiled for two minutes, did not crystallize on being cooled to −10°. Removing the acetic anhydride *in vacuo* and dissolving the residue in 3 ml. of ethyl acetate, evaporating, and thrice repeating, the residue was again dissolved in the same solvent and treated with ethereal diazomethane. The product was crystallized from methyl alcohol, yielding the tetramethyl ester of XIII, m.p. 196°.

The tetramethyl ester was prepared from 10 ml. of a 5% solution of XIII in methyl alcohol in the usual way. The product crystallized on concentration, 0.3 g. of colorless prisms, m.p. 196°. For analysis it was recrystallized from methyl alcohol.

Anal. Calc'd for $C_{26}H_{28}O_9$: C, 64.4; H, 5.8.
Found: C, 63.9, 64.2; H, 5.7, 5.8.

The oxime of XIII. A solution of 0.7 g. of XIII in 3.5 ml. of 2 *N* sodium hydroxide was mixed with 0.5 g. of hydroxylamine hydrochloride in 2 ml. of water. After boiling for twenty minutes, it was cooled, made acid with 6 ml. of 2 *N* HCl, and was kept in the ice-box for one day. The product (0.3 g.) was recrystallized four times from water and dried *in vacuo* at 100° over phosphorus pentoxide; colorless prisms, m.p. 234–237°.

Anal. Calc'd for $C_{22}H_{21}NO_9$: C, 59.6; H, 4.8; N, 3.2; neutr. equiv., 110.99.
for $C_{22}H_{21}NO_9 + 2H_2O$: C, 55.0; H, 5.2; N, 2.9; neutr. equiv., 119.8.
for $C_{22}H_{21}NO_9 + 3H_2O$: C, 53.1; H, 5.5; N, 2.8; neutr. equiv., 124.33.
Found: C, 54.4; H, 5.7; N, 3.0; neutr. equiv. 120.2.

For a more sharp analytical characterization the *tetramethyl ester* was used, which was prepared from the oxime by treatment of a methyl alcoholic solution with ethereal diazomethane. The ester was recrystallized from methyl alcohol, yield 65 mg. from 100 mg. of starting material; colorless needles, m.p. 192°, decomp. For analysis it was dried *in vacuo* at 100° over calcium chloride.

Anal. Calc'd for $C_{26}H_{29}NO_9$: C, 62.5; H, 5.8; N, 2.8.
Found: C, 62.5, 62.3; H, 5.7, 5.9; N, 3.0.

The condensation of Acid B (Xb) with phenylhydrazine to XV. A solution of 5 g. of Acid B (Xb) in 30 ml. of warm water was mixed with a solution of 3 g. of phenylhydrazine hydrochloride in 10 ml. of water and boiled for thirty minutes. The oil (3.2 g.) was freed by decantation from the still-warm aqueous solution, washed with water and crystallized from 60% methyl alcohol. The product, needles (2.3 g.), was twice recrystallized from 20 ml. of 80% methyl alcohol and dried *in vacuo* over calcium chloride. It melted at 217–220°, after softening at 204°. For complete removal of hydrate water, drying at 5 mm. and 135° over phosphorus pentoxide was necessary. The dry product was somewhat hygroscopic.

Anal. Calc'd for $C_{28}H_{24}N_2O_7$: C, 67.2; H, 4.8; N, 5.6. for $C_{28}H_{24}N_2O_7 + \frac{1}{2}H_2O$: neutr. equiv., 263.7.
Found: C, 67.5, 67.4; H, 4.7, 4.9; N, 5.4; neutr. equiv., 269.0.

The dimethyl ester was prepared in the usual way in methyl alcoholic solution with ethereal diazomethane and was recrystallized from methyl alcohol, yield 0.6 g. from 1 g. of starting material, m.p. 220°.

Anal. Calc'd for $C_{30}H_{28}N_2O_7$: C, 68.1; H, 5.3.
Found: C, 67.5; H, 5.6.

The reaction between Acid B (Xb) and hydroxylamine. A mixture of 5 g. of Acid B and 3 g. of hydroxylamine hydrochloride was boiled with 20 ml. of water for twenty minutes and kept overnight in the ice-box. The product was washed with water, dried *in vacuo* at room temperature over phosphorus pentoxide, (3.4 g.), giving on four recrystallizations from 30 ml. of water and subsequent drying, a dihydrate, which was converted by sharp drying at 135° *in vacuo* over phosphorus pentoxide into hygroscopic anhydrous material.

Anal. Calc'd for $C_{22}H_{19}NO_8$: C, 62.1; H, 4.5; N, 3.3. for $C_{22}H_{19}NO_8 + 2H_2O$: neutr. equiv., 153.8.
Found: C, 62.3; H, 4.9; N, 2.3; neutr. equiv., 154.0.

The product (0.5 g.) in 10 ml. of methyl alcohol gave with ethereal diazomethane 0.3 g. of the ester which was recrystallized from 200 ml. of methyl alcohol; very slender needles, m.p. 275° after softening at 250°. The product appears to be a *trimethyl ester of the bis-condensate of Acid B and hydroxylamine.*

Anal. Calc'd for $C_{25}H_{25}NO_8$: C, 64.2; H, 5.4; N, 3.0; OCH_3, 20.5.
Found: C, 63.9, 64.2; H, 5.8, 5.7; N, 2.9, 2.9; OCH_3, 20.3.

Oxidation of Acid B (Xb) *with hydrogen peroxide.* A solution of 10 g. of Acid B in 150 ml. of glacial acetic acid was kept at 80° and mixed within 30 minutes with 110 ml. of 33% hydrogen peroxide, warming being continued for another hour. It was then concentrated to incipient crystallization and kept in the ice-box. The product was washed with cold water and dried *in vacuo* at room temperature over sodium hydroxide and phosphorus pentoxide; yield, 4.5 g. For analysis it was recrystallized four times from small amounts of water (charcoal), giving 0.8 g. of colorless, thin needles, m.p. 325–330°. This was dried at 5 mm. and 100° over phosphorus pentoxide.

Anal. Calc'd for $C_{22}H_{20}O_{10}$: C, 59.5; H, 4.5. for $C_{22}H_{20}O_{10} + 2H_2O$: neutr. equiv., 160.1.
Found: C, 59.3, 59.3; H, 4.7, 4.8; neutr. equiv., 163.0.

The usual esterification with diazomethane (with 0.5 g. of the acid in 8 ml. of absol. methyl alcohol) gave 0.22 g. of crystalline methyl ester, which was recrystallized from 200 ml. of methyl alcohol; thin colorless needles, m.p. 291–295°.

Anal. Calc'd for $C_{25}H_{26}O_{10}$: C, 61.7; H, 5.4; OCH_3, 19.1.
Found: C, 61.4, 61.4; H, 5.6, 5.5; OCH_3, 19.6.

Thermal decomposition of bis-adduct IIIc. One gram of bis-adduct IIIc was distilled at 1 mm. from a 300° metal-bath. The distillate was mixed with 10 ml. of *N* sodium hydroxide and warmed at 100° to give an emulsion, which was cooled and extracted with ether. The extract was treated with charcoal, concentrated to a small volume, and cooled with ice-salt mixture; 0.2 g. of a crystalline product. Recrystallization from ether gave faintly yellow plates, m.p. 78°, alone or mixed with authentic 1-phenyl-1-(*p*-methoxyphenyl)-ethylene.

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REFERENCES

(1) WAGNER-JAUREGG, *Ber.*, **63**, 3213 (1930).
(2) WAGNER-JAUREGG, *Ann.*, **491**, 1 (1931)
(3) DIELS AND ALDER, *Ann.*, **486**, 191 (1931); CLAR, *Ber.*, **64**, 1676 (1931).
(4) BERGMANN, SZMUSZKOWICZ, AND FAWAZ, *J. Am. Chem. Soc.*, **69**, 1773 (1947); SZMUSZKOWICZ AND BERGMANN, *J. Am. Chem. Soc.*, **69**, 1779 (1947); BERGMANN AND SZMUSZKOWICZ, *J. Am. Chem. Soc.*, **69**, 1777 (1947).
(5) HUDSON AND ROBINSON, *J. Chem. Soc.*, **141**, 715 (1941).
(6) BRUCKNER, *Ber.*, **75**, 2034 (1942).
(7) BRUCKNER AND KOVÁCS, *Nature*, **161**, 650 (1948); *J. Org. Chem.*, **13**, 641 (1948); **14**, 65 (1949).
(8) LORA TAMAYO, *Nature*, **162**, 969 (1948).
(9) ALDER AND STEIN, *Angew. Chem.*, **50**, 510 (1937).
(10) BAYER, *Ann.*, **258**, 214 (1890).