ultraviolet absorption spectrum of the material (Fig. 1) indicated an appreciable change had occurred. The viscous material was soluble in ethanol. Although it was not examined further, it appeared likely that the change had occurred as a result of polymerization, or autooxidation, or both, of II.

Ultraviolet absorption spectra were determined by means of a Beckman Quartz Spectrophotometer.

2,2',4,6'-Tetramethylbiphenyl (III) was prepared from (II) by means of the same procedure which converted the carbinol I to III.[1] The crude yellow liquid product (1.5 g., 23%) from 6.5 g. of II, which contained some sulfur, had $n^{20}D$ 1.5635. The liquid was not purified, but was identified with III by converting it to its **tetranitro derivative.**[1] From 0.5 g. of crude III, 0.1 g. of the crude tetranitro derivative, m. p. 210–217°, was obtained. This impure material was dissolved in a mixture of 100 cc. of benzene and 100 cc. of petroleum ether (b. p. 40–60°), and the solution was allowed to trickle through a column (1.2 × 25 cm.) of chromatographic alumina. The column was developed with 100 cc. of benzene. When the washings were concentrated to 2 cc., the tetranitro derivative crystallized from the solution. Three recrystallizations from petroleum ether (b. p. 65–110°) containing a little benzene gave pale yellow needles, m. p. 235–237°, alone or when mixed with an authentic specimen.

Summary

1. 1-(2,4-Dimethylphenyl)-2,6-dimethyl-1-cyclohexanol (I) has been dehydrated to 1-(2,4-dimethylphenyl)-2,6-dimethyl-1-cyclohexene (II) by heating I at 200–220° with anhydrous oxalic acid.

2. A comparison of the ultraviolet absorption spectra of I and II with those of compounds of similar structure indicates that a relationship may exist between the difficulty with which hindered carbinols, such as I, are dehydrated and the absorption spectra of their dehydration products.

PITTSBURGH, PENNSYLVANIA
RECEIVED SEPTEMBER 5, 1946

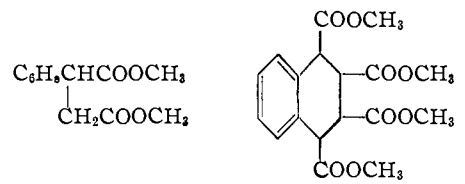
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Vinyl Polymers. XXIV. The Reaction of Benzoyl Peroxide and Maleic Ester[1]

BY C. S. MARVEL, E. J. PRILL[2] AND D. F. DETAR[3]

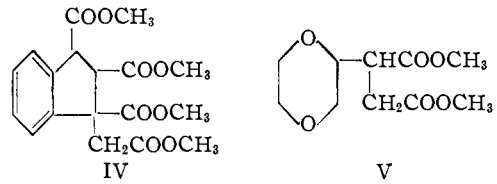
Earlier work in this Laboratory[4] has indicated that *l*-menthyl maleate reacts in the presence of benzoyl peroxide, even though maleic esters do not form high polymers under these conditions. A continuation of this study with dimethyl and diethyl maleate has shown that maleic esters do unite with themselves to a limited extent to yield crystalline products containing peroxide and solvent residues. Since the start of this work, which was interrupted by the war and only recently resumed, several articles have appeared reporting the presence of chemically-bound fragments of peroxides[5,6] and solvents[7] in polymers, and reporting the addition[8] of compounds such as benzene diazonium chloride and carbon tetrachloride to double bonds in the presence of peroxides.

The reaction of two moles of dimethyl maleate with one mole of benzoyl peroxide yields a complex mixture from which there may be isolated unchanged ester (about 15%), a small amount (5% based on the maleic ester) of dimethyl phenylsuccinate (I), larger amounts (25%) of two crystalline esters, $C_{18}H_{20}O_8$ (IIA, m.p. 149°; IIB, m.p. 95°), and a considerable amount of non-volatile material (30–40%) containing more than two maleic ester residues. Compounds IIA and IIB are probably stereoisomeric forms of either tetramethyl 1,2,3,4-tetralintetracarboxylate (III) or tetramethyl 1-methylhydrindene-



I III

tetracarboxylate (IV). It may be noted that the tetraline derivative (III) can exist in four racemic and two meso forms, and the hydrindene derivative (IV) in four racemic forms.



IV V

When the above reaction is carried out in dioxane solution, the same products are formed, and additional products containing the dioxane group, such as dimethyl dioxanylsuccinate (V), are formed.

The elementary analyses of the higher boiling fractions also indicate the presence of dioxane-containing compounds of which VI is a possible

(1) For the twenty-third communication see THIS JOURNAL, **68**, 1088 (1946).

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(3) Present address: Department of Chemistry, Cornell University, Ithaca, New York.

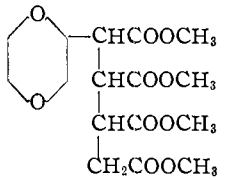
(4) Marvel and Frank, THIS JOURNAL, **64**, 1675 (1942).

(5) Price, Kell and Krebs, *ibid.*, **64**, 1103 (1942); Price and Durham, *ibid.*, **64**, 2508 (1942); Price and Tate, *ibid.*, **65**, 517 (1943); Pfann, Salley and Mark, *ibid.*, **66**, 983 (1944).

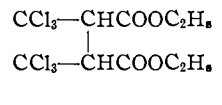
(6) Bartlett and Cohen, *ibid.*, **65**, 543 (1943).

(7) Springer, *Kautschuk*, **14**, 159, 197, 212 (1938); *C. A.*, **33**, 3629 (1939); Breitenbach and Maschin, *Z. physik. Chem.*, **A187**, 175 (1940).

(8) Koelsch, THIS JOURNAL, **65**, 57 (1943); Koelsch and Boekelheide, *ibid.*, **66**, 412 (1944); Kharasch, Urry and Jensen, *ibid.*, **67**, 1626 (1945); *Science*, **102**, 128 (1945).



VI



VII

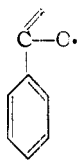
example. In addition to these compounds, another ester $C_{12}H_{20}O_8$ of undetermined structure was isolated in about 1% yield from the reaction in dioxane. An estimation of the molecular weight of the non-volatile residue indicates the presence of molecules containing an average of about four maleic ester groups.

Substitution of diethyl maleate for dimethyl maleate leads to the ethyl esters of the compounds described above.

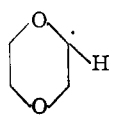
In carbon tetrachloride solution, the products isolated were hexachloroethane[9a] and chlorobenzene[9a] (arising from the reaction of the benzoyl peroxide with the solvent), and dimethyl α,α'-bistrichloromethylsuccinate[9b] (VII).

The formation of the above products can be accounted for on the basis of the generally accepted theories of vinyl polymerization.[10] The initiation reaction is represented by decomposition of the benzoyl peroxide to yield benzoyloxy radicals (VIII) and phenyl radicals. Chain transfer reactions[9,10,11] with the solvents give rise to dioxanyl (IX) and trichloromethyl radicals.

Addition of one of these radicals to dimethyl maleate to form radical X (eq. 1) followed by a

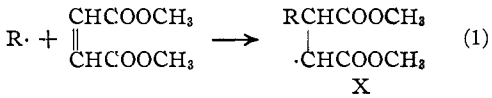


VIII



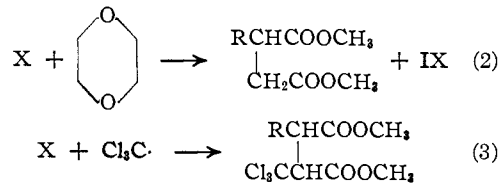
IX

chain transfer reaction[11] with dioxane (eq. 2) or with some other constituent of the reaction mixture accounts for the formation of dimethyl phenylsuccinate (I) and dimethyl dioxanylsuccinate (V).



(1)

X

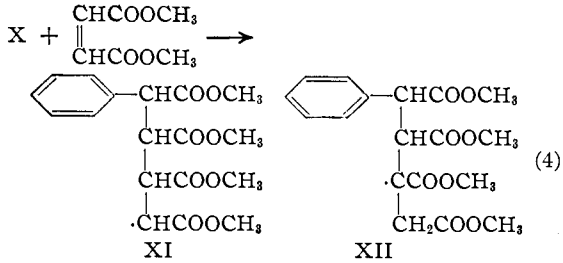


(2)

(3)

Combination of radical X with another radical such as trichloromethyl (eq. 3) can account for the formation of diethyl α,α'-bis-trichloromethylsuccinate when the reaction is carried out in carbon tetrachloride as solvent.

The reaction of radical X with a second molecule of dimethyl maleate in a propagation step (eq. 4) forms radical XI, which by an internal

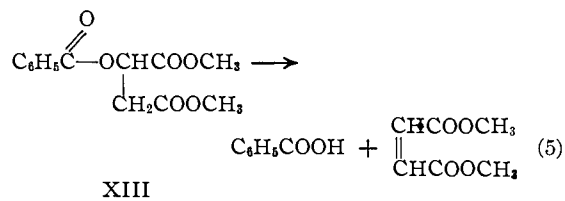


(4)

XI XII

chain transfer coupling typical of aromatic residues (formally $ArH + R\cdot \rightarrow ArR + H\cdot$)[12a] can lead to tetramethyl tetralintetracarboxylate (III). Prior rearrangement[12b] of radical XI to XII would lead to tetramethyl methylhydrindenetetracarboxylate (IV).

The formation of benzoic acid on distillation of the reaction mixtures in spite of destruction of unreacted benzoyl peroxide and removal of acids by washing with bicarbonate solution indicates the presence of pyrolyzable benzoyloxy-containing residues in the products. Participation of benzoyloxy radicals[6] (VIII) in reactions according to eqs. (1) and (2) would lead to the benzoate of malic ester (XIII) which would be expected[13] to pyrolyze readily, eq. 5. Another source of benzoyloxy-containing products is the cleavage of



(5)

XIII

benzoyl peroxide by radicals such as radical XII as suggested by Bartlett and Nozaki.[14]

The dimethyl phenylsuccinate (I) obtained from the reactions was identified by comparison of the ester and the acid with authentic specimens.

(9) (a) Böeseken and Gelissen, *Rec. trav. chim.*, **43**, 869 (1924); Wieland and Tsatsas, *Ann.*, **514**, 163 (1934); Kharasch, Kane and Brown, THIS JOURNAL, **63**, 526 (1941); Kharasch and Dannley, *J. Org. Chem.*, **10**, 406 (1945).

(b). The analogous formation of *bis*-triphenylmethylsuccinic acid from maleic acid and triphenylmethyl has been described by Conant and Chow, *ibid.*, **55**, 3475 (1933).

(10) Price, *Ann. N. Y. Acad. Sci.*, **44**, 365 (1943); Mayo, *ibid.*, **65**, 2324 (1943).

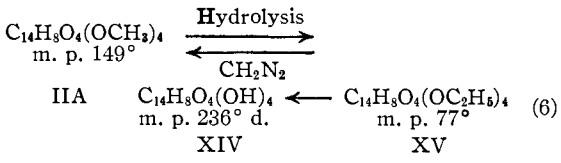
(11) Kharasch, Brown and Chao, *ibid.*, **62**, 3435 (1940); Kharasch, Kane and Brown, *ibid.*, **64**, 1621 (1942); Kharasch and Gladstone, *ibid.*, **65**, 15 (1943); Kharasch, Engelmann and Urry, *ibid.*, **65**, 2428 (1943); Kharasch, Jensen and Urry, *J. Org. Chem.*, **10**, 386 (1945); Kharasch, McBay and Urry, *ibid.*, **10**, 394, 401 (1945).

(12) (a) Hey and Waters, *Chem. Rev.*, **21**, 182 (1937). (b) However, Kharasch, Kane and Brown[9] report that *i*-propyl and *n*-propyl radicals do not rearrange on reaction with carbon tetrachloride, and Kharasch and Dannley[9a] report that α- and β-naphthyl radicals also do not rearrange with that solvent.

(13) *Cf.* Anschütz, *Ber.*, **18**, 1952 (1885).

(14) Bartlett and Nozaki, THIS JOURNAL, **68**, 1501 (1946).

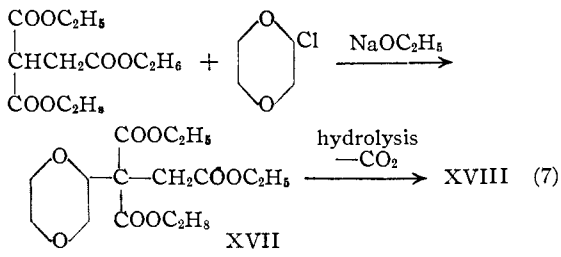
Evidence for the structure of compounds IIA and IIB is based on analyses and degradation. Compound IIA or the corresponding ethyl ester



(XV), isolated from the reaction of diethyl maleate, can be hydrolyzed to an acid (XIV), which can be converted to compound IIA by the action of diazomethane. These relationships are shown in eq. (6). Oxidation of compound XIV with alkaline permanganate gives phthalic anhydride, indicating a benzene ring with two vicinal side chains. Tests for unsaturation—treatment with dilute permanganate in aqueous dioxane and attempted hydrogenation over platinum black at room temperature and low pressure or over nickel at 100° and 2000 pounds hydrogen pressure—were negative. The only reasonable structures based on the starting materials and the above evidence are structures III and IV. Compound XIV yielded a dianhydride on treatment with acetic anhydride. Numerous attempts were made to dehydrogenate compound IIA using palladium-on-carbon (Linstead's method[15]), chloranil,[16] or selenium[17] but either unchanged starting material or else low yields of mixtures of substances were obtained. Attempts to synthesize ester III by the double Michael condensation of *o*-phenylenediacetic ester and acetylenedicarboxylic ester were also unsuccessful.

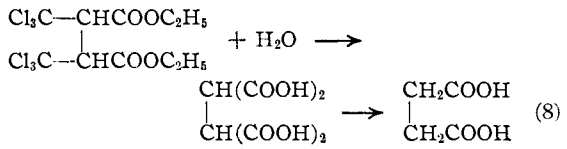
Compound IIB was hydrolyzed to an acid $C_{14}H_8O_4(OH)_4$ (XVI) which yielded phthalic anhydride on oxidation. It is likely that compounds IIA and IIB are stereoisomers.

The structure of dimethyl dioxanylsuccinate ester (V) was determined by hydrolysis of the ester to dioxanylsuccinic acid (XVIII), which was synthesized by the scheme shown in eq. (7). 1,1,2-Tricarbethoxyethane was

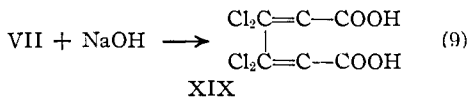


alkylated with chlorodioxane and the product (XVII) was hydrolyzed and decarboxylated to give dioxanylsuccinic acid (XVIII). The dimethyl ester from the reaction and the dimethyl ester from synthetic dioxanylsuccinic acid (XVIII) reacted with ammonia to give a monoacid amide and a diamide. Treatment of the acid (XVIII) with acetyl chloride yielded the anhydride.

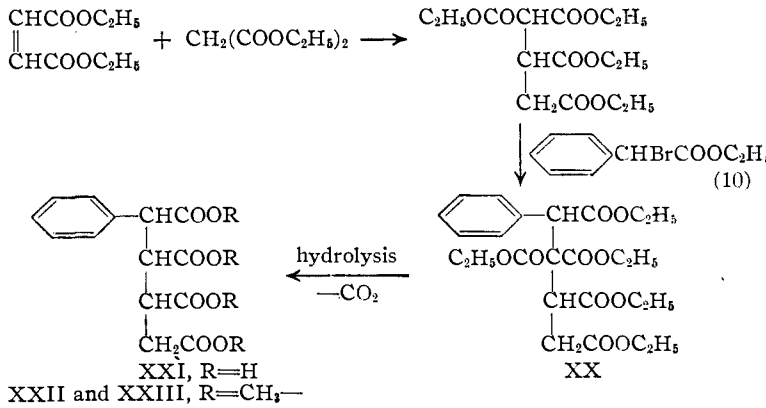
The structure of α,α'-bis-trichloromethylsuccinic ester (VII) was established by acid hydrolysis of the ester to succinic acid (eq. 8) and by



alkaline hydrolysis to a compound whose analysis suggests structure XIX, α,α'-bis-dichloromethylenesuccinic acid (XIX) (eq. 9).



Phenylbutanetetracarboxylic acid (XXI) has been synthesized by the reactions given in eq. (10). Two different methyl esters (XXII and XXIII) have been obtained from acid XXI which



appear to represent two of the four possible racemic forms. These esters (XXII and XXIII) are appreciably more soluble in water than compounds IIA or IIB, and a mixture of the isomeric acids (XXI) yielded benzoic acid on oxidation as expected.

Experimental[18,19]

Polymerization of Maleic Esters.—A mixture of the maleic ester and from one-half to one-third the molar proportion of benzoyl peroxide was kept at 55° for from one hundred and seventy to seven hundred hours. Some experiments were carried out in the absence of added solvent, and others were carried out in dioxane (400 cc. per mole of ester). Variations in the duration of the reaction, or in the manner of adding the peroxide (in one portion or in several portions) had no significant effect on the yields

(15) Fieser, "Laboratory Manual of Organic Chemistry," 2nd ed., D. C. Heath and Co., Boston, Mass., 1941, p. 458.

(16) Barclay and Campbell, *J. Chem. Soc.*, 530 (1945).

(17) Ref. 15, p. 456.

(18) Microanalyses by Miss Theta Spoor and Mrs. Margaret Ledyard, University of Illinois.

(19) Melting points are uncorrected unless otherwise noted.

TABLE I

POLYMERIZATION OF MALEIC ESTER AT 55°

Reactants: Maleic ester, g.	Reactants: Benzoyl peroxide, g.	Solvent, cc.	Time, hours	Products, per cent. of maleic ester obtained as: Recovered ester	Phenyl and dioxanyl-succinates	Tetralin-tetracarboxylates, etc.	Non-volatile residue[a]
Me 200	168[b]	None	700	14	3	24	43
Me[c] 500	300[b]	Dioxane 800	500	6	10	16	15
Me 200	111	Dioxane 300	480	10	10	16	43
Et 114	80	None	700	14	6	24	30
Et 300	140	Dioxane 300	400	21	8	4	40
Et 171	80	Dioxane 500	340	3	17	28	35
Et 171	80	Dioxane 400	170	19	15	10	40
Et 57	40	Dioxane 200	170		15	14	38
Et 57	40	Dioxane 200	80	20	28	14	18

[a] The residue was assumed to consist of 80% ester. [b] Added in several portions. [c] Part of reaction mixture was lost.

of, or the proportions of, products. At the completion of the reaction the solvent was removed under slightly reduced pressure in a stream of air, and unreacted peroxide was destroyed by the addition of a solution of sodium iodide in acetone. After removal of the acetone, the residue was taken up in ether and thoroughly washed with aqueous sodium bicarbonate. The ether solution was dried (sodium sulfate) and the residue remaining after removal of the ether was distilled under reduced pressure. Benzoic acid, which was present in the distillate, was removed by washing with bicarbonate solution before further fractionation.

Figure 1 represents the distillation curve obtained in a typical fractionation. The products shown here were obtained from the reaction of dimethyl maleate in dioxane. Table I illustrates the relative proportions of the fractions obtained in other experiments. Because of the difficulties involved in the fractionation of high-boiling material, the estimates in Table I are only approximate.

Redistillation of the various fractions eventually dielded samples which crystallized or which could be hyvrolyzed to crystalline acids.

Isolation of Dimethyl Phenylsuccinate (I).—The 105–118° (1 mm.) fraction on redistillation yielded a series of fractions which ranged in refractive index from an initial high of $n^{20}D$ 1.492 to a low of $n^{20}D$ 1.459. The former fractions solidified on seeding with a crystal of dimethyl phenylsuccinate and melted at 54.5–55.5° after pressing on a porous plate. Hydrolysis by twelve-hour refluxing with constant-boiling hydrochloric acid yielded an acid, m. p. 166–167°, which gave no depression of the melting point when mixed with an authentic specimen of phenylsuccinic acid. Wren[20] reports a melting point of 167–168° for the acid and 57.8–58.5° for the ester.

Isolation of Dimethyl Dioxanylsuccinate (V).—The fractions of low refractive index from the above fractionation yielded on alkaline hydrolysis a crystalline acid, m. p. 126–128°, which did not depress the melting point of synthetic dioxanylsuccinic acid (XVIII).

Anal. Calcd. for $C_8H_{12}O_6$: C, 47.08; H, 5.88. Found: C, 47.48; 47.42; H, 5.89, 5.99.

The same acid was obtained on hydrolysis of a fraction, b. p. 187–188° (4 mm.), $n^{20}D$ 1.4578, from the reaction with diethyl maleate.

Isolation of the Tetracarboxylic Acid Ester (IIA).—The 182–195° (1 mm.) fraction on redistillation partly crystallized to yield a methyl ester (IIA), colorless prisms, m. p. 149.4–149.8° (cor.) on recrystallization from methanol. The ester was obtained from reactions in dioxane and from reactions carried out without an added solvent.

Anal. Calcd. for $C_{18}H_{20}O_8$: C, 59.33; H, 5.53. Found: C, 59.33; H, 5.41.

Hydrolysis of the ester (20 g.) by refluxing with 6 *N* hydrochloric acid (100 ml.) for eighteen hours with removal of methanol by a fractionating column gave on cooling 10.8 g. of colorless crystals of the acid (XIV) m. p. 236° (gas evolved) after two recrystallizations from constant boiling hydrochloric acid.

Anal. Calcd. for $C_{14}H_{12}O_8$: C, 54.55; H, 3.93. Found: C, 54.10; H, 4.09.

A fraction, b. p. 188–196° (1 mm.), from the reaction of diethyl maleate and benzoyl peroxide yielded a colorless crystalline ethyl ester (XV), m. p. 77–78°.

Anal. Calcd. for $C_{22}H_{28}O_8$: C, 62.84; H, 6.71. Found: C, 62.96; H, 6.60.

This ethyl ester on acid hydrolysis yielded an acid, m. p. 228° (gas evol.) unrecrystallized sample, which was converted by the action of diazomethane into a methyl ester, m. p. 149–150° (cor.) on recrystallization. The ester gave no depression of melting point when mixed with compound IIA.

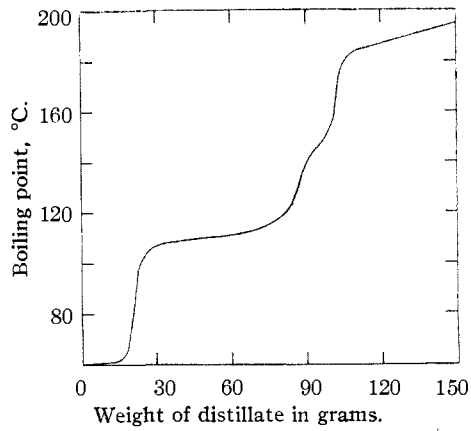


Fig. 1.—Redistillation curve for the product from the reaction of benzoyl peroxide (300 g.), and dimethyl maleate (500 g.) in dioxane for 500 hours at 55°. From the preliminary distillation there were obtained 235 g. of distillate and 100 g. of non-volatile residue.

Isolation of the Tetracarboxylic Acid Ester (IIB).—The corresponding acid (XVI) was obtained by alkaline saponification of the fractions, b. p. 190–200° (1 mm.), from several reactions with both dimethyl and diethyl maleate with or without dioxane as a solvent. Usually only a small proportion of the hydrolysate crystallized due to the presence of acid XIV and possibly of other isomers. Crystallization from ethyl acetate in which it is only slightly soluble yielded the acid in the form of a colorless powder, m. p. 222° (gas evolved).

Anal. Calcd. for $C_{14}H_{12}O_8$: C, 54.55; H, 3.93. Found: C, 53.91; H, 4.23.

(20) Wren, *J. Chem. Soc.*, **113**, 215 (1918).

The acid was converted to the methyl ester, colorless needles from aqueous methanol; crystals from ethyl acetate–petroleum ether (30–60°), m. p. 95–96°.

Anal. Calcd. for $C_{18}H_{20}O_8$: C, 59.33; H, 5.53. Found: C, 59.61; H, 5.26.

A fraction of the product of the reaction of diethyl maleate and benzoyl peroxide in the absence of dioxane which consisted of a mixture of the ethyl ester XV and of the ethyl ester of acid XVI had the constants: b. p. 199–202° (1 mm.), $n^{20}D$ 1.4997. Both acid XVI and acid XIV were obtained on hydrolysis.

Anal. Calcd. for $C_{22}H_{28}O_8$: C, 62.84; H, 6.71; mol. wt., 420; sapn. equiv., 105. Found: C, 62.66; H, 6.43; mol. wt. (f. p. dioxane[21]), 384; sapn. equiv., 98.

Indication of the Presence of Dioxane Residues in High-Boiling Fractions (VI).—The high-boiling (190–200° at 1 mm.) fractions from the reactions carried out in the absence of dioxane have carbon–hydrogen analyses which agree accurately with the formula $C_{22}H_{28}O_8$ for the ethyl esters as shown directly above. The corresponding fractions from reactions carried out in dioxane solution have lower carbon analyses as is to be expected if compounds containing dioxane residues are present in these fractions.

Anal. Calcd. for $C_{16}H_{24}O_{10}$ (VI): C, 51.06; H, 6.43; calcd. for compound IIA, see above. Found for fraction b. p. 193–195° (1 mm.); C, 55.5; H, 5.51; for fraction b. p. 215–220° (1–2 mm.); C, 52.36; H, 5.80.

Similar results were obtained with the ethyl esters.

Anal. Calcd. for $C_{20}H_{32}O_{10}$ (ethyl ester corresponding to methyl ester VI): C, 55.54; H, 7.46; calcd. for ester XV, see above. Found for fraction b. p. 178–180° (1 mm.): C, 57.36; H, 6.86; for fraction b. p. 222–223° (1 mm.): C, 56.23; H, 6.81.

Isolation of the Ester $C_{14}H_{20}O_8$.—The fraction, b. p. 140–144° (1 mm.) (Fig. 1) on redistillation, was analyzed.

Anal. Calcd. for $C_{14}H_{20}O_8$: C, 53.16; H, 6.37. Found: C, 52.76; H, 6.03.

Hydrolysis with 20% potassium hydroxide yielded an acid, m. p. 185–187° on crystallization from a mixture of ethyl acetate and ethanol. Both the ester and the acid decolorized dilute permanganate solution.

Anal. Calcd. for $C_{10}H_{12}O_8$: C, 46.16; H, 4.65. Found: C, 45.29; H, 4.68.

Reaction of Diethyl Maleate with Benzoyl Peroxide in Carbon Tetrachloride Solution.—One-half mole of benzoyl peroxide and one mole of diethyl maleate were refluxed in 1200 cc. of dry carbon tetrachloride for thirty-six hours. The solvent was removed, the residue taken up in ether and washed with bicarbonate solution, the ether layer dried and distilled to yield 87 g. of distillate (up to 200° at 1 mm.) and 131 g. of dark non-volatile residue.

Isolation of Chlorobenzene.—From the first fractions, on redistillation, a liquid was obtained, b. p. 129–132° (atm.), $n^{20}D$ 1.5214, m. p. of dinitro derivative 50–52°. These values agree with those reported[22] for chlorobenzene; b. p. 132°, $n^{20}D$ 1.5245, dinitro derivative, m. p. 51°.

Isolation of Hexachloroethane.—The crystalline material of camphor-like odor which sublimed into the Dry Ice trap had a melting point of 184–185° (sealed tube) on recrystallization from ethanol, as reported[9a] for hexachloroethane.

Isolation of α,α′-bis-Trichloromethylsuccinic ester (VII).—From fractions, b. p. 130–150° (1 mm.), crystals separated which on sublimation under reduced pressure and crystallization from 50% ethanol were obtained as colorless needles, m. p. 93.5–94.5°.

Anal. Calcd. for $C_{10}H_{12}O_4Cl_6$: C, 29.37; H, 2.96; Cl, 52.02. Found: C, 29.37; H, 3.29; Cl, 51.44.

Diethyl α-Dioxanyl-α-carbethoxysuccinate (XVII).—Chlorodioxane[23] (20 g., 0.163 mole), prepared from dioxane *via* dichlorodioxane[24] and dioxene,[23] was added dropwise with stirring to an ice-cooled mixture of 42 g. (0.171 mole) of 1,1,2-tricarbethoxyethane[25] ($n^{20}D$ 1.4288) and a solution of 3.76 g. (0.163 mole) of sodium in 100 cc. of absolute ethanol. The mixture was stirred for two hours at 0°, then refluxed for two hours, and most of the alcohol removed by distillation. The residue was treated with water, taken up in ether, dried and distilled to give ethoxydioxane, some malonic ester, and 15 g. of compound XVII, $n^{20}D$ 1.4530, b. p. 150–152° (1 mm.).

Anal. Calcd. for $C_{15}H_{24}O_8$: C, 54.21; H, 7.28. Found: C, 54.16; H, 7.13.

The ethoxydioxane formed as a by-product by the reaction of chlorodioxane and sodium ethoxide was obtained as a colorless liquid, b. p. 81–82° (50 mm.), $n^{20}D$ 1.4258.

Anal. Calcd. for $C_6H_{12}O_3$: C, 54.52; H, 9.16. Found: C, 54.85; H, 9.29.

Hydrolysis of ethoxydioxane with 0.5 *N* hydrochloric acid and conversion of the product to the *p*-nitrophenylhydrazone gave a product, m. p. 139–141° after two recrystallizations from 50% ethanol. Summerbell and Rochen[26] report a melting point of 142° for the *p*-nitrophenylhydrazone of 3-oxa-5-hydroxypentanal.

Dioxanylsuccinic Acid (XVIII).—A mixture of 11 g. of compound XVII and 90 cc. of 20% potassium hydroxide was refluxed for nine hours. After cooling, the solution was neutralized with dilute sulfuric acid and then refluxed for one-half hour to complete the decarboxylation. The solution was acidified and extracted with ether in a continuous extractor. The ether was removed and the residue crystallized from ethyl acetate–petroleum ether (30–60°) to yield 4.7 g. (70%) of colorless crystals, m. p. 124–125.5° after two recrystallizations. For analyses see above.

Dimethyl Dioxanylsuccinate (V).—Compound XVIII (7 g.) was esterified with diazomethane and distilled to give 6.5 g. of the methyl ester (V), b. p. 113–114° (1 mm.), $n^{20}D$ 1.4592.

Anal. Calcd. for $C_{10}H_{16}O_6$: C, 51.69; H, 6.94. Found: C, 51.70; H, 6.75.

Dioxanylsuccinamic Acid and Dioxanylsuccinamide.—The mono- and diamides of dioxanylsuccinic acid (XVIII) were prepared from the methyl ester of the synthetic acid and from the esters isolated from the reaction of benzoyl peroxide on maleic ester. The ester was allowed to remain in contact with five times its volume of concentrated aqueous ammonia for a week with occasional shaking. By crystallization from ethanol the monoamide and the diamide were separated; monoamide, colorless crystals from ethyl acetate–ethanol, m. p. 160–161°, water-soluble, acidic toward phenolphthalein with sharp end-point.

Anal. Calcd. for $C_8H_{13}O_5N$: C, 47.29; H, 6.45; N, 6.90. Found: C, 47.20; H, 6.45; N, 7.08.

The diamide separated as colorless needles from ethanol, m. p. 234–235° d., and could be sublimed at 220° (1 mm.).

Anal. Calcd. for $C_8H_{14}O_4N_2$: C, 47.51; H, 6.98; N, 13.86. Found: C, 47.75; H, 7.22; N, 13.3.

Dioxanylsuccinic Anhydride.—Synthetic dioxanylsuccinic acid (XVIII) (1 g.) was refluxed for one hour with 5 cc. of acetyl chloride. After removal of excess chloride, crystallization from ethyl acetate–petroleum ether, and sublimation, colorless crystals of anhydride, m. p. 121–123°, were obtained.

Anal. Calcd. for $C_8H_{10}O_5$: C, 51.61; H, 5.41. Found: C, 51.78; H, 5.41.

Oxidation of the Tetracarboxylic Acid (XIV).—Compound XIV (0.500 g.) was heated on the steam-bath for three hours with a mixture of 1.90 g. of potassium permanganate, 30 cc. of water, and 2 cc. of 1 *N* sodium hy-

(21) It was found that molecular weight determinations on butane-1,2,3,4-tetracarbethoxylate were about 10% too low when measured in benzene solution, but were satisfactory in dioxane solution.

(22) Prager and Jacobsen, "Beilsteins Handbuch der organischen Chemie," 4th ed., Julius Springer, Berlin, 1922, Vol. 5, pp. 199, 200, 263.

(23) Summerbell and Umhoefer, THIS JOURNAL, **61**, 3016 (1939).

(24) Kucera and Carpenter, *ibid.*, **57**, 2346 (1935).

(25) Bischoff, *Ann.*, **214**, 38 (1882).

(26) Summerbell and Rochen, THIS JOURNAL, **63**, 3241 (1941).

droxide. The mixture was acidified with sulfuric acid and extracted in two portions for three hours each with ether in a small continuous extractor operating at the rate of 500 cc. of ether per hour. After drying the ether layer and removal of the solvent, the residue was sublimed slowly over a hot plate, yielding 60 mg. (22%) of needles which on resublimation had the m. p. 131.3–131.6° (cor.); mixed melting point with authentic phthalic anhydride 130.6–131.0° (cor.). Phthalanilic acid was prepared from the oxidation product,[27] m. p. 168.5–169° (cor.), solidified and remelted at 200–201° (cor.). The reported[27] melting point of phthalanilic acid is 169–170°, and of phthalanil, 207°.

Anhydride of XIV.—Compound XIV (1.00 g.) and 7 cc. of acetic anhydride were refluxed for five minutes to dissolve the acid, then excess acetic anhydride was removed by evaporation in a beaker. The residue was taken up in 1 cc. of acetic anhydride and 10 cc. of benzene added; almost colorless dense crystals separated, m. p. 192.7–194.4° (cor.) on recrystallization.

Anal. Calcd. for $C_{14}H_8O_6$: C, 61.77; H, 2.96. Found: C, 61.87; H, 3.36.

Tests for Unsaturation of Compound IIA.—Small amounts of compound IIA, of the acid XIV, and of the ethyl ester XV were dissolved in aqueous dioxane and a drop of dilute permanganate solution added. Both blanks and controls were run, but none of the tetracarboxylic acid derivatives gave any trace of decolorization.

To 0.98 g. of compound IIA in methanol solution was added Raney nickel and the solution was treated with hydrogen at 2000 lb./sq. in. at 100° for two and one-half hours; 0.71 g. of unchanged ester was recovered.

Compound IIA (1.14 g.) in methanol was refluxed with Raney nickel for one hour, filtered, 20 mg. of platinum oxide was added, and the solution treated for fifteen hours with hydrogen at 50 lb./sq. in. at room temperature; 0.98 g. of unchanged ester was recovered.

Attempted Dehydrogenation of Compound IIA.—Tetralin was dehydrogenated over palladium-on-charcoal in an apparatus similar to that described by Fieser,[15] and provided with a source of carbon dioxide (Dry Ice) and a simple azotometer. Upon refluxing, hydrogen was evolved and colorless crystals of naphthalene separated on the condenser. Using the proved catalyst attempts were made to dehydrogenate compound IIA in refluxing butylbenzene (b. p. 173°), in refluxing α-methylnaphthalene (b. p. 240° cor.), and by heating without solvent with a bath temperature of 240–280°. Unchanged ester was recovered in the respective amounts: 95, 63, 69%, and no evolution of hydrogen was detectable. When compound IIA was heated for six hours at 300° with palladium on charcoal in a sealed tube and with nitrobenzene as a hydrogen acceptor, only a tar was obtained. With two and one-half hours at 260–270° (cor.) with the same reactants, much unchanged ester was present.

The ester (IIA) (0.500 g.) was refluxed with 0.680 g. of chloranil[16] in 20 cc. of xylene for thirty-five hours; 70% of unchanged ester was recovered.

Attempted selenium dehydrogenations[17] of 100-mg. samples of the methyl ester IIA, the acid XIV, and the ethyl ester XV yielded only 5–10 mg. of mixtures which were not separable by crystallization from benzene–petroleum ether or from methanol.

Attempted Synthesis of Tetralintetracarboxylic Acid Ester (III).—Dimethyl *o*-phenylenediacetate (prepared[23] *via* *o*-xylene, *o*-xylylene bromide, *o*-phenylenediacetonitrile, *o*-phenylenediacetic acid) was mixed with an equimolar portion of dimethyl acetylenedicarboxylate[29] in the presence of various catalysts. After all attempts, the irritating odor of acetylenedicarboxylate was detectable, and hydrolysis of several reaction mixtures led to the isolation of considerable *o*-phenylenediacetic acid. The catalysts tried were piperidine,[30] one drop of sodium methoxide,[31] one drop of Triton B (40% aqueous solution of benzyltrimethylammonium hydroxide), and sodium sand. The reactants were allowed to stand for several days at room temperature or slightly above and were heated at 100° for several hours. *o*-Phenylenediacetonitrile also failed to react.

Oxidation of the Tetracarboxylic Acid (XVI) from Ester IIB.—Following the procedure used for acid XIV, a 38% yield of phthalic anhydride, m. p. 131.0–131.4° (cor.) was obtained.

Hydrolysis of Diethyl α,α′-Bis-trichloromethylsuccinate (VII).—A mixture of 4.0 g. of compound VII and 85 cc. of 70% by weight sulfuric acid was refluxed for thirty-eight hours, then extracted with ether in a continuous extractor. Removal of the ether left 0.3 g. of residue, m. p. 183–184.5°, which gave no depression with an authentic specimen of succinic acid. By the action of acetyl chloride, it was converted to the anhydride, colorless needles from chloroform, m. p. 117–118.5°. The reported[27] melting point of succinic acid is 185° and of succinic anhydride is 120°.

A mixture of 2.5 g. of compound VII and 30 cc. of 20% potassium hydroxide was refluxed for twelve hours, then acidified and extracted with ether in a continuous extractor. The residue obtained on removal of the ether was recrystallized three times from ethyl acetate–petroleum ether (30–60°) to give colorless cubes, m. p. 219° d.

Anal. Calcd. for $C_6H_2O_4Cl_4$: C, 25.75; H, 0.72. Found: C, 25.78; H, 1.13.

1-Phenyl-1,2,2,3,4-pentacarbethoxybutane (XX).—To a hot solution of 6.7 g. of sodium in 100 cc. of absolute ethanol was added 107.5 g. of 1,1,2,3-tetracarbethoxypropane[32] (b. p. 188–189° (8 mm.), $n^{20}D$ 1.4393). After one-half hour 70.0 g. of ethyl α-bromophenylacetate[33] (obtained in 78% yield from phenylacetic acid; b. p. 146–149° (16 mm.), $n^{20}D$ 1.5375) was added and the mixture was refluxed for five hours. After removal of most of the ethanol by distillation, water was added, the organic layer was taken up in ether, washed with dilute sulfuric acid, dried over sodium sulfate, and then distilled. After considerable forerun, 31 g. of compound XX distilled, b. p. 210–230° (2 mm.). A redistilled portion, b. p. 195–200° (1 mm.), $n^{20}D$ 1.4913, was analyzed.

Anal. Calcd. for $C_{25}H_{34}O_{10}$: C, 60.72; H, 6.93. Found: C, 61.47; H, 6.81.

1-Phenylbutane-1,2,3,4-tetracarboxylic Acid (XXI).—A 22.5-g. portion of compound XX was hydrolyzed by refluxing for thirty-two hours with 250 cc. of 20% potassium hydroxide. The solution was acidified, refluxed for an hour to complete the decarboxylation, and then extracted with ether in a continuous extractor. The ether was removed and the residue treated with cold ethyl acetate and petroleum ether. The 2-g. portion which was insoluble, was recrystallized from glacial acetic acid, m. p. 202–204°.

Anal. Calcd. for $C_{14}H_{14}O_8$: C, 54.19; H, 4.55. Found: C, 53.72; H, 4.76.

From the residue lower melting samples of the acid (m. p. 167.5–168.7°) were obtained.

Tetramethyl-1-phenylbutane-1,2,3,4-tetracarboxylate (XXII and XXIII).—The tetramethyl ester of the isomer (m. p. 202°) was prepared using diazomethane. It was obtained as colorless needles, m. p. 142.5–143.5° after two crystallizations from methanol.

Anal. Calcd. for $C_{18}H_{22}O_8$: C, 59.01; H, 6.05. Found: C, 59.02; H, 5.95.

From the acid, m. p. 168°, there was obtained a mixture of methyl esters from which one, m. p. 117–118°

(27) Huntress and Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, New York, 1941.

(28) Moore and Thorpe, *J. Chem. Soc.*, **93**, 175 (1908).

(29) We wish to thank Mr. H. J. Sampson for supplying us with a sample of dimethyl acetylenedicarboxylate.

(30) Connor and McClellan, *J. Org. Chem.*, **3**, 576 (1939).

(31) Koelsch, THIS JOURNAL, **65**, 437 (1943).

(32) Clarke and Murray, "Organic Syntheses," Coll. Vol. I, 272 (1941).

(33) Anschütz, *Ann.*, **354**, 127 (1907).

(cor.), could be isolated in pure form by repeated crystallization from methanol.

Anal. Calcd. for $C_{18}H_{22}O_8$: C, 59.01; H, 6.05. Found: C, 58.99; H, 6.10.

Summary

It has been found that dimethyl and diethyl maleate react in the presence of large quantities of benzoyl peroxide to give the corresponding esters of phenylsuccinic acid and of tetracarboxylic acids which are probably stereoisomeric forms of tetralintetracarboxylic acid. Some higher molecular weight products of unidentified nature are also produced.

When the reaction is carried out in dioxane, dioxyanylsuccinic ester is formed in addition to these products, and in carbon tetrachloride solution, α,α'-bis-trichloromethylsuccinic ester is formed.

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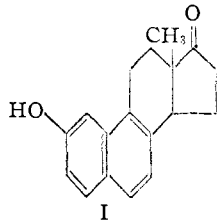
[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

The Synthesis of 2-Hydroxy-17-equilenone

BY W. E. BACHMANN AND W. J. HORTON[1]

2-Hydroxy-17-equilenone[2] (I), the isomer of equilenin in which the OH group is in the 2-position, has been synthesized by the methods employed in the preparation of equilenin[3] and related compounds.[4]

6-Methoxy-1-keto-1,2,3,4-tetrahydrophenanthrene (II), an intermediate in the synthesis, was prepared by cyclization of γ-7-methoxy-1-naphthylbutyric acid. This acid was prepared in



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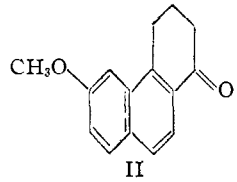

II

three ways: (a) from 1-amino-7-naphthol through the intermediate 7-methoxy-1-iodonaphthalene and β-7-methoxy-1-naphthylethyl alcohol; (b) from 7-methoxy-1-tetralone through the Reformatsky reaction, Bouveault reduction of the dehydrated ester, a malonic ester synthesis on the bromide of the resulting alcohol and dehydrogenation of the product; (c) by Clemmensen reduction of β-7-methoxy-1-naphthoylpropionic acid. The keto acid was obtained from the reaction between 2-methoxynaphthalene and succinic anhydride in the presence of aluminum chloride in carbon disulfide. Substitution in the 8-position of 2-methoxynaphthalene was unexpected, for it had been reported that succinoylation of 2-methoxynaphthalene in carbon disulfide takes place exclusively in the 1-position.[5]

Plimmer, Short and Hill[6] obtained a glass on cyclization of γ-7-methoxy-1-naphthylbutyric acid by phosphorus pentoxide in benzene. We found that cyclization of the acid chloride by stannic chloride gave a mixture of two crystalline compounds, one (m. p. 100–102°) in 70–80% yield and the other (m. p. 81–82.5°) in about 10–15% yield. The higher melting compound was definitely shown to be 6-methoxy-1-keto-1,2,3,4-tetrahydrophenanthrene (II). The lower melting compound is probably the cyclic ketone with a seven-membered ring formed by cyclization to the 8-position,[7] but this has not been established. The particular compound or mixture of compounds which were formed depended on the cyclizing agent and apparently also on certain uncontrollable conditions when phosphorus pentoxide was used, since reproducible results were not always obtained. The most satisfactory methods of preparing II were the method mentioned above and the action of a mixture of phosphorus pentoxide and phosphoric acid on the acid. After this work had been completed, Campbell and Todd[8] reported the formation of crystalline II (m. p. 99–102°) from the reaction between the acid and hydrogen fluoride.

Only one of the two possible forms (*cis* and *trans*) of the final hormone isomer was obtained in the synthesis.

Experimental

γ-7-Methoxy-1-naphthylbutyric Acid. (a) From 1-Amino-7-naphthol.—7-Hydroxy-1-naphthylamine (m. p. 160–166°), which was obtained by alkaline fusion of 1-naphthylamine-7-sulfonic acid, was acetylated by ice cold acetic anhydride; the product was methylated by means of dimethyl sulfate in alkaline solution to **1-acetylamino-7-methoxynaphthalene** in quantitative yield. A sample after recrystallization from water melted at 160–161° (reported,[9] 145°).

Anal. Calcd. for $C_{13}H_{13}O_2N$: N, 6.5. Found: N, 6.7.

A mixture of 22.7 g. of powdered 1-acetylamino-7-methoxynaphthalene, 11.3 cc. of water and 27.4 cc. of concentrated hydrochloric acid was refluxed for one hour. On cooling, the clear solution deposited the hydrochloride of 7-methoxy-1-naphthylamine; yield, 17.4 g. (78%). This was used directly for diazotization. A sample of the free **7-methoxy-1-naphthylamine** after evaporative distilla-

(1) From the Ph.D. dissertation of W. J. Horton, 1942.

(2) For the nomenclature employed for these compounds see Bachmann and Wilds, THIS JOURNAL, **62**, 2084 (1940).

(3) Bachmann, Cole and Wilds, *ibid.*, **62**, 824 (1940).

(4) Preceding paper, Bachmann and Morin, *ibid.*, **66**, 553 (1944).

(5) Short, Stromberg and Wiles, *J. Chem. Soc.*, 319 (1936).

(6) Plimmer, Short and Hill, *ibid.*, 694 (1938).

(7) Compare the cyclization of γ-5-methoxy-1-naphthylbutyric acid to the 8-position [Kon and Soper, *ibid.*, 790 (1939)].

(8) Campbell and Todd, THIS JOURNAL, **64**, 928 (1942).

(9) Davis, *Chem. News*, **74**, 302 (1896).