g. (0.3 mole) of α-*n*-butyl di-*t*-butylmalonate in 125 ml. of ether, followed after 24 hours[11] of stirring and refluxing by 55.8 g. (0.3 mole) of *p*-nitrobenzoyl chloride in 300 ml. of ether essentially as described for II ($X = NO_2$). After stirring and refluxing 18 hours longer, the mixture was decomposed with *t*-butyl alcohol and cold dilute hydrochloric acid. The solvent was removed from the dried ether solution (after washing with saturated sodium bicarbonate solution) and the crude residual acyl malonate dissolved in 200 ml. of anhydrous benzene. A catalytic amount (2.0 g.) of *p*-toluenesulfonic acid was added and the solution refluxed until the evolution of gas ceased (10 hours), in the apparatus described previously.[6] The cooled solution was shaken with water and ether and the organic layer washed with saturated sodium bicarbonate solution followed by water, dried over Drierite, and the solvents distilled. The residue was distilled *in vacuo* to give 38.4 g. (58%) of *p*-nitrocaprophenone, b.p. 160–161° (1 mm.).

Anal. Calcd. for $C_{12}H_{15}O_3N$: C, 65.14; H, 6.83; N, 6.34. Found: C, 65.22; H, 6.97; N, 6.50.

The 2,4-dinitrophenylhydrazone melted at 181–182° after two recrystallizations from ethanol.

Anal. Calcd. for $C_{18}H_{19}O_6N_5$: C, 53.82; H, 4.77; N, 17.45. Found: C, 53.99; H, 4.47; N, 17.54.

The oxime melted at 79–81° after one recrystallization from ethanol–water.

α-Methyl Di-*t*-butylmalonate.—To a stirred solution of potassium *t*-butoxide prepared from 12.3 g. (0.315 mole) of potassium and 200 ml. of anhydrous *t*-butyl alcohol was added 65 g. (0.3 mole) of di-*t*-butylmalonate (prepared from malonyl chloride and *t*-butyl alcohol)[10] followed after a few minutes by 50 g. (0.55 mole) of methyl bromide according to the general method for alkylating malonic esters.[12] There was obtained 48.9 g. (71%) of α-methyl di-*t*-butylmalonate, b.p. 93–96° (10 mm.).

Anal. Calcd. for $C_{12}H_{22}O_4$: C, 62.61; H, 9.64. Found: C, 62.49; H, 9.40.

***p*-Nitropropiophenone.**—This ketone was prepared essentially as described for *p*-nitrocaprophenone, employing 5.3 g. (0.22 mole) of sodium hydride in 125 ml. of ether, 46 g. (0.2 mole) of α-methyl di-*t*-butylmalonate in 100 ml. of ether and 37 g. (0.2 mole) of *p*-nitrobenzoyl chloride in 250 ml. of ether. After hydrolysis and decarboxylation of the crude acyl derivative, there was obtained 13 g. (36%)[13] of *p*-nitropropiophenone which, after one recrystallization from ethanol and three recrystallizations from 60–90° ligroin, melted at 82–85°.

Anal. Calcd. for $C_9H_9O_3N$: C, 60.34; H, 5.06; N, 7.82. Found: C, 60.38; H, 4.89; N, 7.58.

The oxime melted at 143–144° after one recrystallization from ethanol.

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[11] This reaction time could probably be shortened considerably and perhaps the yield of product improved by the use of a higher boiling inert solvent; *cf.* F. W. Swamer and C. R. Hauser, This Journal, **72**, 1352 (1950).

[12] *Cf.* N. Weiner, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 279.

[13] This yield could probably be improved considerably. The sodium hydride available at the time was not of the highest quality and the sodio derivative of α-methyl di-*t*-butylmalonate formed only sluggishly. Since the sodio derivative appeared to be relatively insoluble in ether, the use of dioxane or some other solvent may be advantageous.

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The Hydrogenolysis of Dibutyl Phthalate

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Adkins[1] has shown that esters possessing the carbalkoxy group attached to an aryl group readily undergo hydrogenolysis over copper–chromium oxide at 250° with the resulting conversion of the carbalkoxy group to a methyl group. With the exception of the limited work on diethyl phthalate[2] and diethyl hexahydrophthalate[3] the hydrogenolysis of esters of polybasic aromatic acids has received little attention.

Recent investigations in this Laboratory have been focused upon the water-soluble polycarboxylic aromatic acids produced by the oxidation of bituminous coals. The hydrogenolysis reaction has been used on the butyl esters of these coal acids to convert them to methylated nuclear structures in order to obtain more information concerning the structure of the aromatic nuclei.[4] Along with the anticipated di-, tri- and tetramethylbenzenes in the fractionally distilled hydrogenolysis products there appeared some oxygen-rich fractions which have been characterized as phthalans; higher boiling unidentified materials were also present.

In an effort to ascertain whether the phthalan heterocycle might have been synthesized by the hydrogenolysis reaction from esters of benzene polycarboxylic acids containing the carbalkoxy groups on adjacent positions, one kilogram (7.26 equivalents) of dibutyl phthalate has been subjected to hydrogenolysis. When hydrogen absorption ceased the resulting material was filtered free of catalyst, "topped" free of low boiling products by distillation and subjected to additional stages of hydrogenolysis; even in the fourth stage *o*-xylene was still being produced, while 0.08 equivalent of ester groups remained unconverted. Data for the four stages are given in Table I.

Table I

Hydrogenolysis of 1000 g. of Dibutyl Phthalate

Six hours per stage at 270°; 10% copper chromium oxide by weight; initial pressure = 115–125 atm. (25°)

	Stages			
	1	2	3	4
Equivalents of ester charged	7.26	3.85	1.66	0.94
Moles of hydrogen absorbed	12.82	7.95	2.70	3.38
Grams of products				
a, b.p. < 100°	25	16	6	4
b, water in separated phase	36	37	12	19
c, b.p. 100–120°	348	151	48	34
d, b.p. 120–144°	569	93	29	65
e, b.p. 144–170		288	5	1
f, b.p. 170–190°			26	11
g, b.p. > 190° (residue)			154	20
Equivalents of ester after stage	3.85	1.66	0.94	0.08

For further investigation of chemical composition, the fractions from all four stages with the same boiling point range were combined and refractionated in distillation columns of 50 theoretical plates. Small amounts of *n*-butyraldehyde, *n*-butyl *n*-butyrate, dibutyl ether, 2-methylcyclohexanemethanol, phthalan and hexahydrophthalan were isolated and identified in addition to the expected large quantities of *o*-xylene, butanol and water.

Since the phthalan heterocycle has been shown to be a minor product of the hydrogenolysis of dibutyl

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[1] H. Adkins, "Reactions of Hydrogen," University of Wisconsin Press, Madison, Wisconsin, 1937, p. 101.

[2] H. Adkins, B. Wojcik and L. W. Covert, This Journal, **55**, 1669 (1933).

[3] W. A. Lazier, U. S. Patent 2,105,664 (Jan. 18, 1938).

[4] C. H. Ruof, T. R. Savich and H. C. Howard, This Journal, **73**, 3873 (1951).

phthalate, the isolation of phthalans from the hydrogenolysis products of the esters of the coal acids cannot be regarded as unequivocal evidence for the presence of such heterocycles as nuclei of the coal acids.

Acknowledgment.—We wish to thank Messrs. D. T. Muth, T. R. Savich and J. B. Simsic for their assistance.

Experimental

Hydrogenolyses.—One kg. (7.26 equivalents) of dibutyl phthalate (No. D-30, Fisher Scientific Company), 100 g. of a copper-chromium oxide catalyst prepared as described previously,[4] and 125 atm. of hydrogen were charged to a stainless steel rocking autoclave and heated to 270° for six hours. After cooling, the bomb contents were filtered free of catalyst through a layer of Sil-O-Cel on a medium porosity fritted filter funnel. The catalyst and filter aid were extracted exhaustively in a soxhlet extractor with ether to remove adsorbed products, the ether was evaporated and the extract was combined with the main filtrate. The combined filtrate was then fractionated in a column of 30 theoretical plates until the still temperature reached 270°. The amount of ester present was determined by saponification of 1 g. of the still contents. The still contents were then subjected to the next stage of hydrogenolysis carried out in the same manner. Products from all four stages with the same boiling range were combined and refractionated in columns of 50 theoretical plates.

***n*-Butyraldehyde**.—The combined fractions boiling up to 100° contained mainly butanol and *o*-xylene which had formed a ternary azeotrope with the readily separable water. *n*-Butyraldehyde, 0.5 g., b.p. 74° (740 mm.), was isolated and identified as its 2,4-dinitrophenylhydrazone, m.p. and mixture m.p. 122°.

***o*-Xylene and Butanol**.—The fraction boiling 100–120° was a mixture of butanol and *o*-xylene which form a binary azeotrope[5]; no dimethylcyclohexanes were found. The *o*-xylene was freed of butanol by alternate distillation and washing with 10 volumes of water. The fractions boiling 120–144° consisted almost entirely of *o*-xylene with traces of dibutyl ether which boils close to the *o*-xylene and forms an azeotrope with it[5]; the dibutyl ether was readily removed by adsorption on silica gel. The total amount of *o*-xylene present in all fractions as determined by quantitative ultraviolet absorption spectra was 306 g. or a yield of 80.5%; the yield of butanol was not determined.

***n*-Butyl *n*-Butyrate**.—The fraction boiling 144–170° contained 3 g. of *n*-butyl *n*-butyrate, b.p. 166° (740 mm.), $n^{25}D$ 1.4052, sapn. equiv., 149. The infrared spectrum was identical with that of an authentic sample. The butyric acid was recovered from the saponification and converted to the *p*-phenyl phenacyl ester, m.p. and mixture m.p. 83°.

Hexahydrophthalan.—Redistillation of the fraction boiling 170–190° gave 7 g. of hexahydrophthalan, b.p. 179° (740 mm.), $n^{25}D$ 1.4652, which readily forms an adduct with stannic chloride in pentane.

Anal. Calcd. for $C_8H_{14}O$: C, 76.14; H, 11.18; *MR*, 36.40. Found: C, 75.87; H, 11.21; *MR*, 36.10.

These data and the infrared spectra correspond closely with those recently published for authentic material.[6]

Phthalan and 2-Methylcyclohexanemethanol.—When the hexahydrophthalan was removed from the fraction boiling 170–190° there still remained a mixture of 8 g. of phthalan and 3 g. of 2-methylcyclohexanemethanol quantitatively characterized by comparison with refractive indices and the infrared spectra of authentic material.[6] The phthalan readily formed an adduct with stannic chloride, possessed the characteristic strong benzaldehyde odor, and on heating in air polymerized to a non-volatile red resin[6] from which the 2-methylcyclohexanemethanol was readily separated by distillation, b.p. 194°, $n^{25}D$ 1.4615.

Anal. Calcd. for $C_8H_{16}O$: C, 74.94; H, 12.58; *MR*, 38.26. Found: C, 74.75; H, 12.52; *MR*, 38.49.

Residue.—The 20 g. of black viscous residue contained 0.08 equivalent of esters and 1.1 wt. % hydroxyl groups determined by saponification and acetylation, respectively, but was not investigated further.

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[5] L. H. Horsley, *Anal. Chem.*, **19**, 508 (1947).

[6] J. Entel, C. H. Ruof and H. C. Howard, THIS JOURNAL, **74**, 441 (1952).

Steroidal Sapogenins. XIX.[1] Sodium Borohydride Reduction of 3-Acetoxy-$\Delta^{3,5,7}$-22-isospirostatriene and 3-Acetoxy-$\Delta^{3,5,7,9(11)}$-22-isospirostatetraene

BY HOWARD J. RINGOLD, G. ROSENKRANZ AND CARL DJERASSI[2]

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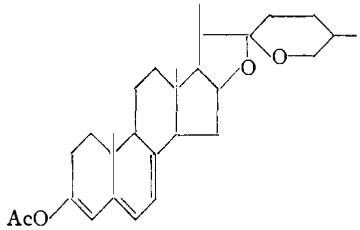
Three independent reports[3–5] have appeared recently on the sodium borohydride reduction of 3-acetoxy-$\Delta^{3,5}$-cholestadiene (Δ^4-cholesten-3-one enol acetate) to cholesterol in 60–75% yield. Since $\Delta^{5,7}$-3β-hydroxy steroids represent the starting materials for the introduction of a C-11 oxygen function into ring C unsubstituted steroids,[6] it seemed pertinent to investigate the applicability of the sodium borohydride reduction to the preparation of such dienes. In fact, Dauben, Eastham and Micheli[7] in a recent preliminary communication reported the formation of 70% of 7-dehydrocholesterol from 3-acetoxy-$\Delta^{3,5,7}$-cholestatriene by such a method. We have independently[8] investigated this procedure in the sapogenin series, where a two-step degradation[9] leads directly to the pregnane series, and would like to record briefly our results.



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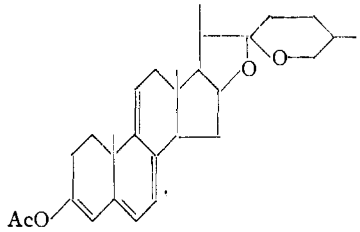

II

3-Acetoxy-$\Delta^{3,5,7}$-22-isospirostatriene[10] (I) be-

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[4] B. Belleau and T. F. Gallagher, THIS JOURNAL, **73**, 4458 (1951).

[5] W. G. Dauben and J. F. Eastham, *ibid.*, **73**, 4463 (1951).

[6] E. M. Chamberlain, W. V. Ruyle, A. E. Erickson, J. M. Chemerda, L. M. Aliminosa, R. L. Erickson, G. E. Sita and M. Tishler, *ibid.*, **73**, 2396 (1951); L. F. Fieser, J. E. Herz and W. Huang, *ibid.*, **73**, 2397 (1951); G. Stork, J. Romo, G. Rosenkranz and C. Djerassi, *ibid.*, **73**, 3546 (1951).

[7] W. G. Dauben, J. F. Eastham and R. A. Micheli, *ibid.*, **73**, 4496 (1951).

[8] Mexican patent application No. 31855 (August 3, 1951).

[9] C. Djerassi, J. Romo and G. Rosenkranz, *J. Org. Chem.*, **16**, 754 (1951).

[10] R. Yashin, G. Rosenkranz and C. Djerassi, THIS JOURNAL, **73**, 4654 (1951).