take a planar configuration, *i.e.*, a doubly bonded pair of carbons and the four atoms singly bonded to them are all in a plane. Thus there is no strain with respect to possible twist in double bonds. The structure is such as to be able to readily adjust to C=C—C angles in the vicinity of 120° so that there is no reason to assume strain from this source. The twist angle about the C–C single bonds is near 90° which presumably prevents any first order conjugation between successive double bonds but does not otherwise cause significant strain. Thus the tub structure is a strain-free configuration.

The heat of formation of cycloöctatetraene measured by Prosen, Johnson and Rossini[4] and converted to the absolute zero with the calculated functions of Lippincott and Lord[5] yields ΔH_f = 76.33 kcal./mole at 0°K. Using the bond energies given recently,[6] and in particular the 81.0 kcal. value appropriate for the C—C single bond in the larger hydrocarbons, one calculates a heat of formation of 86.4 kcal./mole. The difference of 10 kcal./mole can be plausibly ascribed to hyperconjugation in the tub model.

One further check on the tub model is readily made. The lowest totally symmetric vibration at 194 $cm.^{-1}$ is unequivocably identified in the Raman spectrum by its polarization and is far removed from the next higher frequency of the same type at 873 $cm.^{-1}$. Thus a calculation of the lowest totally symmetric bending frequency should offer a significant comparison. The bond distances were assumed constant and the bond angles involving hydrogen were also held constant. The frequency is not sensitive to the exact bond distances or angles—the values used were C–C, 1.51 Å.; C=C, 1.34 Å.; C=C—C angle, 120°; C–H, 1.09 Å.; C=C—H angle, 120°. The potential function for this vibration was assumed to depend almost entirely on the C=C—C angle bending force constant. This constant in other molecules[7] ranges from 0.6 to 1.4 $\times 10^{-11}$ erg./radian^2. The calculated value from the 194 $cm.^{-1}$ frequency is 0.93 $\times 10^{-11}$ erg/radian^2. Similarly in the deuterated cycloöctatetraene the corresponding frequency at 172 $cm.^{-1}$ yields the same potential constant. This potential constant is evidently well within the expected range.

Calculations in the skeletal approximation for all other modes of vibration gave higher frequencies than for this symmetric deformation vibration in agreement with the observed spectrum.

The D_4 or crown model for cycloöctatetraene involves C=C double bonds twisted by about 80°. All normal olefinic compounds involve planar double bonds. Thus there is no precedent for twisted double bonds; indeed one is tempted to say that such bonds would not be double bonds in the ordinary sense. Magee, Shand and Eyring[8] have studied the torsion of double bonds in detail and their results indicate a triplet electronic state to be the most stable in the twisted configuration. On this basis, the crown model would involve four triplet units which would interact in some unknown manner. To be in agreement with the diamagnetism of cycloöctatetraene, this interaction would have to yield a singlet ground state. In view of these considerations it is not possible to make any accurate calculation of the strain energy of the crown structure, but a lower limit of 60 kcal. can be estimated from activation energies for *cis–trans* isomerizations.[8] Also in this structure there would be no reason to expect the typical olefinic C=C stretching frequencies near 1600–1650 $cm.^{-1}$ which are observed very clearly in cycloöctatetraene.

Calculations[9] to the skeletal approximation indicate that for the D_4 model the lowest totally symmetric vibration should be substantially higher than ring deformation vibrations of lower symmetry. This is contrary to the observed Raman spectrum in which the polarized line is at 194 $cm.^{-1}$ and is definitely the lowest of the Raman bands.

In summary, potential energy considerations from related hydrocarbons are in complete agreement with observed facts on the basis of the tub or D_{2d} structure for cycloöctatetraene. The crown or D_4 structure, which has been interpreted as more consistent with certain physical data,[2,3b] is difficult to understand on the basis of the same potential functions and gives the wrong order for the low frequency ring deformation vibrations. Since this manuscript was prepared, Karle[10] has published a further electron diffraction study of cycloöctatetraene and concluded that this molecule has the D_{2d} structure. While the evidence we have presented in this note would not be conclusive, we believe the net balance of all evidence on cyclooctatetraene strongly favors the tub or D_{2d} model.

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(4) E. J. Prosen, W. H. Johnson and F. D. Rossini, THIS JOURNAL, **72**, 626 (1950).

(5) E. R. Lippincott and R. C. Lord, *ibid.*, **73**, 3889 (1951).

(6) K. S. Pitzer, *ibid.*, **70**, 2140 (1948).

(7) J. E. Kilpatrick and K. S. Pitzer, *J. Research Natl. Bur. Standards*, **38**, 191 (1947); B. Bak, *Kgl. Danske Videnskab. Selskab, Mat-fys Medd.*, **22**, No. 9 (1945); G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., New York, N. Y., 1945, p. 193.

(8) J. L. Magee, W. Shand and H. Eyring, THIS JOURNAL, **63**, 677 (1941); see also R. S. Mulliken, *Phys. Rev.*, **41**, 751 (1932).

(9) Details of this skeletal normal coördinate analysis are presented in the Ph.D. dissertation of Willis B. Person, University of California, 1952.

(10) I. L. Karle, *J. Chem. Phys.*, **20**, 65 (1952).

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Modes of Cleavage of Acylalkylmalonic Esters. Synthesis of *p*-Nitrocaprophenone and *p*-Nitropropiophenone

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RECEIVED JANUARY 10, 1952

The observation of earlier workers[2] that certain crude acyl derivatives of alkylmalonic esters were cleaved by acid at the ketone group to regenerate the carboxylic acid and alkylmalonic ester has been confirmed in the present work with pure acyl derivatives II (X = NO_2, OCH_3 and H). These acyl derivatives, synthesized from the corresponding acid chloride and sodio malonic ester, underwent this mode of cleavage apparently exclusively with dilute sulfuric and acetic acids. For example,

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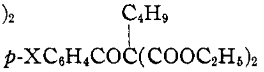
(1) Carbide and Carbon Chemicals Corp. Fellow, 1950–1952.

(2) *Cf.* R. E. Bowman, *J. Chem. Soc.*, 322 (1950).

acyl derivative II ($X = NO_2$) gave *p*-nitrobenzoic acid (90–92%) and caproic acid which resulted presumably from hydrolysis and decarboxylation of regenerated *n*-butylmalonic ester. No *p*-nitrocaprophenone was found.

o- or *p*-$NO_2C_6H_4COCH(COOC_2H_5)_2$

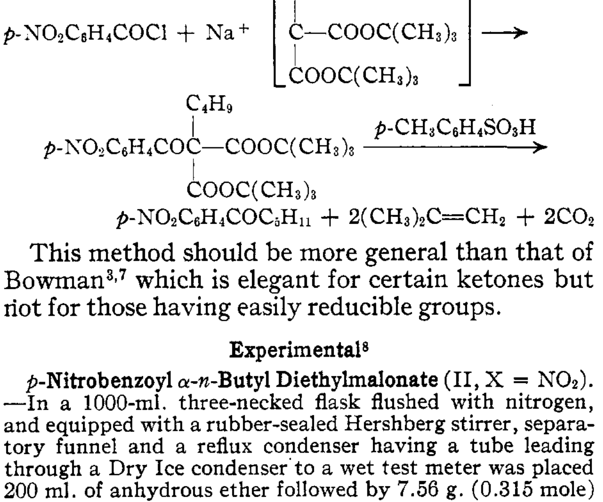
I



$$p\text{-}XC_6H_4CO\overset{\displaystyle C_4H_9}{\overset{|}{C}}(COOC_2H_5)_2$$

II

In contrast to II, acyl derivatives of malonic ester itself, such as I, are hydrolyzed by acid apparently exclusively at the ester groups, yielding, after decarboxylation, methyl ketones.[3,4] Although this excellent method for preparing *o*- and *p*-nitroacetophenones[5] through intermediates I is limited to methyl ketones, a modification of this method employing di-*t*-butyl alkylmalonates instead of the diethyl esters was found applicable to the synthesis of *p*-nitrocaprophenone and *p*-nitropropiophenone. This modification, illustrated below for the former ketone, is based on the procedure devised previously for converting *t*-butyl ethyl acylmalonates to *β*-keto esters.[6] The di-*t*-butyl *n*-butylmalonate was prepared conveniently from commercial diethyl *n*-butylmalonate and converted to its sodium derivative by sodium hydride.



$$p\text{-}NO_2C_6H_4COCl + Na^+ \left[\begin{array}{l} C_4H_9 \\ | \\ C\text{—}COOC(CH_3)_3 \\ | \\ COOC(CH_3)_3 \end{array}\right]^- \longrightarrow$$

$$p\text{-}NO_2C_6H_4CO\begin{array}{l} C_4H_9 \\ | \\ C\text{—}COOC(CH_3)_3 \\ | \\ COOC(CH_3)_3 \end{array} \xrightarrow{p\text{-}CH_3C_6H_4SO_3H}$$

$$p\text{-}NO_2C_6H_4COC_5H_{11} + 2(CH_3)_2C{=}CH_2 + 2CO_2$$

This method should be more general than that of Bowman[3,7] which is elegant for certain ketones but not for those having easily reducible groups.

Experimental[8]

***p*-Nitrobenzoyl *α*-*n*-Butyl Diethylmalonate** (II, $X = NO_2$).—In a 1000-ml. three-necked flask flushed with nitrogen, and equipped with a rubber-sealed Hershberg stirrer, separatory funnel and a reflux condenser having a tube leading through a Dry Ice condenser to a wet test meter was placed 200 ml. of anhydrous ether followed by 7.56 g. (0.315 mole) of sodium hydride.[9] To the stirred mixture was added during one hour 64.8 g. (0.3 mole) of *α*-*n*-butyl diethylmalonate (Eastman Kodak Co.) in 200 ml. of anhydrous ether. The mixture was stirred and refluxed for 1.5 hours, the theoretical quantity of hydrogen being evolved. To this solution of the sodio derivative of *α*-*n*-butylmalonic ester was added dropwise during 3 hours 55.8 g. (0.3 mole) of *p*-nitrobenzoyl chloride in 300 ml. of anhydrous ether. The viscous mixture was then stirred vigorously and refluxed for an additional 15 hours, cooled in an ice-bath, and 35 ml. of ethanol added cautiously to decompose the excess sodium hydride, followed by a cold mixture of 25 ml. of 3 *N* hydrochloric acid and 150 ml. of water. After shaking thoroughly, the ether phase (to which was added an ether extract of the aqueous phase) was washed with saturated sodium bicarbonate solution, then with water and dried over Drierite. The solvent was removed and the residue distilled *in vacuo* to give 54.6 g. (50%) of *p*-nitrobenzoyl *α*-*n*-butyl diethylmalonate, b.p. 215–218° (4 mm.) and at 215–217° (4 mm.) on redistillation.

Anal. Calcd. for $C_{18}H_{23}O_7N$: C, 59.17; H, 6.35; N, 3.83. Found: C, 59.13; H, 5.82; N, 3.85.

Anisoyl *α*-*n*-Butyl Diethylmalonate (II, $X = OCH_3$).—This compound was prepared in a 500-ml. flask from 2.52 g. (0.105 mole) of sodium hydride suspended in 75 ml. of ether, 21.7 g. (0.1 mole) of *α*-*n*-butyl diethylmalonate in 75 ml. of ether, and 17.1 g. (0.1 mole) of anisoyl chloride in 50 ml. of ether essentially as described for the *p*-nitrobenzoyl derivative (refluxed 2 hours). There was obtained 25.7 g. (74%) of anisoyl *α*-*n*-butyl diethylmalonate, b.p. 197–201° (1 mm.) and at 196–197° (1 mm.) on redistillation.

Anal. Calcd. for $C_{19}H_{26}O_6$: C, 65.12; H, 7.48. Found: C, 65.09; H, 7.30.

Benzoyl *α*-*n*-Butyl Diethylmalonate (II, $X = H$).—This compound was prepared from 2.52 g. (0.105 mole) of sodium hydride suspended in 75 ml. of ether, 21.7 g. (0.1 mole) of *α*-*n*-butyl diethylmalonate in 75 ml. of ether, and 14.1 g. (0.1 mole) of benzoyl chloride in 50 ml. of ether, essentially as described for anisoyl *α*-*n*-butyl diethylmalonate. There was obtained 25.0 g. (78%) of benzoyl *α*-*n*-butyl diethylmalonate, b.p. 168–169° (1.5 mm.) and at 165° (1 mm.) on redistillation.

Anal. Calcd. for $C_{18}H_{24}O_5$: C, 67.48; H, 7.55. Found: C, 67.39; H, 7.30.

Cleavage of Acyl Derivatives II.—Mixtures of 0.05 mole of these compounds, 2 ml. of concentrated sulfuric acid, 15 ml. of glacial acetic acid and 10 ml. of water were refluxed 10 to 20 hours, then cooled and water added. The mixtures were extracted with ether and the ether solutions extracted with saturated sodium bicarbonate solution to give, on acidification, the corresponding aromatic acid and some caproic acid. The aromatic acid was collected by suction filtration and washed thoroughly with water.

From the corresponding acylmalonates (II), there were isolated *p*-nitrobenzoic acid, m.p. 236–239° (90%), anisic acid, m.p. 182–184° (71%), and benzoic acid, m.p. 119–120° (66%).

When a mixture of 0.05 mole of II ($X = NO_2$), 15 ml. of glacial acetic acid and 10 ml. of water was refluxed 48 hours, *p*-nitrobenzoic acid, m.p. 235–238°, was obtained in 92% yield.

***α*-*n*-Butyl Di-*t*-butylmalonate.**—A mixtuure of 100 g. (0.463 mole) of *α*-*n*-butyl diethylmalonate, 100 g. (1.79 moles) of potassium hydroxide and 100 ml. of water was refluxed and stirred for 3.5 hours, then evaporated to dryness on the steam-bath. An aqueous solution of the residue was acidified in the cold, and the mixture extracted several times with ether. After drying over Drierite, the solvent was removed, and the cooled semi-solid residue stirred with 30–60° petroleum ether and filtered with suction to give 61.0 g. (82%) *n*-butylmalonic acid, m.p. 96–101°, after drying in air.

This acid (134 g., 0.85 mole) was heated with 2.7 equivalents of thionyl chloride at 40–50° for 24 hours and at 60° for 7 hours, to give, after distilling off the excess thionyl chloride, 145.0 g. (87%) of *n*-butylmalonyl chloride, b.p. 92–96° (22 mm.).

This acid chloride (61 g., 0.31 mole) was treated with 51 g. (0.68 mole) of *t*-butyl alcohol and 80 g. (0.65 mole) of dimethylaniline in 275 ml. of anhydrous ether (refluxed 4.5 hours),[10] to give 76 g. (90%) of *α*-*n*-butyl di-*t*-butylmalonate, b.p. 114–116° (5 mm.).

Anal. Calcd. for $C_{15}H_{28}O_4$: C, 66.18; H, 10.30. Found: C, 66.27; H, 10.39.

***p*-Nitrocaprophenone.**—To a suspension of 7.56 g. (0.315 mole) of sodium hydride in 200 ml. of ether was added 81.6

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[3] H. G. Walker and C. R. Hauser, This Journal, **68**, 1386 (1946).

[4] This remarkable difference in the mode of cleavage of acyl derivatives I and II in the presence of acid might conceivably be due either to the existence of I in the enol form (cleavage at the ketone group thereby being retarded) or to the presence of considerable steric strain in II around the quaternary carbon (cleavage at the ketone group thereby being facilitated) *cf.* H. C. Brown and R. S. Fletcher, *ibid.*, **71**, 1845 (1949).

[5] G. A. Reynolds and C. R. Hauser, *Org. Syntheses*, **30**, 70 (1950). See also K. Schofield and T. Swain, *J. Chem. Soc.*, 384 (1948).

[6] D. S. Breslow, E. Baumgarten and C. R. Hauser, This Journal, **66**, 1286 (1944).

[7] R. E. Bowman, *J. Chem. Soc.*, 325 (1950).

[8] Analyses by Clark Microanalytical Laboratory, Urbana, Ill. Melting points and boiling points are uncorrected.

[9] We are indebted to Metal Hydrides, Inc., for a generous sample of this reagent.

[10] *Cf.* C. R. Hauser, B. E. Hudson, B. Abramovitch and J. C. Shivers, "Organic Syntheses," **24**, 19 (1944).

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).