1000 cm.$^{-1}$, and sharper bands at 1885(m), 1690(s), 1645(s), 1590(s), 870(s).

c. **In the Presence of 2-Mercaptomesitylene.**—Azo-bis-diphenylmethane (0.425 g., 1.21 mmoles) was decomposed as described above in 20 ml. of diphenylmethane-13-C^{14} and 7 ml. of benzene in the presence of 0.357 g. (2.35 mmoles) of 2-mercaptomesitylene. The solvents were removed in vacuum and the residue was treated with 15 ml. of ethanol, leading to tetraphenylethane, 0.145 g. (0.434 mmole), 37% yield, m.p. and mixed m.p. 208–210°. The filtrates were concentrated leading in several portions to a solid 0.130 g., m.p. 118–120°, which was recrystallized from ethanol, dimesityl disulfide, 0.110 g. (0.365 mmole), 30% yield, m.p. and mixed m.p. 120–123°. Infrared spectra of this isolated compound was identical with that of an authentic sample. The infrared absorption maxima of the residue in chloroform and of a mixture of diphenylmethyl mesityl sulfide and dimesityl disulfide are as follows: the band at 1930 cm.$^{-1}$ is not present in diphenylmethane.

Residue (expt. 411): 3300(m) cm.$^{-1}$, 2800(s), 1930(m), 1870(m), 1785(m), 1640(s), 1580(s), 1430(s), 1300–1150(s), 1070(s), 1005(s), 935(s), 910(s), 840(m).

Diphenylmethyl mesityl sulfide and dimesityl disulfide: 3300(m) cm.$^{-1}$, 2800(s), 1930(m), 1865(m), 1785(m), 1715(s), 1585(s), 1450–1410(s), 1290–1160(m), 1070(s), 965(m), 905(m), 845(s).

Decomposition of Azo-bis-diphenylmethane in Benzene at 60°. a.—In some early experiments the decomposition was carried out without exclusion of air. Tetraphenylethane was not isolated, but a white solid was obtained melting over a range, 170–200°. When the decomposition of 0.300 g. (0.83 mmole) was carried out in the presence of 0.205 g. (1.86 mmoles) of thiophenol, tetraphenylethane was not found, but there was found compound III melting at 170–173°, 0.088 g., 30% yield and benzophenone azine, 0.038 g. (0.105 mmole) 13% yield, and a residue, 0.15 g.

b.—Under carbon dioxide the azo compound, 0.479 g. (1.32 mmoles), led to nitrogen, 96%, and to tetraphenylethane, 0.362 g., 85% yield (corr.). The azo compound, 0.500 g., and thiophenol, 0.30 g. (0.04 mole/l.), in 70 ml. of benzene led to nitrogen, 81%, to tetraphenylethane, 0.142 g., 32%, and to compound III, 0.025 g., 5% yield, m.p. 173–175°.

c.—A solution of 0.500 g. (1.38 mmoles) of benzophenone azine and 0.500 g. of the azo compound in 75 ml. of benzene was heated at 60° for five hours under nitrogen and concentrated in vacuum. The residue was crystallized from 80 ml. of ethanol leading to compound III, 0.490 g., 51% yield, m.p. and mixed m.p. 175–177°, and after concentration, to benzophenone azine, 0.140 g., 28% recovered, m.p. and mixed m.p. 162–164°, and finally to tetraphenylethane, 0.130 g., 28% yield (crude), m.p. 200–205°.

Compound III, 0.28 g. (0.081 mmole), was hydrogenated in 20 ml. of acetic acid over platinum oxide, absorbing 4.2 ml. of hydrogen with discharge of color. In another run 0.054 g. was hydrogenated similarly, the solution was concentrated and the residue was crystallized from ethanol leading to tetraphenylethane, m.p. and mixed m.p. 209–211°, 0.030 g., 58% yield.

Radioactivity Measurements.—Solutions of the solvent, diphenylmethane-13-C^{14}, and of the various samples of recovered tetraphenylethane were prepared in dimethylformamide (b.p. 151–152°), 0.3-ml. portions of the solutions were placed in small aluminum dishes and the radioactivity was measured, infinite thickness sample, $^1/_8$″ from thin end-window Geiger counter, on an Atomic Instrument Scaler, model 101. The samples of tetraphenylethane were crystallized several times from carbon tetrachloride and from ethanol. In some experiments 0.5-ml. portions were used. The observed activities of each sample of solvent diphenylmethane-13-C^{14} and of the tetraphenylethane formed in it from the azo compound were converted to counts per minute per unit concentration and the ratio of the two activities was taken as the percentage exchange. The data are summarized in Table IV.

TABLE IV

C^{14} COUNTING DATA

D-$(C_6H_5)_2C^{14}H_2$, solvent; T-$(C_6H_5)_2CH$-$CH(C_6H_5)_2$, product

Expt.	Concn., mg./ml.	Counts/min.	Background	Exchange, %
295,6-D	78	2739	52 ± 5	
295-T	59	75 ± 5	44	1.5 ± 0.5
296-T	105	74 ± 6	38	1.0 ± 0.4
297-D	130	3281	44	
297-T	61	297 ± 11	44	16.7 ± 1.0
298-D	130	3321	44	
298-T	64	334 ± 7	44	18.0 ± 0.7
299-D	60	2520	75	
299-T	42	118 ± 10	75	2.5 ± 0.9
405-D	128	3788	113	
405-T	29	90 ± 2	65	3.0 ± 0.5
402-D	71	1272	74	
402-T	61	110 ± 2	74	3.5 ± 0.5
406-D	85	1662	66	
406-T	32	89 ± 7	66	3.8 ± 2.0
410-D	72	560	60	
410-T	60	55 ± 5	60	0
411-D	73	498	60	
411-T	67	72 ± 5	60	2.6 ± 2.9

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WALTHAM, MASSACHUSETTS

[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY(1)]

Peroxides. IV.[2] Aliphatic Diperacids

BY WINFRED E. PARKER, L. P. WITNAUER AND DANIEL SWERN

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A previously unreported series of peroxides, the C_5–C_{10} and the C_{12} and C_{16} α,ω-diperacids, have been prepared in high yield from the corresponding dibasic acids and 65% aqueous hydrogen peroxide in concentrated sulfuric acid solution. The products were characterized by peroxide oxygen content, X-ray diffraction, polarography and ultimate analysis. The long-spacings of the odd and even diperacids fall on a single line and the angle of tilt is essentially the same as that of dibasic acids, the C-form of aliphatic monocarboxylic acids and the C_9–C_{16} aliphatic monoperacids. Polarograms of the diperacids are similar to those of monoperacids previously described except that the diffusion current constant is only 1.6 times as great.

In contrast to organic monoperacids, of which numerous well-characterized examples are known[3,4] diperacids are almost completely unknown. Bae-

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(2) Paper III is THIS JOURNAL, **77**, 5537 (1955).

(3) W. E. Parker, C. Ricciuti, C. L. Ogg and D. Swern, *ibid.*, **77**, 4037 (1955).

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yer and Villiger[5] and Milas and Panagiotakos[6] reported the preparation of diperterephthalic and diperoxalic acids, respectively, by the reaction of the appropriate acid chloride with hydrogen peroxide, but the products isolated in low yield were not characterized.

In a previous publication,[3] we described a procedure for preparing aliphatic monoperacids in high yield directly from the carboxylic acid and 50–65% hydrogen peroxide in concentrated sulfuric acid solution. This reaction has now been applied to the C_5 through C_{10} and the C_{12} and C_{16} α,ω-dicarboxylic acids to produce the corresponding aliphatic diperacids in good to almost quantitative yield.

$$HO_2C—(CH_2)_n—CO_2H + 2H_2O_2 \xrightarrow[n\ =\ 3-14]{H_2SO_4} HO_3C—(CH_2)_n—CO_3H + H_2O$$

For best results, four moles of hydrogen peroxide (100% excess) are employed per mole of dibasic acid. Three hours reaction time is required for the preparation of the C_5–C_{10}-diperacids and 5 hr. for the longer chain members.

Diperglutaric and diperadipic acids have a substantial solubility in water. They are isolated by diluting the reaction mixtures with saturated ammonium sulfate solution at 0° followed by filtration. The higher diperacids are precipitated by dilution with a half-saturated ammonium sulfate solution. Dipersuccinic acid could not be precipitated from the reaction mixture because of its high solubility even in saturated ammonium sulfate.

Analytically pure samples of dipersuberic and higher diperacids are obtained from the reaction products by recrystallization of the reaction products at 0° from ethanol–water mixtures. The shorter-chain compounds are recrystallized from water. In general only fair yields (60%) of analytically pure products are obtained as a result of a combination of high solvent solubility and hydrolytic decomposition. Temperatures in excess of 45° should be avoided in recrystallization; otherwise most of the peracid decomposes. To reduce the time of contact between diperacid and warm solvent and to keep decomposition at a minimum, the solvent is heated to 40–45° prior to addition of the compound. This is particularly important in large-scale recrystallizations.

The diperacids prepared in this study are soluble in 95% ethanol, acetone, ether and dioxane and insoluble in hydrocarbons. The shorter chain (C_5–C_7) members are soluble in water.

Analytically pure diperacids have variable melting-decomposition temperatures of about 80–100°. It is doubtful that these are true melting points since they are not reproducible and gas evolution is observed in the liquid mass. At room temperature, however, the diperacids are relatively stable and they are not shock-sensitive. For long-term storage they should be kept in the refrigerator. They are flammable and are consumed rapidly and completely (no carbonaceous residue) when plunged into a flame.

The pure diperacids were characterized by ultimate analysis, peroxide oxygen content, polarographic examination and X-ray diffraction. Dipersebacic acid was titrated potentiometrically in aqueous alcohol as rapidly as possible and gave a neutralization equivalent corresponding to two acid groups (percarboxyl) per mole. The point of inflection in the titration curve was two *p*H units higher and the *pK* value three *p*H units higher than those obtained with sebacic acid. This result parallels that obtained in comparing monoperacids with the corresponding carboxylic acids.[3]

Polarograms of the diperacids are essentially the same as those of the monoperacids.[3] The half-wave potential is at the same position but the diffusion current constant is only 1.6 times that of the monoperacids. The polarograph can be used for analysis of the diperacids, but for routine work it is more convenient to use a standard iodometric method with a modified solvent system (see Experimental).

Long-spacings were obtained on the C_6–C_{10}-diperacids, and the results were compared with those obtained on the corresponding dibasic acids and on the monoperacids and carboxylic acids reported previously.[3]

The long-spacings of the diperacids increase regularly as the hydrocarbon chain increases. The long-spacings of the even and odd numbered diperacids do not fall on separate lines, as is the case with the corresponding dibasic acids.[7,8] The long-spacings of the even and odd numbered monoperacids also fall on a straight line.[3]

Figure 1 is a plot of the long-spacings of diperacids and dibasic acids. The plot of the long-spacings of the diperacids is approximately parallel to that of the C_8 and higher dibasic acids containing an even number of carbon atoms. The long-spacings of the diperacids are about 1 Å. larger than those of the corresponding even dibasic acids. The long-spacings of monoperacids and the corresponding monocarboxylic acids show a similar difference.[3]

The average increase in long-spacing for each additional carbon atom in the diperacid chain is about 1 Å., which is lower than the expected projected distance (1.27 Å.) of one C–C bond. This value of projected C–C distance is extremely close to the value found in the dibasic acids, the C-form of the monobasic acids, and the C_9–C_{16}-monoperacids. Thus, all of these compounds crystallize with essentially the same angle of tilt.

We were unable to obtain a powder pattern of diperadipic acid that had a long spacing different from that of adipic acid although the side spacings were different.

Experimental

Starting Materials.—The C_4–C_{10}-dibasic acids were Eastman White Label Organic Chemicals. 1,10-Decanedicarboxylic and 1,14-tetradecanedicarboxylic acids were obtained from the Aldrich Chemical Co. The former had the correct melting point and was used as received. The latter

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TABLE I

ALIPHATIC DIPERACIDS

Diperacid	Reactants,[a] grams H_2SO_4 (95%)	 H_2O_2 (65%)	 Dibasic acid	Yield of diperacid,[b] %	Recrystallized products[c] Peroxide oxygen, % Calcd.	 Found	 Carbon, %[d] Calcd.	 Found	 Hydrogen, %[d] Calcd.	 Found
Diperglutaric (C_5)	60	32	20	69	19.5	18.4	36.6	37.2	4.88	5.15
Diperadipic (C_6)	25	14	10	64	17.9	17.0	40.4	41.6	5.62	6.12
Diperpimelic (C_7)	25	13	10	98	16.6	16.4	43.7	44.2	6.24	6.36
Dipersuberic (C_8)	11	5	3.6	90	15.5	16.0	46.5	46.4	6.78	7.05
Diperazelaic (C_9)	25	11	10	80	14.5	14.4	48.8	50.8	7.20	7.69
Dipersebacic (C_{10})	30	10.5	10	82	13.6	13.6	51.2	51.2	7.75	7.88
1,10-Decanedipercarboxylic (C_{12})	20	4.6	5	96	12.2	11.3	..	..	..	..
1,14-Tetradecanedipercarboxylic (C_{16})	13	3.1	4.3	80	10.0	8.0[e]	..	..	..	..

[a] Reaction time was 3 hr. except for C_{12}- and C_{16}-diperacids, 5 hr. [b] Calculated by multiplying the purity of the crude reaction product by the percentage yield. Purity of crude diperacids usually exceeded 90% except the C_{16}. [c] Recrystallized from water-alcohol mixtures, except for C_5-, C_6- and C_7-diperacids which were recrystallized from water. [d] Because of flashing considerable difficulty was experienced in obtaining good checks. [e] A purer product could not be isolated.

was crystallized twice from 95% ethanol before use. Its melting point was raised to only 120° (lit. 126°). The 65% hydrogen peroxide was generously furnished by J. G. Wallace, E. I. du Pont de Nemours and Co. The 50% commercial grade is also satisfactory.

Dipersebacic Acid.—The preparation of this compound is typical. Ten grams (0.05 mole) of sebacic acid was dissolved in 30 g. of 95% sulfuric acid in an open beaker. With good stirring, 10.5 g. (0.2 mole, 100% excess) of 65% hydrogen peroxide was added dropwise over a 5–10 minute period while maintaining the internal temperature at 20–25° by an ice-water bath.[9] Stirring was continued for an additional 3 hr. Several volumes of a half-saturated aqueous solution of ammonium sulfate (35 g./100 g. H_2O) were added at 0° and the precipitate of dipersebacic acid was filtered off. The product was washed on the funnel with the cold ammonium sulfate solution until the filtrate was free of sulfuric acid (several washes). Alternatively the precipitated reaction product was dissolved in ether and washed acid-free with ammonium sulfate solution. (This procedure resulted in a large loss of product with the shorter-chain diperacids.) The crude product was dried under vacuum at room temperature; yield 10 g. (85%) and 96% purity. Recrystallization from ethanol-water (1:5) yielded an analytically pure product (70%), neutralization equivalent 113 (calcd. 117). Additional analyses are given in Table I.

Other Diperacids.—The C_5–C_9-diperacids were prepared similarly; the C_{12} and C_{16} required 5 hr. reaction time. Purity of crude reaction products exceeded 90% except that of the C_{16} (only 80%). A saturated ammonium sulfate solution at 0° was required to precipitate diperglutaric and diperadipic acids in yields exceeding 70%. Details and analyses are given in Table I.

Iodometric Analysis.—Purity of the diperacids was determined iodometrically.[10] Water-acetic acid (1:5) was used instead of acetic acid–chloroform (3:2) as the solvent system.

Polarographic Behavior.—The procedures have been reported.[3,11]

X-Ray Diffraction.—Long spacings were obtained with a General Electric XRD-3[12] direct recording unit using filtered CuKα radiation (λ 1.5405 Å.), 1° beam slit, 0.1° detector slit, high resolution soller slit, scanning speed 2°/min., chart speed 60 in./hr. linear scale, 4 sec. time constant. To prepare the diperacids for X-ray examination, they were dissolved in a minimum amount of ethanol, and the solution was evaporated to dryness at room temperature. All samples were stored at 0° until examined. The samples were *gently* ground in an agate mortar and mounted in a recessed plastic holder. Long spacings (Å.) were as follows: C_5, 7.19; C_7, 9.30; C_8, 10.39; C_9, 11.47; C_{10}, 12.27.

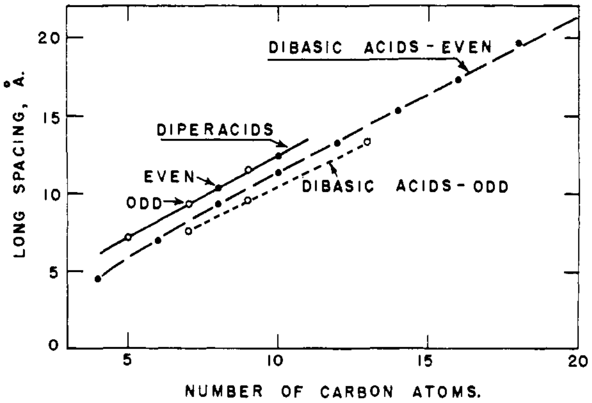

Fig. 1.

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[9] The reaction is highly exothermic. A safety shield should be employed and the operator should wear safety glasses.

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[12] Mention of a specific instrument does not imply endorsement by the Department of Agriculture over similar instruments not mentioned.