in 10 ml. of either glacial acetic acid or chloroform. The mixture was heated on a water-bath and the appropriate phosphorus trihalide (1–2 ml.) was added dropwise with shaking until the suspension completely dissolved. The solution was warmed 10–15 minutes on the water-bath, filtered, and allowed to cool. The crystalline material depositing was recrystallized, usually from chloroform. In this manner were prepared 9-chloroarsafluorene (I), 9-bromoarsafluorene (II), 2-nitro-9-chloroarsafluorene (III), 3-nitro-9-chloroarsafluorene (IV), 5-nitrobiphenyl-2-dichloroarsine (V) and 4′-nitrobiphenyl-2-dichloroarsine (VI). Details are given in Table I. Melting points were obtained with an aluminum block using a calibrated thermometer. Arsenic analysis was accomplished according to the procedure of Robertson.[5]

TABLE I

PREPARATION OF SOME HALOARSINES

Compound	Reaction solvent[b]	Recrystn. solvent[b]	Yield, %[a]	M.p., °C.	Arsenic, % Calcd.	Found
I	A	B	43.2	160–161	...	...
II	B	B	65.1	174–175	24.48	25.55
III	A	B	79.3	186–187	24.43	24.36
IV	A	B	80.1	199–200	24.43	24.47
V	A	B	70.9	105–106	21.84	21.78
VI	B	C	76.5	81–82	21.84	21.35

[a] Yield calculated from weight of recrystallized product. [b] Key to solvents: A, glacial acetic acid; B, chloroform; C, benzene–petroleum ether.

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[5] G. R. Robertson, THIS JOURNAL, **43**, 182 (1921).

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The Preparation of Two Fluorinated *p*-Dihalobenzenes[1]

BY MAX HELLMANN AND ANDREW J. BILBO

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A number of benzene derivatives containing fluorine and other halogens have been reported in the literature.[2] None of these compounds, however, contain two halogen atoms, other than fluorine, in positions para to each other. More recently Finger and co-workers[3] prepared 1,4-dichloro-2,5-difluorobenzene and 1,4-dibromo-2,5-difluorobenzene as the first compounds of this type to be made.

In this paper two new compounds of this series are reported containing one and four fluorine atoms, respectively. They are 1,4-dichloro-2-fluorobenzene, which was prepared from 2,5-dichloroaniline by the Schiemann reaction,[2] and 1,4-dibromo-2,3,5,6-tetrafluorobenzene, which was obtained by brominating *sym*-tetrafluorobenzene. Finger and his associates had prepared this tetrafluorobenzene but found it relatively resistant to further substitution such as nitration and chlorination.[3] Our attempts to brominate this compound failed under mild conditions, but by using fuming sulfuric acid as a solvent, a good yield of the desired product was obtained. The identity of both new compounds was established by chemical analysis and by their ultraviolet absorption spectra.

The ultraviolet absorption data of the two new fluorinated *p*-dihalobenzenes and their non-fluorinated analogs are presented in Table I. The shapes of the ultraviolet absorption curves for these new compounds agree with those generally found for aromatic compounds.[4] It is evident from these data that the introduction of fluorine atoms does not affect the main absorption bands appreciably. The secondary bands appear to be intensified in the fluorinated compounds, but they do not show any significant shifts. More detailed data on the ultraviolet absorption spectra of these and other fluorinated benzenes will be published at a later date.

TABLE I

ULTRAVIOLET ABSORPTION DATA

Compound	Primary band Wave length, Å.	Molar absorbance	Secondary band Wave length, Å.	Molar absorbance
1,4-Dichlorobenzene	2248	12,900	2650	300
			2728	390
			2805	330
1,4-Dichloro-2-fluorobenzene	2240	11,400	2665	780
			2718	1080
			2795	1030
1,4-Dibromobenzene	2278	15,500	2655	290
			2733	300
			2821	195
1,4-Dibromo-2,3,5,6-tetrafluorobenzene	2275	18,400	2480	1750
			2700	1100

Experimental

1. **1,4-Dibromo-2,3,5,6-tetrafluorobenzene.**—The bromination was performed in a 100-ml. three-neck flask equipped with a mercury-sealed stirrer, condenser and a dropping funnel. Into this flask 14 ml. of bromine, 15 ml. of 60% fuming sulfuric acid and 0.5 g. of aluminum bromide were introduced. The mixture was stirred and 10 g. of 1,2,4,5-tetrafluorobenzene was added dropwise. An exothermic reaction occurred with the evolution of white fumes. After the addition was completed, the flask was heated in a water-bath at 50–60° for 4 hours. The contents were then carefully poured over cracked ice. The product settled out as a brownish solid which was filtered and washed successively with sodium carbonate, sodium bisulfite and water. It was then recrystallized from a methanol–water mixture and dried at room temperature; yield 16 g. (78%), m.p. 76–77°.

Anal. Calcd. for $C_6F_4Br_2$: F, 24.68; Br, 51.91; mol. wt., 307.9. Found: F, 24.7; Br, 51.7; mol. wt., 296.

2. **1,4-Dichloro-2-fluorobenzene.**—A suspension of 49.6 g. of 2,5-dichloroaniline hydrochloride in 40 ml. of concentrated hydrochloric acid and 80 ml. of water was stirred and cooled to −5°. A solution of 19.7 g. of sodium nitrite in 60 ml. of water was added dropwise while the temperature was maintained at −5°. After the addition was completed, the solution was stirred for 5 minutes. Any solid that remained at this point was removed by filtration at 0°. To the clear filtrate 42 ml. of 40% fluoboric acid was added rapidly. The resulting suspension of the diazonium fluoborate was stirred vigorously at about 5° for 30 minutes and filtered. The precipitate was washed with 25-ml. portions of 5% fluoboric acid, methanol and ether. The salt was then spread out on a large filter paper and dried in air; yield 46.6 g. (72%).

The diazonium fluoborate was decomposed in a system containing two flasks connected by a bent tube of large bore. The salt was introduced into one flask and the other was cooled in an ice-bath. The receiving flask was connected to a trap, cooled in ice, which had an outlet to the hood. The decomposition was performed by intermittent heating with a Bunsen burner until no more white fumes were given

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[1] This paper is based on work sponsored by the Ordnance Corps, United States Department of the Army.

[2] For references up to 1946 see A. Roe, "Organic Reactions," Vol. V, John Wiley and Sons, Inc., New York, N. Y., 1949, pp. 193–228.

[3] G. C. Finger, F. H. Reed, D. M. Burness, D. M. Fort and R. R. Blough, THIS JOURNAL, **73**, 145 (1951).

[4] L. Doub and J. M. Vandenbelt, *ibid.*, **69**, 2714 (1947).

off. The product which had collected in the receiving flask and the trap was poured back into the decomposition flask from which it was steam distilled. The distillate was extracted with ether, washed with sodium carbonate and dried over Drierite. After removing the ether, the remaining liquid was distilled under reduced pressure; b.p. 91–92° at 60 mm., 168–169° at 750 mm., m.p. 4°, yield 23.5 g. (80%).

Anal. Calcd. for $C_6H_3Cl_2F$: C, 43.68; H, 1.83; Cl. 42.98. Found: C. 43.7; H, 1.9; Cl, 42.8.

3. Measurement of Spectra.—The absorption spectra were determined on solutions in 95% ethanol by means of a Cary Recording Spectrophotometer (Model 12), using 2-cm. matched fused quartz absorption cells against the solvent as reference.

Acknowledgment.—The authors wish to acknowledge the aid of Dr. G. M. Wyman and his associates who made the ultraviolet absorption measurements reported here.

NATIONAL BUREAU OF STANDARDS
WASHINGTON, D. C.

Low Pressure Hydrogenation and Several Properties of Methyl and *n*-Butylketene Dimers[1]

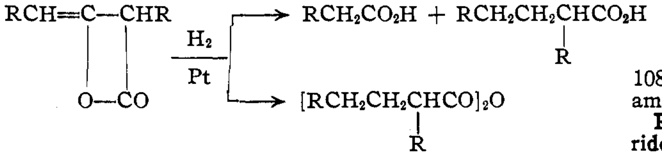
BY CARL M. HILL AND MARY E. HILL

RECEIVED APRIL 7, 1953

It has been demonstrated in this Laboratory that hydrogenation of mono-substituted alkylketene dimers at high pressures and temperatures and in the presence of Raney nickel catalyst produces dialkyl glycols.[2] It was thought profitable to report the response of ketene dimers of this type to hydrogen at low pressures and in the presence of Adams platinum catalyst. It was desired also to study the influence which a reactive solvent might have on the nature of the reduction products.

Treatment of methylketene dimer with hydrogen at 4.8 atm. and in platinum catalyst and petroleum ether gave 2-methylvaleric and propionic acids. Similar results were observed when *n*-butylketene dimer dissolved in petroleum ether was treated with hydrogen at 3.5 atm.

From an experiment in which *n*-butylketene dimer was treated with hydrogen at 3.4 atm. and in acetic acid anhydride, 2-*n*-butyloctanoic acid anhydride and acetic acid were isolated. It is probable that 2-*n*-butyloctanoic acid was formed as an intermediate product but was dehydrated by the acetic anhydride to form 2-*n*-butyloctanoic acid anhydride and acetic acid.



Where R = CH_3 and *n*-C_4H_2.

Experimental[3]

Preparation of Ketene Dimers.—The dimers were prepared by dehydrohalogenation of propionyl and *n*-caproyl chlorides with triethylamine.[4]

Characterization of Ketene Dimers.—Methylketene dimer reacted with concentrated ammonia to yield α-propionylpropionamide, m.p. 83–84° (reported[5] m.p. 82°); with aniline to give α-propionylpropionanilide, m.p. 115–116°; and with water to form diethyl ketone, from which the semicarbazone was prepared. Melting point of the semicarbazone was 135–136°; m.p. of the semicarbazone prepared from an authentic sample of diethyl ketone was 135–136°; mixed m.p. 135–136°. *n*-Butylketene dimer reacted with 15% sodium hydroxide solution to yield di-*n*-amyl ketone, b.p. 225° (755 mm.) and m.p. 14–15°; reported[6] m.p., 14–15°.

Catalytic Hydrogenation of Methylketene Dimer.—A mixture of 5.14 g. (0.04 mole) of methylketene dimer (b.p. 50–52° (9 mm.)) dissolved in 50 ml of petroleum ether and 0.3 g. of platinum oxide was treated with hydrogen at 4.8 atm. for four hours. The catalyst was separated and the solvent removed by distillation. Distillation of the residue from a Claisen flask gave two fractions: propionic acid (9.5%), b.p. 140° (755 mm.), n^{20}_D 1.3950, neutral equivalent calcd. for $C_3H_6O_2$: 74, found: 75; and 2-methylvaleric acid (75%), b.p. 88–90° (8 mm.) and 192° (750 mm.), d^{20}_4 0.9309, n^{20}_D 1.4170, MR_D (calcd.) 31.45, (found), 31.41, neutral equivalent calcd. for $C_6H_{12}O_2$: 116, found, 115. Reported[7] b.p., d^{20}_4 and n^{20}_D of 2-methylvaleric acid are 192–193.6° (748 mm.), 0.9230 and 1.4136, respectively.

Bromination of Methylketene Dimer.—A solution of 6.5 g. of dry bromine in 10 ml. of carbon tetrachloride was added dropwise to a solution of 5 g. of methylketene dimer in 40 ml. of carbon tetrachloride at 0°. Three grams of the reaction product was added slowly to a chilled suspension of 10 ml. of absolute ethanol and 5 g. of pulverized sodium acetate. Removal of the ethanol and distillation of the residue gave 2 g. of product, b.p. 86–88° (4 mm.), d^{20} 1.3200. Saponification equivalent of the product calculated on basis of one ester group and one reactive bromine is 119; found, 119.

Anal. Calcd. for $C_8H_{13}O_3Br$: Br, 33.75. Found: Br, 34.00.

Catalytic Hydrogenation of *n*-Butylketene Dimer.—A mixture of 10.8 g. (0.06 mole) of *n*-butylketene dimer (b.p. 115–116° (4 mm.)) dissolved in 50 ml. of petroleum ether and 0.2 g. of platinum oxide was treated with hydrogen at 3.5 atm. for 45 minutes. Two reduction products were isolated: *n*-caproic acid (22%), b.p. 74–76° (5 mm.), n^{20}_D 1.4170 (n^{20}_D observed for an authentic sample of *n*-caproic acid, 1.4169), d^{20}_4 0.8580; m.p. of amide 100–101° (reported[8] m.p. for *n*-caproamide 101°), neutral equivalent calcd. for $C_6H_{12}O_2$: 116, found, 111; and 2-*n*-butyloctanoic acid (72%), b.p. 156–158° (7 mm.), d^{20}_4 0.8923, n^{20}_D 1.4390, MR_D (calcd.) 59.17, (found) 59.09; neutral equivalent calcd. for $C_{12}H_{24}O_2$: 200, found 197; amide m.p. 108–109°; m.p. of the amide prepared from an authentic sample of 2-*n*-butyloctanoic acid, 108–109°; mixed m.p. 107–108°.

Catalytic hydrogenation of this dimer was repeated using 8.5 g. (0.04 mole) of the dimer, 0.15 g. of platinum oxide, 30 ml. of pure acetic acid anhydride and 3.4 atm. of hydrogen pressure. The theoretical amount of hydrogen was absorbed within 15 minutes. Products isolated were: 2-*n*-butyloctanoic acid anhydride (73%), b.p. 175–177° (3 mm.), d^{20}_4 0.8913, n^{20}_D 1.4440, equivalent weight calcd. for $C_{24}H_{46}O_3$: 191, found 197; and 2 g. of acetic acid. The 2-*n*-butyloctanoic anhydride was further identified by treatment with concentrated ammonia. This gave 2-*n*-butyloctanoamide, m.p. 108–109°, mixed m.p. 107–108°; and 2-*n*-butyloctanoic acid, b.p. 134–135° (4 mm.); amide m.p. 107.5–108.5°.

Reaction of *n*-Butylketene Dimer with Hydrogen Chloride.—Dry hydrogen chloride gas was bubbled through 3 g. of *n*-butylketene dimer at 0° for 2 hours. Distillation of the product gave 1 g. of α-caproylacaproyl chloride boiling at 198–200° (4 mm.).

Anal. Calcd. for $C_{12}H_{21}O_2Cl$: Cl, 15.23. Found: Cl, 15.32.

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[1] The experimental portion of this paper is based largely on the doctoral thesis, "Studies of Ketenes and Their Derivatives," of C. M. Hill, Cornell University, 1941.

[2] C. M. Hill, M. E. Hill, H. I. Schofield and L. Haynes, THIS JOURNAL, **74**, 166 (1952); C. M. Hill, L. Haynes and M. E. Hill, *ibid.*, 3423 (1952).

[3] All melting points are corrected.

[4] J. C. Sauer, THIS JOURNAL, **69**, 2444 (1947).

[5] H. Pingel, *Ann.*, **245**, 87 (1888).

[6] R. R. Briese and S. M. McElvain, THIS JOURNAL, **55**, 1698 (1933).

[7] M. Hommelen, *Bull. soc. chim. Belg.*, **42**, 243 (1933).

[8] I. Simon, *ibid.*, **38**, 47 (1929).