132.2. Found: C, 54.50; H, 9.06; neutral equiv., 133.6.

Ethyl *t*-butylglycolate: b. p. 53° at 5 mm.; $n^{25}D$ 1.4210; d^{25} 0.9661. Calcd. for $C_8H_{16}O_3$: C, 59.97; H, 10.07. Found: C, 59.26; H, 10.03.

Ethyl di-*t*-butylglycolate: b. p. 70° at 3.5 mm.; $n^{25}D$ 1.4431; d^{25} 0.9525. Calcd. for $C_{12}H_{24}O_3$: C, 66.63; H, 11.18; $-OC_2H_5$, 20.84. Found: C, 66.51; H, 11.05; $-OC_2H_5$, 18.73.

Di-*t*-butylpivaloylcarbinol (?): m. p. 113–113.5°. Calcd. for $C_{14}H_{28}O_2$: C, 73.63; H, 12.36. Found: C, 73.48; H, 12.56.

Ethyl *t*-butylglycolate failed to react with semicarbazide, as expected, but did yield a derivative, m. p. 166°, with 2,4-dinitrophenylhydrazine, probably due to oxidation at the *alpha* carbon atom.

The analyses for carbon and hydrogen were carried out by Mr. Charles W. Beazley, Micro-Tech Laboratories, Skokie, Ill.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF NOTRE DAME
NOTRE DAME, INDIANA
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Some New 1,1,1-Trichloro-2,2-bis-(*p*-alkylphenyl)-ethanes

BY G. F. HENNION AND JOSEPH G. WALSH

The condensations of chloral hydrate with toluene,[1] two of the xylenes,[2] *t*-butylbenzene[3] and benzene itself[4] are known to yield crystalline derivatives structurally analogous to DDT. We have recently extended the reaction to several other alkylbenzenes to determine whether it may be used to prepare solid derivatives useful for identification purposes. Furthermore, an assortment of 1,1,1-trichloro-2,2-bis-(*p*-alkylphenyl)-ethanes (I) was desired to explore the possibility of preparing 4,4'-dialkyldiphenylacetylenes (III) from them by elimination of hydrogen chloride and chlorine.

$$\underset{\text{I}}{(R—C_6H_4)_2CH—CCl_3} \xrightarrow{\text{KOH}} \underset{\text{II}}{(R—C_6H_4)_2C{=}CCl_2} \xrightarrow{\text{2Na}} \underset{\text{III}}{R—C_6H_4—C{\equiv}C—C_6H_4—R}$$

The reactions of the alkylbenzenes with chloral hydrate were carried out in concentrated sulfuric acid (96.9%) in the ordinary manner. Toluene and *t*-butylbenzene gave solid products identical with those previously described.[1,3] Ethylbenzene, isopropylbenzene, *n*-butylbenzene, *s*-butylbenzene and 2-*s*-amylbenzene, however, yielded viscous oils which could not be induced to crystallize. The isolation and purification of these products proved somewhat troublesome because dilution of the crude reaction products with water gave emulsions, probably due to appreciable sulfonation as a side reaction. The emulsions were broken with ether and salt and the ethereal extracts finally distilled three times *in vacuo*. The physical constants, yields after the first distillation, and analyses for these compounds are given in Table I.

Each of the seven products (I) was treated with alcoholic potassium hydroxide to prepare the corresponding dichloroethylenes (II). Again the toluene and *t*-butylbenzene derivatives gave solids, as previously reported, while all the other yielded oils. In all cases the dichloroethylenes were insoluble in liquid ammonia and failed to react well with sodium in this medium. An ethereal solution of the di-*p*-tolyl compound, for example, decolorized only a fraction of the theoretical amount of sodium in liquid ammonia and yielded an insoluble, infusible, polymeric substance containing chlorine. All attempts to prepare acetylenes (III) in this manner failed.

TABLE I

1,1,1-TRICHLORO-2,2-*bis*-(*p*-ALKYLPHENYL)-ETHANES

Alkyl group	B. p., °C.	Press., mm.	Yield, %	$n^{25}D$	Chlorine, % Calcd.	Found
Ethyl[a]	183	0.8	51	1.5780	31.2	31.1
Isopropyl	199	1.4	40	1.5672	28.8	28.5
n-Butyl	203	0.4	42	1.5611	26.8	25.6
s-Butyl	204	0.4	36	1.5597	26.8	25.7
2-*s*-Amyl	210	0.4	27	1.5515	25.0	24.2

[a] Wild, *Helv. Chim. Acta*, 29, 497(1946), reported the boiling point to be 180° at 0.2 mm. The refractive index was not given.

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[1] Fischer, *Ber.*, **7**, 1190 (1874).

[2] Elbs, *J. prakt. Chem.*, [2] **39**, 300 (1889).

[3] Cristol, Hayes and Haller, THIS JOURNAL, **68**, 913 (1946).

[4] Baeyer, *Ber.*, **5**, 25 (1872).

Nitration of (*p*-Bromophenyl)-cyclopentane

BY RICHARD D. KLEENE

It was desired to prepare an acetamino derivative of (*p*-bromophenyl)-cyclopentane by the method of Ipatieff and Schmerling[1] for alkyl benzenes. The product obtained was free of halogen as described below.

(3,5-Diacetaminophenyl)-cyclopentane.—One gram of the bromo compound[2] was nitrated with 5 ml. of a mixture of one part of 70% nitric acid and one part of 98% sulfuric acid by volume. The red oil so obtained was dissolved in alcohol and reduced with tin and 36% hydrochloric acid. The amine was then acetylated with acetic anhydride and the resulting solid was recrystallized three times from dilute alcohol. Very fine hair-like needles were formed which melted at 233–234° (uncor.); yield 50%. Analysis showed the complete absence of bromine.

Anal. Calcd. for $C_{15}H_{20}O_2N_2$: C, 69.2; H, 7.70; N, 10.8. Found: C, 68.4; H, 7.57; N, 10.4.

A mixture of this new compound with (2,4-diacetaminophenyl)-cyclopentane[1] (m. p. 228°) melted at 220–225°. The two compounds also appeared dissimilar under the microscope. The removal of the bromine atom indicates that it is probably activated by both nitro groups. This reduces the possibility that the new compound is the 2,5- or the 2,6-diacetamino isomer.

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[1] V. N. Ipatieff and L. Schmerling, THIS JOURNAL, **59**, 1056 (1937); **60**, 1476 (1938).

[2] R. D. Kleene, *ibid.*, **62**, 2883 (1940).

The removal of halogens from aromatic compounds during the reduction of two activating nitro groups is a well-known phenomenon. Thus the reduction of 2,4-dibromo-3,5-dinitrotoluene with tin and hydrochloric acid gives 3,5-diaminotoluene.[3]

In contrast to the nitration with mixed acid as described above, nitration with 70% nitric acid alone according to the method of Mayes and Turner[4] led to a mixture of products from which a considerable amount of 1-nitro-4-bromobenzene was isolated. The other products were not identified.

(3) W. A. Davis, *J. Chem. Soc.*, **81**, 873 (1902).

(4) H. A. Mayes and E. E. Turner, *ibid.*, 500 (1929).

CHICAGO, ILLINOIS RECEIVED MAY 29, 1947

The Acylation of Thiophene and Furan by Means of Boron Trifluoride[1]

BY HOWARD D. HARTOUGH AND ALVIN I. KOSAK[2]

The acetylation of thiophene and furan to form the respective 2-acyl derivatives has been effected previously by means of several catalysts.[3] This reaction has now been effected by means of catalytic amounts of boron trifluoride complexes in ether, methanol, and acetic acid. The yields were satisfactory (70%) with 0.03–0.075 mole of the catalyst per mole of acetic anhydride. When acetyl chloride was used instead of acetic anhydride the yield was poor. The analogous reaction with benzoyl chloride was effected in 22% yield.

Although the nucleus of 2-acetylthiophene is acetylated in the presence of zinc chloride, orthophosphoric acid and phosphorus pentoxide,[3] acetylation at the side chain of this ketone occurred in the presence of a molecular equivalent of boron trifluoride to form a triacetylthiophene in 17% yield; however, the product has not been identified. Acetylation at the side chain might have been anticipated from the work of Meerwein, Pannwitz and Vossen[4] and Hauser and Adams.[5]

With furan, acetic anhydride and a catalytic amount of boron trifluoride in methanol, 2-acetylfuran was obtained in 46% yield.

Boron Trifluoride Complexes.—The boron trifluoride etherate was used as received from the Eastman Kodak Co. The boron trifluoride methanol complex and the boron trifluoride acetic acid complex were prepared by saturating methanol and acetic acid with boron trifluoride gas at 100 p. s. i. pressure in a stirring autoclave.

2-Acetylthiophene.—To a mixture of 252 g. (3 moles) of thiophene and 107 g. (1 mole) of 95% acetic anhydride cooled to 10° by means of an ice-bath was added 4 g. of boron trifluoride–methanol complex (60% boron trifluoride). The temperature rose to 13° and when it finally subsided after five minutes to 5° the ice-bath was removed and the flask warmed to 50° for two hours. Two hundred milliliters of water was added, the mixture agitated for fifteen minutes, the lower organic layer drawn off, washed with 10% sodium carbonate solution until neutral, and distilled. Thiophene, 180 g., was recovered and 84 g. (70%) of 2-acetylthiophene, b. p. 87–88° (8 mm.),[6] $n^{20}\text{D}$ 1.5666, was obtained.

2-Benzoylthiophene.—To 126 g. (1.5 moles) of thiophene and 141 g. (1 mole) of benzoyl chloride was added 4 g. of boron trifluoride–acetic acid complex. No heat of reaction was noted and the mixture was heated at 90–95° for six hours. After cooling, the reaction mixture was washed with 10% sodium hydroxide solution until neutral. Distillation yielded thiophene, 42 g. (22%) of 2-benzoylthiophene, b. p. 146–147° (5 mm.), m. p. 56.5–57°,[7] after recrystallization from ASTM naphtha, and 21 g. of tarry residue.

"2-Triacetylthiophene."—To 42 g. (0.33 mole) of 2-acetylthiophene was added 107 g. (1 mole) of 95% acetic anhydride and 110 g. (0.84 mole) of boron trifluoride etherate. The temperature rose to 38° and after fifteen minutes the mixture was warmed on a steam-bath at 55° for thirty minutes. The hot mixture was poured slowly into one liter of water containing 120 g. of sodium acetate and shaken until the oily liquid crystallized. The crystals were filtered, washed with cold benzene, and purified by vacuum sublimation, yielding 12 g. (17%) of bright yellow crystals, m. p. 176–177°.[8]

Anal. Calcd. for $C_{10}H_{10}O_3S$: S, 15.31, Found: S, 14.92.

Oxidation with alkaline permanganate gave 2-thiophenecarboxylic acid, m. p. and mixed m. p. 127–128.5°.

2-Acetylfuran.—A procedure, analogous to that employed for to 2-acetylthiophene, was used but the temperature of the reaction mixture was maintained at 25° instead of 50° for two hours. Distillation yielded 53 g. (48%) of 2-acetylfuran, b. p. 89–90° (43 mm.),[9] m. p. 30–32°,[9] $n^{30}\text{D}$ 1.5015.

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(1) Paper VII of this series.

(2) Present address: Ohio State University, Columbus, Ohio.

(3) (a) Hartough and Kosak, THIS JOURNAL, **68**, 2639 (1946); (b) **69**, 1012 (1947); (c) **69**, 3093 (1947); (d) **69**, 3098 (1947); (e) Hartough, Kosak and Sardella, *ibid.*, **69**, 1014 (1947); (f) Hartough and Conley, *ibid.*, **69**, 3096 (1947).

(4) Meerwein, *Ber.*, **66B**, 411 (1933); Meerwein and Pannwitz, *J. prakt. Chem.*, **141**, 123 (1934); Meerwein and Vossen. *ibid.*, **141**, 149 (1934).

(5) Hauser and Adams, THIS JOURNAL, **66**, 345 (1944).

(6) Reported data (ref. 3a): b. p. 77–78° (4 mm.) and $n^{20}\text{D}$ 1.5666.

(7) Reported data (ref. 3b); b. p. 143–144 (4 mm.) and m. p. 56.5–57°.

(8) Alternate purification procedures involved numerous recrystallizations from benzene or precipitation of the material from ethyl acetate by addition of petroleum ether yielding brown crystals, m. p. 173–175°.

(9) Reported data (ref. 3c): m. p. 30–32° and b. p. 45–50° (5 mm.).

SOCONY-VACUUM LABORATORIES
RESEARCH AND DEVELOPMENT DEPARTMENT
PAULSBORO, N. J.

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Derivatives of Diethylamino Compounds

BY NELSON J. LEONARD, FELICE MARY KRAFT AND VIVIAN WOLFMAN

In connection with studies in progress on reactions of aminoalcohols and aminoketones involving possible rearrangement, it was desirable to obtain readily identifiable derivatives of certain diethylamino compounds. The compounds of interest included amines, aminoethers, aminoalcohols and aminoketones, in all of which the amine function was tertiary. Derivatives have been formed with picric acid, picrolonic acid and ethyl iodide. Diethyl-*n*-propylamine has been obtained