under reduced pressure and in an atmosphere of nitrogen did not effect the transformation analogous to I→II, but led rather to intractable tars.

Bromination of III with one mole of bromine resulted in a substitution product, formulated tentatively as the 5-bromo derivative of III. Treatment of III with an excess of bromine led to an unstable compound $C_6H_7O_3SBr_3$, formulated tentatively as the 5-bromo-3,4-dibromide of III.

Experimental

Mesityl Oxide Cyclic Sulfonic Ester (III).—Mesityl oxide (19.6 g.) was added to 41 g. acetic anhydride and the mixture was cooled to 0°. Chlorosulfonic acid (22.3 g.) was added dropwise while the temperature was kept at 0° with an ice–salt-bath. The mixture was stirred for one-half hour after the addition of the acid was complete, and then placed in the cold-room overnight. The reaction mixture was decomposed by pouring it into an equal volume of ice–water with vigorous stirring. The light-yellow precipitate which formed was separated and purified by crystallization from methanol to yield 13 g. (41%) of stout, colorless prisms of m. p.[3] 65–67°.

Anal. Calcd. for $C_6H_8O_3S$: C, 45.0; H, 5.03. Found: C, 45.1; H, 5.19.

After several weeks a sample of the compound suddenly decomposed with violence, the production of sulfur dioxide and a black tar.

Bromination of the Cyclic Sulfonic Ester of Mesityl Oxide.—A 5.0-g. sample of the ester (III) was dissolved in carbon tetrachloride (25 ml.) and bromine was added dropwise during ten minutes until the decolorization of it became slow. A precipitate formed rapidly and hydrogen bromide was evolved. A slight excess of bromine was removed with sodium thiosulfate solution and the solvent was removed by distillation. The crude product was crystallized from alcohol to give 3.0 g. of white, crystalline material of m. p. 75–76° (mixed with III, m. p. 46–47°).

Anal. Calcd. for $C_6H_7O_3SBr$: C, 30.1; H, 2.95. Found: C, 30.4; H, 3.36.

The substance is a powerful skin irritant and is formulated as the 5-bromo derivative of the cyclic sulfonic ester of mesityl oxide (III).

A 5.0-g. sample of the cyclic sulfonic ester (III) was dissolved in 25 ml. of carbon tetrachloride and 10 g. of bromine was added rapidly. The mixture was allowed to stand for a day and the precipitate that formed was separated and washed thoroughly with methanol–water (1:1). The white crystalline product turned dark near its melting point and then melted with decomposition at 156–60°.

Anal. Calcd. for $C_6H_7O_3SBr_3$: C, 18.2; H, 1.88. Found: C, 18.3; H, 1.77.

This substance is formulated as the **5-bromo-3,4-dibromide** of the cyclic sulfonic ester (III).

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[3] Melting points are not corrected.

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The Reaction of *t*-Butylmagnesium Chloride with Ethyl Oxalate

BY G. F. HENNION AND CHARLES F. RALEY

In connection with another problem we have recently had occasion to re-examine the reaction of *t*-butylmagnesium chloride with ethyl oxalate.[1] Our observations are not entirely in accord with the previous report which states that the reaction gives a mixture of products containing *t*-butylglycolic acid, ethyl *t*-butylglycolate, α-ethoxy-β,β-dimethylbutyric acid and smaller amounts of substances thought to be *t*-butyl neopentyl ketone and *sym*-di-*t*-butylglycol. *t*-Butylglycolic acid and its ethyl ester were obtained in the present study but the other products could not be found; instead, several other compounds were isolated.

We have carried out the reaction in three ways: addition of ethyl oxalate to the Grignard reagent (1:4); addition of the Grignard reagent to the ester (2:1); and simultaneous reaction of magnesium (2.5), *t*-butyl chloride (2.0), and ethyl oxalate (1.0). In each case there was considerable evolution of gas, evidently isobutylene, and after working up the products in the usual way complex mixtures were encountered. In view of the latter fact the reaction seems to have little preparative value.

Experimental

A. **Direct Addition.**—When 0.385 mole of ethyl oxalate was added dropwise to 1.54 moles of *t*-butylmagnesium chloride in anhydrous ether (previously filtered through glass wool), 0.7 mole of isobutylene was recovered by absorption in sulfuric acid. After hydrolysis of the reaction mixture with ice and hydrochloric acid in the usual way, extraction of the ether layer with sodium bicarbonate solution removed 18 g. of impure *t*-butylglycolic acid. The neutral components, after removal of the ether, were saponified and thus yielded an additional 10 g. of the acid. It was best purified by vacuum distillation (b. p. 110–117° at 4 mm.), followed by crystallization from water; m. p. 85–86°. Smaller amounts of other products were formed also; of these only hexamethylethane and diisobutylene were recognized.

B. **Reverse Addition.**—In this experiment, when 1.35 moles of filtered Grignard reagent was added to 0.676 mole of ester, the only acidic substance recovered was 2.5 g. of impure oxalic acid. There was obtained by distillation of the ether layer after hydrolysis, etc., 27 g. of ethyl *t*-butylglycolate and 30 g. of a substance whose analysis corresponds to $C_{12}H_{24}O_3$. There was good evidence that the latter compound is the previously unknown ethyl di-*t*-butylglycolate, $(t\text{-}C_4H_9)_2C(OH)COOC_2H_5$. In addition to these two compounds there was 26 g. of higher boiling material.

C. **Barbier Reaction.**—When this method was employed with 2.5 gram atoms of magnesium, 2.0 moles of *t*-butyl chloride and 1.0 mole of ethyl oxalate (the latter mixed and added slowly to the magnesium under ether), hydrolysis and removal of the ether left 137 g. of pale yellow oil. Distillation *in vacuo* through a helix-packed column yielded 38 g. of impure ethyl *t*-butylglycolate and 40 g. of ethyl di-*t*-butylglycolate. The remainder of the product was distilled at 2.5–3.0 mm. without the column and appeared to decompose somewhat in the process. The distillate (39 g.) deposited a crystalline solid; after removal and crystallization from aqueous alcohol it melted at 113–113.5°. The analytical data corresponded with the formula $C_{14}H_{28}O_2$. Despite the oxygen content this substance gave none of the tests specific for alcohols, carbonyl compounds, etc. It was tentatively decided that the compound is di-*t*-butylpivaloycarbinol, $(t\text{-}C_4H_9)_2C(OH)COC(CH_3)_3$. Decomposition by strong heating and the failure to respond to functional group reactions are consistent with this structure.

The physical properties and the analytical data for purified samples of the various products are summarized below.

***t*-Butylglycolic acid**: b. p. 118° at 9 mm.; m. p. 85–86°. Calcd. for $C_6H_{12}O_3$: C, 54.52; H, 9.15; neutral equiv.,

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[1] Egorova, *J. Russ. Phys.-Chem. Soc.*, **41**, 1454 (1909); *Chem. Zentr.*, **81**, 1003 (1910).

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.

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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.

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.	Chlorine, % 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.

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.

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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).