from the mother liquor after crystallization of the benzoic acid. These experiments indicate the presence of the rearrangement product, *p*-ethyltoluene, in the *n*-propylbenzene and constitute an additional example of rearrangement occurring with benzylmagnesium chloride.[2]

Experimental

Benzyl Chloride.—Two samples were purified for use. The first was obtained by washing 700 g. of commercial benzyl chloride with cold water, 2% sodium bicarbonate and drying with sodium sulfate. The material was fractionated through a packed column and a middle fraction boiling from 178.2–179.2° (cor.) collected (*p*-chlorotoluene boils at 162°). Oxidation of 10 g. of this benzyl chloride by the procedure below gave only benzoic acid and no *p*-chlorobenzoic acid which was easily separated because of its low solubility in hot water. A sample of benzyl alcohol was made by means of the crossed Cannizzaro reaction[3] from purified benzaldehyde. This benzyl alcohol was halogen free as shown by a negative Beilstein test and was converted to benzyl chloride by reaction with concentrated hydrochloric acid. This sequence of reactions insured the absence of any chlorotoluenes in the benzyl chloride. Both samples of benzyl chloride behaved alike when used for the preparation of *n*-propylbenzene.

***n*-Propylbenzene.**—The procedure described in "Organic Syntheses"[1] was followed exactly using the precautions recommended for the exclusion of moisture, carbon dioxide and air. The product was collected over the range specified, 155–160°, and amounted to 175 g. Two runs were combined and the 350 g. fractionated through a 50-cm. packed column using a reflux ratio of about 10 to 1. A 6-ml. forerun was collected from 155.2–159.2° (cor.) and the balance of the material was split into 32 fractions by volume, the boiling points of which rose steadily from 159.2 to 161.2° (cor.). The last three fractions boiling 160.2 to 161.2° were combined and refractionated into 11 cuts. The last fraction (No. 11B) had properties similar to those given in the literature[4] for *p*-ethyltoluene.

Compound	B. p. (cor.), °C.	n^{20}_D	d^{20}_4
n-Propylbenzene	159.2	1.4919	0.8618
o-Ethyltoluene	164.8	1.5041	.8810
p-Ethyltoluene	161.8	1.4952	.8612
Fraction 11B	161–161.3	1.4963	.8690

However, oxidation as described below gave only a 5% yield of terephthalic acid. No higher boiling fraction corresponding to *o*-ethyltoluene (b. p. 164.8°) was obtained and it seems evident that the compounds codistil since volume–temperature plots showed no plateaus. Also, oxidation of the last three fractions gave small amounts of terephthalic acid.

Oxidation Procedure.—A mixture of 600 ml. of water, 4 ml. of 10% sodium hydroxide solution and 8 g. of Fraction 11B was heated to 85° and vigorously stirred with a Hershberg stirrer while 102 g. of powdered potassium permanganate was added. The mixture was heated to gentle reflux for one hour and the excess permanganate reduced by addition of sodium bisulfite. Then 50 ml. of concentrated sulfuric acid was added slowly and more sodium bisulfite to dissolve the manganese dioxide. The decolorized solution was subjected to steam distillation to remove any unchanged hydrocarbon but no appreciable amount was recovered. The hot solution was filtered through a hot funnel and the precipitate consisting of terephthalic acid and a little manganese dioxide was treated with 20 ml. of 10% sodium hydroxide. The mixture was filtered and the filtrate acidified with sulfuric acid. The terephthalic acid (0.5 g.) separated as a white powder which sublimed at 305–306°. It was converted to the dimethyl ester by refluxing with 75 ml. of methanol and 10 ml. of concentrated sulfuric acid. The ester separated from the mixture on cooling and was washed thoroughly with 5% sodium bicarbonate solution and recrystallized from benzene. White needles, melting sharply at 140.5° (cor.) were obtained. It was compared with a specimen prepared from pure *p*-xylene which was oxidized by the same procedure as described above to give an 85–90% yield of terephthalic acid subliming at 305–306° and a methyl ester melting at 140.5°. A melting point of a mixture of the two samples of the ester showed no depression.

Examination of different batches of *n*-propylbenzene prepared at different times by different workers showed variations in the amounts of terephthalic acid obtained. Calculations indicate that the amount of *p*-ethyltoluene formed in the reaction between benzylmagnesium chloride and ethyl sulfate ranged from 0.4 to 5.0% in different preparations.

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[2] Gilman and Kirby, THIS JOURNAL, **54**, 345 (1932); Austin and Johnson, *ibid.*, **54**, 647 (1932).

[3] "Organic Syntheses," Coll. Vol. 2, 590 (1943).

[4] Doss, "Physical Constants of the Principal Hydrocarbons," 3rd ed., The Texas Co., 1942, pp. 75, 76.

Formation of N-Phenylsuccinimide in Ziegler[1] Reactions Carried Out in Benzene

BY DAVID R. HOWTON

Various investigators[2] have reported that N-bromosuccinimide (NBS) does not attack benzene at an appreciable rate in the absence of other materials. In connection with studies of the Ziegler bromination of certain four-membered-ring olefins,[3] we have noted that small but significant amounts of N-phenylsuccinimide are formed when benzene is employed as a solvent; details of the isolation of this compound from a reaction in which the olefin was cyclohexene are given in the Experimental part.

Whereas the yield of N-phenylsuccinimide in this instance is only 1%, more (14% in one case[3]) is formed in the presence of olefins reacting with NBS at a slower rate; there is also evidence[3] that the reaction leading to the formation of N-phenylsuccinimide is favored by the addition of catalysts such as dibenzoyl peroxide. Preliminary experiments show that in the absence of α-methylene olefins reaction between NBS and benzene is not complete after several days at 80° in the presence of dibenzoyl peroxide (*cf.* ref. 2c) or in the presence of this peroxide plus ethylene.

The formation of N-phenylsuccinimide under these conditions is of interest because of possible bearing it may have on the mechanism of the Ziegler reaction and of free-radical reactions in general, and because it represents a new type of direct amidation[4] (or amination) of benzene.

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[1] Ziegler, *et al.*, *Ann.*, **551**, 80 (1942).

[2] (a) Buu-Hoï, *Ann.*, **556**, 1 (1944); (b) Ettlinger, Ph.D. Dissertation, Harvard University, December 15, 1945, p. 86; (c) Schmid, *Helv. Chim. Acta*, **29**, 1144 (1946).

[3] Buchman and Howton, to be published.

[4] Schmid and Karrer, *Helv. Chim. Acta*, **29**, 573 (1946), have observed a similar amidation in the reaction of NBS with acridine.

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Experimental

A mixture of 45.9 g. (0.26 mole) of NBS, 27.1 g. (0.33 mole) of cyclohexene (found by iodometric titration to contain 0.05 mole of cyclohexene hydroperoxide per liter), and 185 ml. of C. P. anhydrous benzene was stirred and brought to reflux in twenty-six minutes; six minutes later the NBS was shown by testing with potassium iodide to be completely consumed. After cooling and filtering off succinimide, the filtrate was fractionally distilled; in addition to solvent and unchanged cyclohexene, 21.0 g. (50.3%) of 3-bromocyclohexene, b. p. 45–47° at 10 mm. and 6.7 g. of a colorless oil, b. p. 51–57° at 1 mm.,[5] were obtained. Careful fractional recrystallization of solids which separated from the residues left after removal of each of the above liquid fractions gave a total of 0.44 g. (1%, based on NBS) of N-phenylsuccinimide, m. p. 155.2–155.7° (cor.) unchanged by admixture with an authentic sample.

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(5) On long standing at 0°, this oil deposited 1.31 g. of massive colorless crystalline material, tentatively identified as 3,6-dibromocyclohexene[1] (m. p. 107.5–108.3° (cor.). *Anal.* Calcd. for $C_6H_8Br_2$: C, 30.03; H, 3.36. Found: C, 30.43; H, 3.61); the residual oil was shown to consist of at least 60% 1,2-dibromocyclohexane (b. p., m. p., mixed m. p. with an authentic sample; separated from reactive unsaturated dibromides by virtue of its inertness toward trimethylamine at room temperature).

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The Bromine-Sensitized Photochemical Formation of Hexabromoethane from Carbon Tetrabromide

BY L. B. SEELY, JR., AND J. E. WILLARD

When very dilute solutions (10^{-3} *M*) of bromine in purified and degassed liquid carbon tetrabromide were illuminated at 95° with light of wave length between 4100 and 4500 Å., more bromine was produced. We have assumed that this was due to the formation of hexabromoethane from two molecules of carbon tetrabromide with the consequent liberation of one molecule of bromine.

Our interest in this reaction was occasioned by the simplicity and symmetry of the reacting molecules, the unusual nature of the process as characterized by the formation of a carbon-to-carbon bond, the relation of this reaction to other reactions involving an attack by a light-activated halogen on a halogen–carbon bond and, lastly, the possibility of tracer studies as a means of investigating the mechanism.

Precise studies of this reaction have been carried out on carbon tetrachloride solutions. The carbon tetrachloride was purified according to procedures previously described.[1] The carbon tetrabromide was purified by repeated recrystallizations from carbon tetrachloride. The bromine was distilled in vacuum from anhydrous calcium bromide and sealed in small bulbs for later introduction into the reaction mixture. The mixture of tetrahalides was purified and degassed by flushing with pure nitrogen, evacuating while frozen and distilling several times in vacuum.

At 0.5 *M* carbon tetrabromide, 2 × 10^{-3} *M* bromine and 50° the reaction proceeded with a quantum yield of about 1.0 × 10^{-3} mole of bromine per einstein of light absorbed. Under other conditions quantum yields between 10^{-4} and 10^{-2} were recorded. An increase in the bromine concentration caused a decrease in the quantum yield. The quantum yield increased with increase in the carbon tetrabromide concentration but the quantitative dependence on this concentration varied with the bromine concentration. The temperature coefficients were likewise dependent on the bromine concentration.

The explanation of this behavior appears to be the existence of two reaction mechanisms, prevailing in different bromine concentration ranges, with a transitional range between. At bromine concentrations above 3 × 10^{-3} *M* (0.5 *M* carbon tetrabromide, 50°) the reaction followed the rate law

$$\frac{d[C_2Br_6]}{dt} = \frac{kI_{abs}f([CBr_4])}{[Br_2]^2}$$

The experimental evidence to date indicates that f([CBr_4]) should be the first power. This has been hard to rationalize in terms of the usual mechanisms, since two carbon tetrabromide molecules are required to produce one hexabromoethane molecule, and since the light dependency is first power.

At bromine concentrations below 1 × 10^{-3} *M*, there is evidence that the rate law becomes independent of both carbon tetrabromide and bromine, following the law

$$d[C_2Br_6]/dt = k'I_{abs}$$

This is the law to be expected if the process determining the concentration of tribromomethyl free radicals is the combination of these radicals. Further studies in this region may provide experimental evidence concerning such processes.

At bromine concentrations above 1 × 10^{-3} *M* the quantum yield for the photo-activated exchange of free bromine with the bromine in carbon tetrabromide (determined by means of radiobromine) was very much higher than the quantum yield for the formation of hexabromoethane and was very sensitive to trace amounts of impurities.

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(1) Dickinson and Leermakers, THIS JOURNAL, **54**, 3853 (1932).

The Glycogen Content of *Phymatotrichum Sclerotia*[1]

BY DAVID R. ERGLE

In a recent chemical study[2] of the mycelial and sclerotial stages of ***Phymatotrichum omnivorum***

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(1) Published with the approval of the Director of the Texas Agricultural Experiment Station as Technical Paper No. 996.

(2) Ergle and Blank, *Phytopathology*, **37**, 153–161 (1947).