and a device for adding solids[4] was placed 94 g. (0.80 mole) of benzyl cyanide, 110 g. (0.80 mole) of β-diethylaminoethyl chloride, and 270 ml. of benzene (dried over potassium hydroxide). To this was added slowly 32 g. (0.80 mole) of sodium amide while the flask was kept well cooled in an ice bath. The contents was then allowed to warm up to room temperature and finally heated in an oil-bath at 80° for one hour. The reaction mixture was allowed to stand overnight and then treated with 150 ml. of water with stirring. The two layers which formed were separated and the benzene layer was dried over "Drierite." Evaporation of the solvent and distillation of the residue gave 128 g. of γ-diethylamino-α-phenylbutyronitrile, b. p. 120–122° (1 mm.). This yield is 74%.

The above preparation is an improvement on the method of Eisleb,[5] giving a 14% increase in yield.

Methyl γ-Diethylamino-α-phenylbutyrate.—A solution of 86.6 g. (0.40 mole) of γ-diethylamino-α-phenylbutyronitrile in 80 g. each of water, sulfuric acid and glacial acetic acid was refluxed for thirty-five hours in an oil-bath kept at 130°. The water and acetic acid were removed by distillation under reduced pressure. Two 100 ml. portions of methanol were added and also removed under reduced pressure. To the residue was added 240 ml. of methanol and 120 ml. of sulfuric acid. The solution was refluxed for nine and one-half hours, cooled, poured onto ice and made strongly alkaline with ammonium hydroxide. The ester was extracted with three-200 ml. portions of ether. The extracts were dried over "Drierite" and distilled. The yield was 83.8 g. or 84% of theory; b. p. 130–135° (3 mm.), $n^{25}\mathrm{D}$ 1.495.

***p*-Chlorobenzyl γ-Diethylamino-α-phenylbutyrate.**—In a 50-ml. Erlenmeyer flask was placed 28.5 g. (0.20 mole) of *p*-chlorobenzyl alcohol, 10 g. (0.04 mole) of methyl γ-diethylamino-α-phenylbutyrate, and about 0.3 g. of solid sodium ethoxide. The flask was heated for sixteen hours in an oil-bath maintained at 150°. The excess alcohol was removed by distillation. The *p*-chlorobenzyl ester was collected at 165–167° (1 mm.) and weighed 11.2 g. The yield was 78% based on methyl ester of 48.5% based on phenylacetonitrile.

3,4-Diethoxybenzyl γ-Diethylamino-α-phenylbutyrate.—This ester could not be directly distilled from the the reaction mixture. It was extracted from the reaction mixture with 5% hydrochloric acid. The acid solution was then made alkaline with ammonium hydroxide and extracted with ether. The ester could then be distilled after evaporating off the ether.

Substituted Benzyl Alcohols.—Most of the substituted benzyl alcohols were prepared by the reduction of the corresponding benzaldehydes by the method of Adams and Carothers.[6]

Summary

Nineteen new esters of γ-diethylamino-α-phenylbutyric acid have been prepared to be tested for antispasmodic and anticonvulsant activity. The best method for the preparation of these compounds was found to be by the use of an ester interchange reaction, using the methyl ester as the starting compound.

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(4) Swift and Billman, *Ind. Eng. Chem.*, **17**, 600 (1945).

(5) Eisleb, *Ber.*, **74B**, 1433 (1941).

(6) Carothers and Adams, This Journal, **45**, 1071 (1923); **46**, 1680 (1924).

NOTES

Rearrangement in the Reaction between Benzylmagnesium Chloride and Ethyl Sulfate

By Jerome G. Burtle and R. L. Shriner

During a study of the influence of emulsifying agents on the oxidation of alkyl benzenes, it was observed that the alkaline permanganate oxidation of 6 g. of *n*-propylbenzene produced 0.3 g. of terephthalic acid in addition to benzoic acid. Investigation disclosed that this sample of *n*-propylbenzene had been made by the reaction between benzylmagnesium chloride and ethyl sulfate[1] and that it had been collected over a rather wide boiling point range, 155–160° (uncor.). The question arose as to whether the terephthalic acid was formed by the oxidation of *p*-ethyltoluene formed by a *para*-rearrangement during the course of the Grignard reaction, or whether it came from impurities in the benzyl chloride used to make the Grignard reagent. Since benzyl chloride is produced by chlorination of boiling toluene, any *p*-chlorotoluene present would form *p*-tolylmagnesium chloride which would also form *p*-ethyltoluene by reaction with ethyl sulfate. The latter explanation was excluded by repeating the preparation with carefully purified benzyl chloride which was shown to contain no *p*-chlorotoluene by the fact that no *p*-chlorobenzoic acid was produced by oxidation. Also a purified sample of benzaldehyde was converted to benzyl alcohol by the Cannizzaro reaction and this benzyl alcohol (which was halogen free) converted to benzyl chloride which was then used for the preparation of *n*-propylbenzene. In each case, oxidation of the fraction corresponding to *n*-propylbenzene produces terephthalic acid.

The boiling points of *n*-propylbenzene, *o*-ethyltoluene and *p*-ethyltoluene lie rather close together and repeated fractional distillation failed to give any pure fractions of either *o*-ethyltoluene or *p*-ethyltoluene. Apparently the three compounds show a marked tendency to co-distil. The presence of *p*-ethyltoluene was shown by oxidation with alkaline potassium permanganate solution and separation of the terephthalic acid from benzoic acid by means of its very low solubility in hot water. No phthalic acid could be separated

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(1) "Organic Syntheses," Coll. Vol. 1, 471 (1941).

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.