

XCI.—*Investigations on the Dependence of Rotatory Power on Chemical Constitution. Part XXVIII. d-sec.-Butylbenzene.*

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OF the compounds which have been examined in the study of the relationship between chemical constitution and optical activity, very few have been hydrocarbons, probably because of the experimental difficulties in preparing this type of compound in an optically active condition.

Mention may be made, however, of *d*-methylethyl-*n*-propylmethane with  $[\alpha]_D^{20} + 9.5^\circ$ , which was prepared by Marckwald (*Ber.*, 1904, **37**, 1046) by the action of sodium on a mixture of ethyl iodide and *d*-amyl iodide. Klages and Sautter (*Ber.*, 1904, **37**, 649) prepared *d*- $\alpha$ -phenyl- $\gamma$ -methylpentane ( $[\alpha]_D^{25} + 17.2^\circ$ ) by the reduction of *d*- $\alpha$ -phenyl- $\gamma$ -methyl- $\Delta^{\alpha}$ -pentene ( $[\alpha]_D^{25} + 43^\circ$ ), which was obtained by the interaction of active amyl iodide ( $[\alpha]_D^{25} + 5.78^\circ$ ) and benzaldehyde in presence of magnesium. The same authors (*Ber.*, 1905, **38**, 2312), by analogous reactions, prepared *d*- $\gamma$ -*m*-isopropylphenyl- $\gamma$ -methylpentane ( $[\alpha]_D^{25} + 15.91^\circ$ ) and *d*- $\gamma$ -*m*-isopropylphenyl- $\gamma$ -methyl- $\Delta^{\alpha}$ -pentene ( $[\alpha]_D^{25} + 41.89^\circ$ ).

This communication describes the preparation of *sec.*-butylbenzene in what is believed to be an optically pure condition.

The preparation has proved to be so tedious and laborious that the question of preparing other optically active hydrocarbons will be held in abeyance until a more convenient procedure has been devised.

The method of preparing *d*-*sec*-butylbenzene is briefly as follows: The inactive hydrocarbon was nitrated and the *p*-nitro-*sec*-butylbenzene, which is the principal product of the reaction, was reduced to *p*-amino-*sec*-butylbenzene. The latter was then converted into the *hydrogen tartrate*, which was submitted to systematic prolonged fractional crystallisation until a salt of constant rotatory power was obtained. The amino-group of the optically active base obtained by the decomposition of this salt was then eliminated in the usual way, giving optically active *sec*-butylbenzene.

The resolution of *sec*-butylbenzene into its optically active isomerides had been attempted previously. Klages (*Ber.*, 1906, **39**, 2131) converted the hydrocarbon into its sulphonic acid and obtained therefrom a number of crystalline salts by combining it with several of the commoner alkaloids. Fractional crystallisation of these salts, however, brought about no resolution.

*p*-Amino-*sec*-butylbenzene was obtained in an optically active condition by Glattfeld and Wertheim (*J. Amer. Chem. Soc.*, 1921, **43**, 2682) by the crystallisation of the salt with *d*-camphorsulphonic acid. The rotatory power of the amine quoted by these authors is, however, far too low, being some sixty times smaller than the value obtained in the course of the present work.

Each of the compounds now described exhibits a very high optical rotatory dispersive power:  $\alpha_{4359}/\alpha_{5461} = 1.87$  for the amine and 1.81 for the hydrocarbon, whilst an examination of the rotatory powers shows that in no case do they satisfy the simple dispersion equation  $\alpha = K/(\lambda^2 - \lambda_0^2)$ .

As it is possible that the high optical rotatory dispersive power may be due to these compounds containing a benzene nucleus in the molecule, several attempts were made to reduce *sec*-butylbenzene to *sec*-butylcyclohexane to ascertain what effect, if any, the loss of aromatic character would have on the rotatory dispersive power. However, under the conditions employed, namely, agitation of the substance with hydrogen in the presence of colloidal platinum or palladium, little, if any, reduction was effected.

#### EXPERIMENTAL.

*dl*-*sec*-Butylbenzene was prepared by the method of Klages (*Ber.*, 1902, **35**, 2641). The methylethylphenylcarbinol obtained by the interaction of magnesium ethyl chloride and acetophenone was slowly distilled at the ordinary pressure, and the resulting

$\beta$ -phenyl- $\Delta^{\beta}$ -butylene (75% yield) reduced rapidly with sodium and absolute alcohol. *sec.*-Butylbenzene was collected at 168—173° and obtained in 87% yield.

*p*-Nitro-*sec.*-butylbenzene.—To *dl*-*sec.*-butylbenzene (200 g.) was added during 3 hours a mixture of nitric acid (128 c.c.; *d* 1.42) and sulphuric acid (160 c.c.; *d* 1.84) at such a rate that the temperature of the reaction was maintained at 15—20°; external cooling was resorted to, and the mixture kept vigorously stirred. The principal product of the reaction was *p*-nitro-*sec.*-butylbenzene—shown by the production of *p*-nitrobenzoic acid in good yield on oxidation—accompanied by a relatively small amount of a lower-boiling fraction which was presumably *o*-nitro-*sec.*-butylbenzene. Only a rough separation was possible at this stage, owing to the difficulty of obtaining a fraction of constant boiling point. Further purification was, however, easily effected after the next operation by the recrystallisation of the *oxalates* of the mixed amines.

*dl*-*p*-Amino-*sec.*-butylbenzene.—The *p*-nitro-compound was very easily reduced to the corresponding amine by tin and concentrated hydrochloric acid. After decomposition of the stannic chloride compound of the base by caustic soda, the amine was isolated by distillation in steam.

The mixture of neutral oxalates of the amines was crystallised several times from hot water and it was found by determining the density of the amine recovered that one crystallisation was sufficient to remove almost completely the lower-boiling isomeride of greater density. The amine thus obtained distilled constantly at 118°/15 mm.; its density ( $d_4^{20}$  0.949), and the melting point (123°) of its acetyl derivative were unaltered after further recrystallisation of the neutral oxalate. Reilly and Hickinbottom (J., 1920, 117, 120) give 125—126° as the melting point of *p*-*sec.*-butylacetanilide; that prepared by the present authors melts at 123° even after several recrystallisations.

*Resolution of dl*-*p*-Amino-*sec.*-butylbenzene.—Salts of the *dl*-amine with several optically active acids were prepared—that with *l*-malic acid was excessively soluble and could not be crystallised; those with *d*-camphoric and *d*-camphorsulphonic acids were crystalline, but their separation into enantiomorphous forms by fractional crystallisation was too slow to be of use. The compound with *d*-hydroxymethylenecamphor was also prepared, but fractional crystallisation of this failed to effect any resolution. (This is in agreement with the observation of Glattfeld and Wertheim, *loc. cit.*).

After many preliminary attempts it was found that the *d*-hydrogen

tartrate was the most promising of all the salts tried. *p*-Amino-*sec*-butylbenzene (285 g.) was added to a hot solution of *d*-tartaric acid (300 g.) in water (1100 c.c.); the clear solution on standing deposited a crop of crystals (which titration showed to be the *hydrogen tartrate*) in very small, prismatic rods. These were systematically recrystallised until the rotatory power of the amine obtained by decomposing successive crops of the crystals became constant. The rate of the resolution is indicated by the following data :

After four recrystallisations of the hydrogen tartrate, the observed rotatory power ( $\alpha_{5461}^{20}$ ;  $l = 100$  mm.) of the liberated base was  $+ 16^\circ$ , after eight  $+ 23^\circ$ , after twelve  $+ 28^\circ$ , after sixteen  $+ 31^\circ$ , after twenty-two  $+ 37^\circ$ , after twenty-five  $+ 38.2^\circ$ , after twenty-seven  $+ 38.7^\circ$ , after thirty  $+ 38.7^\circ$ .

This prolonged process of recrystallisation is very wasteful and the *d-p*-amino-*sec*-butylbenzene obtained by decomposition of the various crops of salt of constant rotatory power amounted to only 10 g. The amine had b. p.  $114^\circ/12$  mm. and  $d_{20}^{20} 0.945$ .

Various attempts were made to isolate the *laevorotatory* form of *p*-amino-*sec*-butylbenzene in an optically pure condition, but without success. By the decomposition of the most soluble fractions of the hydrogen tartrate, portions of amine of rotatory powers lying between  $\alpha_{5461} - 12^\circ$  and  $- 20^\circ$  were obtained. The *d*-camphorsulphonate of the base with  $\alpha_{5461} - 20^\circ$  was prepared and recrystallised several times; the *laevorotation* of the amine obtained from the less soluble fractions of this salt increased, but at so slow a rate as to render the method valueless. Recrystallisation of the hydrochloride and of the oxalate of the partially active amine was also without effect on the rotatory power. Other solvents besides water were tried in all the above cases for recrystallisation of the various salts, but they bring about separation with even greater slowness than does water.

*d-sec*-Butylbenzene was readily prepared by mixing a solution of *d-sec*-butylbenzenediazonium chloride (from 6 g. of amine) with a strongly alkaline solution of sodium stannite and distilling the mixture in a current of steam. The hydrocarbon was obtained as a colourless liquid which distilled constantly at  $172^\circ$ ; the yield was 2 g. = 40% of the theoretical (compare Friedländer, *Ber.*, 1889, 22, 587).

Although it was considered unlikely that any racemisation would occur during the elimination of the amino-group situated at the end of the molecule remote from the asymmetric carbon atom, yet the following experiments were carried out to gain some information on this important point. Partially active *d*- and *l-p*-amino-*sec*-butylbenzenes of various degrees of rotatory power were diazotised

*Determinations of Rotatory Power.*

d-p-Amino-sec-butylbenzene.  $d_{4}^{20}$  0.9449.

Solvent.	G. of solute in 100 c.c. of soln.	l in mm.	$\alpha_{\lambda}^{20}$ Observed.		$[\alpha]_{\lambda}^{20}$ .							
			$\lambda$	$\lambda$	$\lambda$	$\lambda$						
Homogeneous	—	25	6708.	5896.	6708.	5896.	5790.	5461.	4359.	4359.		
Ethyl alcohol	4.94	100	+5.85°	+8.00°	+8.37°	+9.68°	+18.10°	+24.75°	+33.86°	+35.42°	+40.98°	+76.6°
Carbon disulphide	5.01	100	1.31	1.76	—	2.05	3.75	26.5	35.6	—	41.5	75.8
Chloroform	5.02	100	1.45	2.00	—	2.44	4.96	28.9	39.9	—	48.7	99.0
			1.15	1.63	1.72	2.00	3.72	22.9	32.5	34.3	39.8	74.1

d-p-sec-Butylacetanilide. M. p. 124°.

Chloroform	4.99	100	0.97	1.34	1.40	1.58	2.90	19.4	26.8	28.0	31.6	58.1
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d-sec-Butylbenzene.  $d_{4}^{20}$  0.8639.

Homogeneous	—	25	4.41	5.90	6.19	7.14	12.96	20.42	27.31	28.66	33.15	60.0
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*Density.*

*Refractive Index ( $n_{\lambda}^{25}$ ).*

	$\lambda$	$\lambda$
d-sec-Butylbenzene	6708.	5896.
d-p-Amino-sec-butylbenzene	6708.	5790.
dl-p-Nitro-sec-butylbenzene	6708.	5461.
	5896.	5461.
	1.4838	1.4890
	1.5284	1.5356
	—	1.5322
	—	1.5363
	—	1.5622

d-sec-Butylbenzene	$d_{4}^{15}$ 0.8681,	$d_{4}^{20}$ 0.8639,	$d_{4}^{25}$ 0.8590.
d-p-Amino-sec-butylbenzene	$d_{4}^{15}$ 0.9475,	$d_{4}^{20}$ 0.9449,	$d_{4}^{25}$ 0.9411.
dl-p-Nitro-sec-butylbenzene	$d_{4}^{20}$ 1.063.		

and treated with sodium stannite under different experimental conditions; the ratio of the rotatory power of the original amine to that of the hydrocarbon obtained from it in each of the several cases was quite constant, thus rendering it highly improbable that any racemisation had taken place.

The authors desire to express their thanks to the Government Grant Committee of the Royal Society for a grant with which some of the materials used in this investigation were purchased. Two of them (J. R. S. and P. W. B. H.) wish also to acknowledge their indebtedness to the Department of Scientific and Industrial Research for maintenance grants which enabled them to participate in the work.

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[*Received, December 22nd, 1925.*]

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