NOTES.

ββ′β″-*Trichlorotriethylamine.* By H. McCombie and D. Purdie.

Pure crystalline ββ′β″-trihydroxytriethylamine (100 g., obtained from commercial triethanolamine by distillation at 1—2 mm.) is dissolved in 150 c.c. of dry chloroform in a 1500 c.c. bolthead flask, and a mixture of 270 g. (12% excess) of thionyl chloride and 150 c.c. of chloroform added slowly through the condenser, with frequent shaking; cooling is advisable, as the addition can then be carried out faster. The whole is boiled on the water-bath for 4—5 hours and allowed to cool; the heavy crop of ββ′β″-trichlorotriethylamine hydrochloride is filtered off and washed with chloroform, giving snow-white crystals, m. p. 133°, sufficiently pure for anything but analysis. It may be recrystallised from water, alcohol, or a mixture of the two, and then has m. p. 133·5°. Yield, 140—150 g. (Found : Cl, 58·7. Calc., 58·9%).

The free base is prepared by adding caustic soda to a concentrated aqueous solution of the hydrochloride. Separated in chloroform and vacuum-distilled, it is obtained as a heavy oily liquid, b. p. 137—138°/15 mm., m. p. − 4°, having vesicant properties. On distillation at the ordinary pressure it decomposes, giving mainly the hydrochloride of the trichloro-base, and it also decomposes on long standing (Found : Cl, 52·0. Calc., 52·1%).

The chlorine atoms of ββ′β″-trichlorotriethylamine are reactive, but only a short study was made of the products obtainable from it; the best defined of those prepared was ββ′β″-trithiophenoxytriethylamine, m. p. 57° (Found: S, 22·7. Calc., 22·6%).

The platinichloride of ββ′-dichlorodiethylamine (see Mann, J., 1934, 463) forms orange needles, m. p. 215° (decomp.) (Found: Pt, 27·7. Calc., 28·1%). That of ββ′β″-trichlorotriethylamine forms buff needles, which decompose on heating (Found: Pt, 23·8. Calc., 23·8%).—UNIVERSITY CHEMICAL LABORATORIES, CAMBRIDGE. [*Received, June 5th,* 1935.]

An Unusual Case of Racemisation.

By ERNST BERGMANN and RICHARD HARTROTT.

IN the course of experiments on the synthesis of optically active αα-diphenyl-β-methylpentane, $CH_2Me{\cdot}CH_2{\cdot}CHMe{\cdot}CHPh_2$, we studied the interaction of lævorotatory ethyl α-methyl-*n*-valerate with phenylmagnesium bromide. The product was the desired carbinol, but it was optically inactive and identical with the carbinol obtained from the racemic ester.

Now it is an axiom of stereochemistry that racemisation of a tetrahedral atom can only occur if (a) the tetrahedral atom participates in a substitution reaction or if (b) it loses temporarily its asymmetric structure. Obviously, the first alternative is inapplicable, and only two possibilities can be contemplated in connection with (b): the ester undergoes enolisation before it reacts with the Grignard compound (or after the interaction with the first Grignard molecule, in the form of the ketone $CHMePr{\cdot}COPh$) or the reaction product is racemised. Since dialkylated ethyl acetates are not easily racemised (Conant and Carlson, *J. Amer. Chem. Soc.*, 1932, **54**, 4048), the loss of activity must occur in the end product. We suggest that the carbinol (or its bromomagnesium derivative), when formed, undergoes spontaneously reversible dehydration,

$$CHMePr{\cdot}CPh_2{\cdot}OH \rightleftharpoons CMePr{:}CPh_2$$

which must be accompanied by racemisation. The easy dehydration of diphenylalkylcarbinols is well known.

The observed racemisation, if occurring in the above manner, finds analogy in the fact that a substituted ammonium hydroxide $NR_1R_2R_3H(OH)$, although asymmetric, cannot exist in optically active forms.

EXPERIMENTAL.

α-Methyl-*n*-valeric acid was prepared by coupling methyl methylmalonate (200 g.) with propyl bromide (150 g.) by means of sodium (26·5 g.) in methyl alcohol (450 g.), saponification of the isolated methyl methylpropylmalonate (b. p. 109—111°/20 mm.; yield, 200 g.) by means of 10% methyl-alcoholic potassium hydroxide (2·2 mols.), and decarboxylation by heat. It had b. p. 102—105°/12 mm. (see Stiasny, *Monatsh.*, 1891, **12**, 594); yield, 62 g. A partial resolution of the racemic acid was carried out by means of brucine according to Levene and Bass (*J. Biol. Chem.*, 1927, **70**, 216). The brucine salt, m. p. 78—80°, gave a lævorotatory acid, b. p. 190—193°, $[\alpha]_D - 5{\cdot}25°$ (in acetone). From 5 g. of that preparation, the methyl ester (5 g.) was obtained by means of 1 g. of diazomethane; b. p. 135—136°, $[\alpha]_D - 6{\cdot}95°$ (in acetone).

Interaction between Methyl (—) *α-Methyl-*n*-valerate and Phenylmagnesium Bromide.*—The lævorotatory ester (5 g.) was added to a Grignard solution (magnesium, 2·5 g.; bromobenzene, 18·5 g.) and heated for 30 minutes, and the product decomposed by means of ice and ammonium chloride. The residue of the ethereal layer, repeatedly distilled in a vacuum, gave *αα-diphenyl-β-methyl-*n*-amyl alcohol* as a colourless oil (3·5 g.), b. p. 195—197°/14 mm., which showed no optical activity in acetone or alcohol (Found: C, 85·3; H, 8·6. $C_{18}H_{22}O$ requires C, 85·0; H, 8·7%). The methyl ether too, prepared by the procedure described below, was optically inactive.

For comparison, the same procedure was applied to the racemic methyl ester (b. p. 135—137°) (7 g.), which with magnesium (3·5 g.) and bromobenzene (26 g.) gave the same racemic alcohol, (7 g.), b. p. 194—196°/15 mm., 186—187°/11 mm. (Found: C, 85·3; H, 8·7%).

Synthesis of Racemic αα-Diphenyl-β-methylpentane.—The carbinol (5 g.) was dissolved in dry xylene, and the calculated amount of potassium added, which dissolved on slight heating. When most of the metal had disappeared, three times the theoretical amount of methyl iodide was added, and the whole heated for 4 hours. Some drops of alcohol were then added and the xylene was washed with water, dried, and evaporated in a vacuum. Distillation of the residue gave *α-methoxy-αα-diphenyl-β-methylpentane* (4 g.), a colourless oil, b. p. 174—176°/13 mm. (Found: OMe, 10·4. $C_{19}H_{24}O$ requires OMe, 11·6%. Vieboeck's method, *Ber.*, 1930, **63**, 2812, 3207). Methylation of the carbinol with methyl-alcoholic sulphuric acid according to Ziegler and Schnell (*Annalen*, 1924, **437**, 228) gave a similar product (Found: OMe, 9·1%), but dehydration occurred to a still larger extent.

αα-Diphenyl-β-methylpentane was prepared by shaking the methyl ether (3 g.) in ethereal solution with sodium powder for 3 months, decanting the dark brown-red solution, and adding alcohol to it until the colour disappeared; distillation of the ethereal residue gave 1·2 g. of the hydrocarbon, b. p. 163—164°/13 mm. (Found: C, 90·7; H, 9·5. $C_{18}H_{22}$ requires C, 90·8; H, 9·2%).

The experiments were partly carried out in the Laboratory of the Friedrich Wilhelm University, Berlin.—THE DANIEL SIEFF RESEARCH INSTITUTE, REHOVOTH, PALESTINE.

[*Received, March* 6*th*, 1935.]

N-*Benzhydryl*-N′-*arylformamidines*.

By Leonard E. Hinkel, Ernest E. Ayling, and John H. Beynon.

BENZHYDRYLFORMAMIDINE (Gattermann and Schnitzspahn, *Ber.*, 1898, **31**, 1770), on heating with primary aromatic amines, yields a series of *N*-benzhydryl-*N′*-arylformamidines. The unsymmetrical formamidines on acid hydrolysis yield *N*-benzhydrylformamide and the aryl amine, thus behaving similarly to benzhydrylformamidine itself (*idem, ibid.*), and to diarylformamidines (Dains, *Ber.*, 1902, **35**, 2496), which yield the *N*-substituted formamide and either ammonia or arylamine respectively.

N-*Benzhydryl*-N′-*phenylformamidine* reacts similarly to symmetrically substituted diarylformamidines with compounds containing reactive methylenic hydrogen, *viz.*, phenylacetonitrile, ethyl acetoacetate, and ethyl malonate (compare Dains, *loc. cit.*), aniline elimination occurring with the nitrile and anilide formation with the acetoacetate and malonate. The formation of the anilides (II, R = Me or OEt) with the esters is in agreement with the view (Dains and Brown, *J. Amer. Chem. Soc.*, 1909, **31**, 1148) that the initial reaction yields the substituted aminomethylene derivative (I) and free amine, a secondary reaction being possible between these if the former contains a carbethoxy-group.

$$\text{(I.)}\quad CHPh_2{\cdot}NH{\cdot}CH{:}C(CO_2Et){\cdot}COR \xrightarrow{NH_2Ph} CHPh_2{\cdot}NH{\cdot}CH{:}C(CO{\cdot}NHPh)COR \quad \text{(II.)}$$

Condensation of Benzhydrylformamidine with Primary Aromatic Amines.—A solution of benzhydrylformamidine (1 mol.) and the aromatic amine (1 mol.) in dry benzene was heated under reflux on the water-bath for 2—3 hours until the evolution of ammonia was complete; after removal of the benzene, the solid product was crystallised from light petroleum (b. p. 60—80°).

Aniline (7 c.c.) yielded N-*benzhydryl*-N′-*phenylformamidine* (19 g.; 86%) in long colourless needles, m. p. 126·5° (Found: N, 9·8. $C_{20}H_{18}N_2$ requires N, 9·8%). *p*-Toluidine (2·1 g.) yielded N-*benzhydryl*-N′-p-*tolylformamidine* (5 g., 85%) in colourless prismatic needles, m. p. 131° (Found: N, 9·2. $C_{21}H_{20}N_2$ requires N, 9·3%). *p*-Chloroaniline (3·8 g.) yielded N-*benzhydryl*-N′-p-*chlorophenylformamidine* (7·5 g., 78%) in long colourless needles, m. p. 124° (Found: N, 8·7. $C_{20}H_{17}N_2Cl$ requires N, 8·7%). *p*-Anisidine (2·3 g.) yielded N-*benzhydryl*-N′-p-*methoxyphenylformamidine* (5 g., 85%) in colourless needles, m. p. 137° (Found: N, 8·8. $C_{21}H_{20}ON_2$ requires N, 8·9%). β-Naphthylamine (3 g.) yielded N-*benzhydryl*-N′-β-*naphthylformamidine* (6 g., 85%) in colourless needle-shaped crystals, m. p. 115° (Found: N, 8·1. $C_{24}H_{20}N_2$ requires N, 8·3%).

Hydrolysis of the Benzhydrylarylformamidines.—*N*-Benzhydryl-*N′*-phenylformamidine (6 g.) was boiled with 4*N*-hydrochloric acid (50 c.c.) for 1 hour. Crystallisation of the solid, which gradually separated during the heating, from aqueous alcohol yielded benzhydrylformamide (4 g., 90%) in colourless needles, m. p. and mixed m. p. 132°. The acid filtrate from the hydrolysis yielded aniline on basification and distillation in steam.

The other compounds similarly yielded benzhydrylformamide and the corresponding amine.

Condensation of N-*Benzhydryl*-N′-*phenylformamidine with Phenylacetonitrile*.—The amidine (7 g., 1 mol.) and phenylacetonitrile (3·1 c.c., 1 mol.), heated together at 150—160° for 2·5 hours, yielded a viscous liquid, which slowly solidified on cooling. The solid was washed with alcohol and crystallisation from alcohol yielded β-*benzhydrylamino*-α-*phenylacrylonitrile* (3 g., 40%) in colourless flat needles, m. p. 141° (Found: N, 8·95. $C_{22}H_{18}N_2$ requires N, 9·0%).

Condensation of N-*Benzhydryl*-N′-*phenylformamidine with Ethyl Malonate*.—The amidine (4 g., 1 mol.) and ethyl malonate (2·6 c.c., 1·125 mols.) were heated for 3 hours at 145—150°. The resulting viscid liquid slowly solidified on cooling and, after washing with alcohol, the *anilide* of *ethyl benzhydrylaminomethylenemalonate* (3·1 g., 55%) crystallised from ether–light petroleum (b. p. 40—60°) in colourless prismatic needles, m. p. 145° (Found: N, 6·9. $C_{25}H_{24}O_3N_2$ requires N, 7·0%).

Condensation of N-*Benzhydryl*-N′-*phenylformamidine with Ethyl Acetoacetate*.—The amidine (6 g., 1 mol.) and ethyl acetoacetate (4·1 c.c., 1·5 mols.) were heated at 145—150° for 1·5 hours. The solid, slowly formed from the viscous liquid on cooling, was washed with alcohol, and the *anilide* of *benzhydrylaminomethyleneacetoacetic acid* (2 g., 26%) crystallised from alcohol in long, white, glistening needles, m. p. 154° (Found : N, 7·5. $C_{24}H_{22}O_2N_2$ requires N, 7·6%).

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n-*Propyl and* n-*Butyl Gallate.* By R. M. Harris and J. C. Smith.

An attempt to use the solid *n*-butyl gallate for the purification of *n*-butyl alcohol (Clarke, Robinson, and Smith, J., 1927, 2648) led to the observation that admixture with *n*-propyl gallate raised the m. p. of the ester.

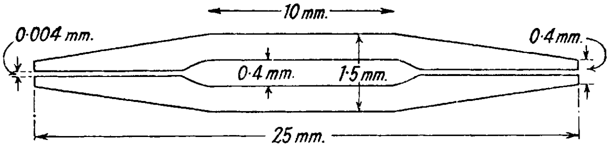
The binary system has now been investigated with distilled esters crystallised from toluene.

n-Propyl gallate, mols. %	0·0	2·5	7·1	10·0	16·5	23·0	37·5	44·3
M. p. (liquidus)	142·4°	143·1°	144·5°	145·8°	148·0°	150·2°	153·0°	153·3°
n-Propyl gallate, mols. %	52·5	56·5	67·0	74·8	86·5	94·0	97·5	100
M. p. (liquidus)	153·5°	153·6°	153·4°	152·7°	151·3°	150·1°	149·2°	148·6°

No compound is formed and the system is one of the rare cases of a continuous series of solid solutions with a maximum m. p. (153·6°, 57% *n*-propyl) (Type II). Mackenzie and Müller (J., 1909, **95**, 547) state that the amyl gallates form solid solutions.—The Dyson Perrins Laboratory, Oxford University. [*Received, June* 15*th*, 1935.]

A Micropyknometer Method for Density Determinations. By G. R. Clemo and A. McQuillen.

In recent work on hexadeuterobenzene, it was necessary to determine the density of small quantities of liquid (*ca.* 2 mg.). The usual method of measuring the length of a thread of liquid in a capillary tube was abandoned owing to the difficulty of obtaining tubes of uniform bore. A small pyknometer (see fig.) was devised from a short length of capillary tubing drawn out at each end to a strong tip with a fine hair-like bore. This filled itself from tip to tip by mere immersion of one end in the experimental liquid, cooled to *ca.* 0·2° below the balance-room temperature, which the liquid attained after some 5 mins.' standing; the slight excess of liquid was discharged and completely evaporated, the size of the capillaries being such that no further loss of benzene by evaporation could be detected by repeated weighings during ½ hour. All weighings were carried out with a microbalance, a tare very similar to the pyknometer itself being used. All manipulations were carried out with bone-tipped forceps, and in each case the outside of the instrument was dried with a glass cloth, dusted with a camel-hair brush, and allowed to stand in the balance case for 15 mins. before being weighed.



The pyknometer was weighed alternately empty and filled with benzene. It was emptied by centrifuging (so that some 6 mg. sufficed for eight separate determinations), dried at 80° for 2 hours in a stream of dry air, and the experiment repeated with hexadeuterobenzene, and finally with distilled water. Ordinary benzene was used after both the heavy benzene and the water determination in order to prove that no change occurred in the adsorbed film. The following results were obtained at 17·2° :

Wt. of C_6H_6, mg. [2·236], 2·258, 2·253, 2·241, 2·253, 2·244, 2·264, 2·254, 2·252, 2·259; mean 2·253.
Wt. of C_6D_6, mg. [2·430], 2·431, 2·441, 2·451, 2·437, 2·445, 2·450, 2·441, 2·432; mean 2·441.
Wt. of H_2O, mg. [2·551], 2·575, 2·552, 2·564, 2·561, 2·576, 2·570, 2·559, 2·563; mean 2·564.
After C_6D_6 : [2·269], 2·258, 2·249; mean 2·254.
After H_2O : [2·268], 2·250, 2·245; mean 2·248.

If the first weighing (in brackets) in each series be omitted, the mean deviation from the mean of all these weighings is 0·005 mg., thus giving the density of ordinary benzene as 0·879 and of hexadeuterobenzene as 0·954.—Armstrong College, University of Durham, Newcastle-upon-Tyne. [*Received, July* 18*th*, 1935.]