# **204.** *The Attempted Resolution of Phenyl αβ-Dideuteroethyl Ketone by an Indirect Method.*

By J. B. M. Coppock, J. Kenyon, and S. M. Partridge.

In an investigation of the optical properties of the system $CHDRR_1$ an attempt has been made to separate crystalline diastereoisomeric esters of (+) phenyl-αβ-dideuteroethylcarbinol by fractional crystallisation.

Reduction by deuterium of (+) phenylvinylcarbinyl *p*-xenylurethane to (+) *phenyl-αβ-dideuteroethylcarbinyl* p-*xenylurethane* and subsequent crystallisation failed to reveal any significant difference in solubility, melting point and rotatory dispersion between the least and the most soluble fractions.

In a second series of experiments (+) phenyl-αβ-dideuteroethylcarbinol was prepared by direct reduction of (−) phenylvinylcarbinol by deuterium and converted into the 3 : 5-dinitrobenzoate. This was fractionally crystallised in order to separate the mixed diastereoisomerides, and the carbinol regenerated by hydrolysis from the least soluble fraction. The original centre of asymmetry was removed by oxidation of the carbinol to phenyl αβ-dideuteroethyl ketone, and after purification through the semicarbazone this ketone was found to be optically inactive.

These results suggest that the system $CHDRR_1$ does not give rise to appreciable optical activity.

In a previous communication (Kenyon and Partridge, J., 1936, 1313) experiments were described which show that addition of bromine to (+) γ-phenyl-α-methylallyl alcohol (I) leads to the production of diastereoisomerides (II) and (III) in unequal amounts :

$$\text{(I) (+) CHPh:CH·CHMe·OH} \begin{array}{l} \nearrow \text{ (II) (+) CHPhBr·CHBr·CHMe·OH} \\ \qquad\qquad\quad \text{(m. p. 112°)} \\ \searrow \text{ (III) (−) CHPhBr·CHBr·CHMe·OH} \\ \qquad\qquad\quad \text{(m. p. 88°)} \end{array}$$

$$\text{(IV) CHPhD·CHD·CHMe·OH} \qquad\qquad \text{CH}_2\text{Ph·CH}_2\text{·CHMe·OH (V)}$$

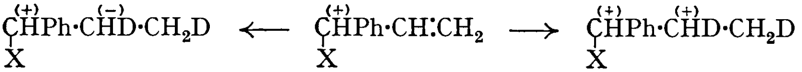
Oxidation of the *unseparated* mixture of (II) and (III) yields the ketone CHPhBr·CHBr·COMe in an optically active condition, thus showing that an asymmetric synthesis has taken place during the combination of (I) with bromine.

In a second communication (Coppock and Partridge, *Nature*, 1936, **137**, 907) it was shown that the alcohol (I) combines with deuterium to produce (IV) and with hydrogen to produce (V), and that (IV) and (V) possess, within the limits of experimental accuracy, identical rotatory powers : and furthermore that oxidation of (IV) yields a ketone devoid of optical activity. Two obvious explanations of this second result are (*a*) that the addition of deuterium to (I) proceeds symmetrically (suggesting that diastereoisomerides which contain as one centre of asymmetry the group $CHDRR_1$ do not differ greatly in the energy required for their formation) and (*b*) that the addition of deuterium to (I) takes place dissymmetrically, as in the case of the addition of bromine, and that an asymmetric centre of the type $CHDRR_1$ is incapable of giving rise to measurable optical activity. A further explanation has since been suggested to us, namely, that the ketone derived from (IV), unlike the dibromo-ketone, may possess little optical stability and may be easily racemised under the conditions of the final oxidation and isolation. Presumably such racemisation would proceed by way of enolisation of the ketone; this we regard as unlikely, since the oxidation is effected in acid solution, *i.e.*, under conditions unfavourable to the keto $\longrightarrow$ enol change.

The object of the present work was to determine whether reduction of similar compounds by deuterium would lead to solid diastereoisomerides sufficiently different in physical properties to be separated by fractional crystallisation, and distinguishable by methods in common use in organic chemistry. A process has been devised whereby, if separation takes place during the fractional crystallisation of the mixture of diastereoisomerides, one centre of asymmetry may be destroyed, leaving a compound of the type $CHDRR_1$ in which one enantiomorph is in excess of the other, and which, if compounds of this type are capable of it, should possess a measurable optical activity.

In a preliminary experiment, optically pure (—) phenylvinylcarbinol, prepared by Duveen's method (in course of publication, preliminary note, *Compt. rend.*, 1938, **206**, 1185), was converted into its *p*-xenylurethane and reduced with both hydrogen and deuterium. As will be observed from scheme I, reduction with deuterium leads to the formation of phenyl-αβ-dideuteroethylcarbinyl *p*-xenylurethane having two asymmetric centres, the second due to a configuration of the type $CHDRR_1$; the latter compound should exist as a mixture of diastereoisomerides.

Scheme I.



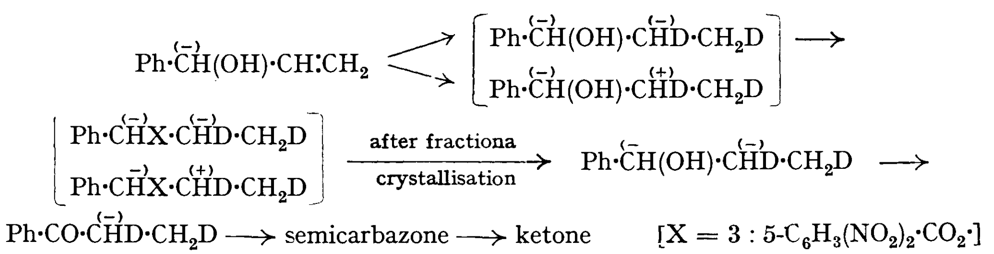
$$\underset{X}{\overset{(+)}{C}}HPh\cdot\overset{(-)}{C}HD\cdot CH_2D \longleftarrow \underset{X}{\overset{(+)}{C}}HPh\cdot CH{:}CH_2 \longrightarrow \underset{X}{\overset{(+)}{C}}HPh\cdot\overset{(+)}{C}HD\cdot CH_2D$$

$(X = p\text{-}C_6H_5\cdot C_6H_4\cdot NH\cdot CO_2.)$

An attempt was made to separate these compounds by fractional crystallisation from benzene–light petroleum, the melting point of each crop being taken in a carefully standardised apparatus capable of reproducing successive determinations on the same material to an accuracy of ± 0·1°. As the crystallisation proceeded, a slight rise in the melting points of successive crops was noted, which ceased after the third recrystallisation (see Table II). However, the same behaviour was noticed during the fractional crystallisation of phenylethylcarbinyl *p*-xenylurethane, and the conclusion was reached that the slight rise in melting point was not more than could be accounted for by the removal of traces of impurity during the process. Solubility determinations on the final products of fractional crystallisation of both the deuterium-reduced and the hydrogen-reduced material led to the same conclusion (Table II). If the group of the type $CHDRR_1$ were capable of contributing to the total rotatory power of the molecule, and any separation had taken place during the process of crystallisation, it might be expected that the rotatory dispersion of the more soluble and the less soluble crops of phenyl-αβ-dideuteroethylcarbinyl *p*-xenylurethane should differ, each displaying anomalous rotatory dispersion to some extent. The optical rotatory powers, determined in benzene solution with a modern instrument capable of an accuracy of ± 0·01° when the brighter lines of mercury and sodium vapour are used, are given in Table I, and within the limits of accuracy of the determinations show no significant difference. Young and Porter (*J. Amer. Chem. Soc.*, 1937, **59**, 328) have reported a slight diminution in rotatory power when hydroxylic hydrogen is replaced by deuterium in methylhexylcarbinol. But as the determinations were made for light of one wave-length only and the laboratory detail was scanty, it is difficult to estimate the value of the result.

As the failure to detect any separation during crystallisation may be due to chance formation of mixed crystals, as sometimes happens in the ordinary methods of resolution, it was decided to repeat the crystallisation process on another compound, and to extend the investigations according to scheme (II).

Scheme II.



$$\mathrm{Ph{\cdot}\overset{(-)}{C}H(OH){\cdot}CH{:}CH_2} \begin{array}{c}\nearrow\\ \searrow\end{array} \left[\begin{array}{l}\mathrm{Ph{\cdot}\overset{(-)}{C}H(OH){\cdot}\overset{(-)}{C}HD{\cdot}CH_2D}\\ \mathrm{Ph{\cdot}\overset{(-)}{C}H(OH){\cdot}\overset{(+)}{C}HD{\cdot}CH_2D}\end{array}\right] \longrightarrow$$

$$\left[\begin{array}{l}\mathrm{Ph{\cdot}\overset{(-)}{C}HX{\cdot}\overset{(-)}{C}HD{\cdot}CH_2D}\\ \mathrm{Ph{\cdot}\overset{-)}{C}HX{\cdot}\overset{(+)}{C}HD{\cdot}CH_2D}\end{array}\right] \xrightarrow[\text{crystallisation}]{\text{after fractiona}} \mathrm{Ph{\cdot}\overset{(-}{C}H(OH){\cdot}\overset{(-)}{C}HD{\cdot}CH_2D} \longrightarrow$$

$$\mathrm{Ph{\cdot}CO{\cdot}\overset{(-)}{C}HD{\cdot}CH_2D} \longrightarrow \text{semicarbazone} \longrightarrow \text{ketone} \qquad [\mathrm{X = 3:5\text{-}C_6H_3(NO_2)_2{\cdot}CO_2{\cdot}}]$$

Optically pure (—) phenylvinylcarbinol was reduced with deuterium to (+) phenyl-αβ-dideuteroethylcarbinol, and a search was made for a crystalline ester of the latter from which the carbinol could be readily recovered; the (+) hydrogen phthalic and the (+) *p*-nitrobenzoic esters could not be induced to crystallise, but (—) phenylethylcarbinyl 3 : 5-dinitrobenzoate proved a well-crystalline substance, m. p. 52—53°, which was smoothly hydrolysed by warm alcoholic potash.

(+) Phenyl-αβ-dideuteroethylcarbinol (15 g.) was converted into the 3 : 5-*dinitrobenzoic* ester (31 g.), which was recrystallised from warm ethyl alcohol three times, leaving the less soluble fraction of the ester (14·5 g.). This fraction was reconverted into the alcohol (5·6 g.), $\alpha_{5461}^{17^\circ} + 8{\cdot}43^\circ$ (*l*, 0·5), from which phenyl αβ-dideuteroethyl ketone (4·2 g.), m. p. 19·5°, was obtained by oxidation with chromic anhydride in acetic acid. This ketone showed a small dextrorotation, $\alpha_{5461}^{19^\circ} + 0{\cdot}14^\circ$ (*l*, 0·25), but this was probably due to a trace of unoxidised alcohol. The ketone was therefore converted into the semicarbazone (5·6 g.), m. p. 175°, which showed no trace of optical activity either in acetic acid (*c*, 5·2; *l*, 2) or in acetone solution (*c*, 1; *l*, 4). The semicarbazone was too sparingly soluble in other solvents to enable further determinations of rotatory power to be made. The mother-liquors from the semicarbazone preparation, after addition of water and cooling had induced the crystallisation of the last traces of semicarbazone, were extracted with ether and this extract was dried and concentrated. This showed a slight dextrorotation, $\alpha_{5461}^{18^\circ} + 0{\cdot}04^\circ$ ($\pm$ 0·01°), which must have been due to unchanged carbinol, as the semicarbazone is insoluble in ether.

Phenyl αβ-dideuteroethyl ketone recovered from the semicarbazone had zero rotation (α ± 0·01°; *l*, 0·25).

The series of reactions described above (scheme II) constitute a synthesis and simultaneous method of resolution of a saturated ketone by crystallisation of the mixed diastereoisomerides derived from the corresponding carbinols, followed by the destruction of the original centre of asymmetry by oxidation. This method might be expected to be more efficient than the usual methods of resolution, which depend for their success on the crystallisation of salts of optically active acids or bases. This view arises from the fact that when asymmetric syntheses of high efficiency have been reported, the asymmetric directing group has always been in covalent union with, and adjacent to, the group under synthesis (cf. Kenyon, Partridge, and Phillips, J., 1937, 207).

The only apparent weakness in the method appears to be the chance formation of mixed crystals of the diastereoisomerides, making their separation by methods of crystallisation difficult even though they may be distinct chemical individuals. This phenomenon is rare, however, with unsolvated covalent organic compounds. It may be assumed, therefore, that as fractional crystallisation has been applied to two different derivatives of the carbinol without any indication of separation in either case, the second asymmetric group $\mathrm{CHDRR_1}$ does not cause sufficient molecular diastereoisomerism to prevent the compound behaving as a homogeneous crystalline substance.

Even if it were possible to resolve a substance containing such a group, it appears doubtful if it would display measurable optical activity, since the most soluble and the least soluble fractions of (+) phenyl-αβ-dideuteroethylcarbinyl *p*-xenylurethane appeared to be identical with each other and with (+) phenylethylcarbinyl *p*-xenylurethane in rotatory dispersion over the visible range, showing that the contribution of the group $\mathrm{CHDRR_1}$

to the total rotatory power of the molecule was immeasurable over this range of wavelengths.

Previous work of the authors (*loc. cit.*) and the results obtained in an analogous case by Erlenmeyer, Fischer, and Baer (*Helv. Chim. Acta*, 1937, **20**, 1012) have led to the conclusion that the molecular diastereoisomerism due to the group $CHDRR_1$ is insufficient to result in unsymmetrical synthesis of the latter. The work of Clemo and McQuillen (J., 1936, 808) on α-pentadeuterophenylbenzylamine suggests that the second type of group $CX_HX_DRR_1$, where $X_H$ and $X_D$ are phenyl and pentadeuterophenyl respectively, is capable not only of resolution by the ordinary method, but also of displaying a small rotatory power, $[\alpha]^{16°}_{5893}$ − 5·7° and + 5·0° respectively. On the other hand, Erlenmeyer and Schenkel (*Helv. Chim. Acta*, 1936, **19**, 1169) were unable to detect any optical activity in the analogous compound phenylpentadeuterophenylacetic acid prepared from *l*-phenylbromoacetic acid. Similarly, McGrew and Adams (*J. Amer. Chem. Soc.*, 1937, **59**, 1497) record the failure to observe any optical activity in a case where the groups $X_H$ and $X_D$ were aliphatic. Their method depended on the reduction of highly active *l*-$\Delta^{\alpha}$-pentinen-γ-ol with deuterium. As the last two cases were independent of the uncertainties of a resolution, they offer positive evidence of the optical inactivity of the asymmetric group.

Thus, except in the outstanding case of α-pentadeuterophenylbenzylamine, the evidence suggests that the differences which exist between hydrogen and deuterium as substituents in the systems $CHDRR_1$ and $CX_HX_DRR_1$ are insufficient to give rise to measurable optical activity.

TABLE I.

*Specific Rotations in Benzene Solution at* 20° (*l*, 2).

| | Phenylethylcarbinyl *p*-xenylurethane. | | Phenyl-αβ-dideuteroethylcarbinyl *p*-xenylurethane. | |
|---|---|---|---|---|
| | From (+) phenylethylcarbinol (*c*, 2·616). | By reduction (*c*, 2·514). | Least sol. (*c*, 2·580). | Most sol. (*c*, 2·519). |
| $[\alpha]_{6438}$ | — | — | + 95·9° | + 97·7° |
| $[\alpha]_{5893}$ | + 119·1° | + 122·9° | + 119·9 | + 121·1 |
| $[\alpha]_{5780}$ | + 128·7 | + 129·7 | + 129·5 | + 128·6 |
| $[\alpha]_{5461}$ | + 147·4 | + 150·4 | + 148·8 | + 148·5 |
| $[\alpha]_{5086}$ | — | — | + 179·3 | + 180·2 |
| $[\alpha]_{4800}$ | — | — | + 213·0 | + 213·2 |
| $[\alpha]_{4678}$ | — | — | + 223·6 | + 227·3 |
| $[\alpha]_{4358}$ | + 289·9 | + 292·2 | + 288·8 | + 285·2 |

TABLE II.

*Solubilities and Melting Points.*

| | Phenylethylcarbinyl *p*-xenylurethane. | | Phenyl-αβ-dideuteroethylcarbinyl *p*-xenylurethane. | |
|---|---|---|---|---|
| | Less sol. crops. | More sol. crops. | Less sol. crops. | More sol. crops. |
| G. in 25 c.c. | 0·1063 | 0·1119 | 0·1114 | 0·1218 |
| | 0·1061 | 0·1125 | 0·1116 | 0·1226 |
| *S* | 4·25 | 4·49 | 4·46 | 4·89 |
| M. p. | 138·6—138·9° | 138·4—138·6° | 137·9—138·4° | 136·7—137·5° |

Solubility *S* (g. per l.) in benzene–*cyclo*hexane mixture (1 : 4 by vol.) at 25·0°.

## EXPERIMENTAL.

In an exploratory experiment, (−) phenylvinylcarbinol (6·7 g.), prepared by Duveen's method (*loc. cit.*), was added to *p*-xenylcarbimide (10 g.) and kept at 98° for 20 minutes. The reaction mixture, which set solid on cooling, was extracted with benzene. (+) Phenylvinylcarbinyl *p*-xenylurethane (13 g., m. p. 134·5°) separated on addition of light petroleum. This on recrystallisation had m. p. 134·8—135·2°. Rotatory powers in benzene solution and comparative data with Duveen's results are in Table III.

*Reduction with Deuterium.*—(+) Phenylvinylcarbinyl *p*-xenylurethane (10 g.) in ether (250 c.c.) was mixed with the platinum oxide catalyst (0·1 g.) (Adams, Vorhees, and Shriner, " Organic Syntheses," **8**, 92) in a vessel which could be shaken when connected with a supply of deuterium prepared from 98% deuterium oxide (Coppock and Partridge, *loc. cit.*) under **2**

TABLE III.

| | (−)Phenylvinylcarbinol. | Phenylvinylcarbinyl *p*-xenylurethane (1). | Phenylethylcarbinyl *p*-xenylurethane (A) prepared from (1), compared with specimen prepared from phenylethylcarbinol obtained by reduction of (−) phenylvinylcarbinol (B) (Duveen). | |
|---|---|---|---|---|
| | | | A. | B. |
| | $[\alpha]^{18^\circ}$ ($l$, 0·5). | $[\alpha]^{20^\circ}$ ($l$, 2; $c$, 2·602). | $[\alpha]^{20^\circ}$ ($l$, 2; $c$, 2·514). | $[\alpha]^{20^\circ}$ ($l$, 2; $c$, 2·616). |
| λ 5893 ............ | − 4·50° | — | — | — |
| | − 4·25 * | + 107·1° | + 122·9° | + 119·1° |
| λ 5780 ............ | − 4·66 | + 112·9 | + 129·7 | + 128·7 |
| λ 5461 ............ | − 5·64 | — | — | — |
| | − 5·65 * | + 131·1 | + 150·4 | + 147·4 |
| λ 4358 ............ | −14·06 | + 257·8 | + 292·2 | + 289·9 |
| B. p. | 111°/18 mm. | — | — | — |
| M. p................ | — | + 134·5° | 138·3—138·7° | 138·3—138·7° |
| | | | mixed m. p. 138·2—138·5° | |
| $n_D^{19^\circ}$ ............... | 1·5398 | — | — | — |

* Values recorded by Duveen (*loc. cit.*).

atms. pressure. After an induction period of about 10 minutes the reduction proceeded very rapidly for about 15 minutes, during which time about 375 c.c. (the calculated amount) were absorbed. The pressure continued to fall, however, for about 1½ hours and a further 50 c.c. of deuterium were absorbed. This phenomenon has been previously observed by us during deuterium reductions, but does not appear to take place in similar catalytic reductions with hydrogen.

After removal of the catalyst, light petroleum (1 l.) was added to the ethereal solution; (+) *phenyl-αβ-dideuteroethylcarbinyl* p-*xenylurethane* then separated in long needles, m. p. 137·3—137·5°. Four recrystallisations from benzene–light petroleum (b. p. 60—80°) (1 : 2) yielded needles (2·8 g.), m. p. 137·9—138·4° (Found: C, 80·0; H + D, 6·6. $C_{22}H_{19}D_2O_2N$ requires C, 79·3; H + D, 6·9%). The solubilities are in Table II. Careful recrystallisation of second crops produced a further 2 g. of material of approximately equal purity, m. p. 138·0—138·3°. A collection of material was made from the mother-liquors, yielding crystals (2 g.) m. p. 136·5—137·5° (solubility in Table II, rotations in Table I).

*Hydrogenation.*—(+) Phenylvinylcarbinyl *p*-xenylurethane (5·5 g.) in ether (125 c.c.) was reduced with hydrogen in the same apparatus; hydrogen (190 c.c.) at 2 atms. pressure was absorbed during the reaction, which was complete in 30 minutes. After removal of the catalyst, light petroleum was added to the warm ethereal solution; (+) phenylethylcarbinyl *p*-xenylurethane then separated in large rectangular prisms (3·3 g.), m. p. 138·3—138·7° (Found: C, 80·0; H, 6·3. Calc. for $C_{22}H_{21}O_2N$ : C, 80·0; H, 6·3%). Mixed with an authentic specimen, it had m. p. 138·2—138·5°. The rotatory powers are in Table III.

In order to determine the degree of utility of the melting-point and solubility methods in following any separation during the recrystallisations of the dideutero-compound it was decided to repeat the recrystallisation process with phenylethylcarbinyl *p*-xenylurethane. The melting points and solubilities are in Table II.

Although phenylvinylcarbinyl *p*-xenylurethane is readily hydrolysed by hot dilute hydrochloric acid, phenylethylcarbinyl *p*-xenylurethane proved to be unexpectedly difficult to hydrolyse. The material remained unchanged in boiling 3N-sodium hydroxide or -hydrochloric acid. In an attempt to hydrolyse it, phenylethylcarbinyl *p*-xenylurethane (4·8 g.) was heated with 30% (vol.) sulphuric acid in a paraffin-bath at 180°. Carbon dioxide was evolved, leaving a crystalline residue. After cooling and dilution with water, this residue was removed by filtration (3·0 g.) (theory, calculated as 4-aminodiphenyl sulphate, 3·1 g.). From this, 4-aminodiphenyl was obtained, which crystallised in pale yellow needles, m. p. 53—54°, from ether–light petroleum. From the dried ethereal extract of the filtrate, crystals of unchanged phenylethylcarbinyl *p*-xenylurethane (0·4 g.) separated. The crude material had m. p. 134°, $[\alpha]_{5893}$ + 112·4° ($c$, 2·02; $l$, 2).

After evaporation of the ether, and removal of the last traces of unchanged urethane by addition of light petroleum, the residual oil had a slight dextrorotation in petroleum solution, but on fractional distillation was found to consist of a heavy oil, b. p. 200°/20 mm., and a fraction, b. p. 70—80°/20 mm., showing that hydrolysis had led to decomposition of the carbinyl residue.

*Second Series of Experiments.*—These were made with a larger quantity of starting material according to scheme II. (−) Phenylvinylcarbinol (15 g.) (b. p. 107°/16 mm.; $\alpha_{5893}^{19·5^\circ}$ − 4·31°, *l*, 0·5) was catalytically reduced with deuterium (2·5 l. at N.T.P. absorbed). The reduction was carried out within an hour of the preparation of the deuterium.

*Preparation of the deuterium.* Deuterium oxide (10 g. of 99·6%) was added dropwise to 4% sodium amalgam (freshly prepared) and gently warmed. Deuterium was evolved smoothly and collected over water. A trap containing concentrated sulphuric acid was interposed between the gas holder and the reaction vessel to prevent back-diffusion of water vapour into the latter.

*Phenyl-αβ-dideuteroethylcarbinyl* 3 : 5-*Dinitrobenzoate.*—(+) Phenyl-αβ-dideuteroethylcarbinol (15 g., b. p. 207°) in pyridine (15 g.) was mixed with 3 : 5-dinitrobenzoyl chloride (25·5 g.) in small portions, the temperature being kept below 75°. The pasty mass, which still retained its light colour, was then warmed at 75° for ½ hour and subsequently treated with cold dilute sodium carbonate solution, followed by dilute hydrochloric acid, and the ester extracted with ether. The dried ethereal extract was evaporated to dryness and on trituration with a little petrol the residue (31 g.) solidified at once. *Phenyl-αβ-dideuteroethylcarbinyl* 3 : 5-*dinitrobenzoate* was recrystallised from 96% alcohol at 45°, the liquors being placed in a refrigerator for a time before filtration. The third crop (14·5 g.) had m. p. 52—53° and consisted of large colourless plates. $[\alpha]_{5893}$ − 37·7°, $[\alpha]_{5780}$ − 39·24°, $[\alpha]_{5461}$ − 45·57°, $[\alpha]_{4358}$ − 98·32° (*c*, 2·929; *l*, 2) (Found: N, 8·2. $C_{16}H_{12}D_2O_6N_2$ requires N, 8·4%). This (14·5 g.) immediately developed an intense violet coloration on addition of potassium hydroxide (4 g.) in ethyl alcohol (50 c.c.), but after ½ hour's heating on a steam-bath and subsequent steam-distillation (+) phenyl-αβ-dideuteroethylcarbinol was obtained colourless and in good yield (5·6 g.), b. p. 207°; $\alpha_{5893}$ + 7·04°, $\alpha_{5780}$ + 7·45°, $\alpha_{5461}$ + 8·43°, $\alpha_{4358}$ + 14·11° (*l*, 0·25; *t*, 77°).

The (+) carbinol (5·6 g.) was mixed with glacial acetic acid (30 c.c.), and chromic anhydride (4 g.) added in small portions at a rate sufficient to keep the mixture at 75—80°. Sodium hydroxide solution in excess was then added, and the mixture steam-distilled. The distillate was salted with potassium carbonate and extracted with ether; from the extract, phenyl αβ-dideuteroethyl ketone (4·2 g.) crystallised in colourless plates, m. p. 19·5°, b. p. 208°, having $\alpha_{5893}$ + 0·10°, $\alpha_{5780}$ + 0·14°, $\alpha_{5461}$ + 0·24° (*l*, 0·25; *t*, 20°). From this (4·2 g.), the semicarbazone of phenyl αβ-dideuteroethyl ketone (5·3 g.), m. p. 175°, was prepared, having α ± 0·01° in glacial acetic acid (*c*, 5·25; *l*, 2) and also in acetone (*c*, 1·0; *l*, 4). Mixed with the semicarbazone of phenyl ethyl ketone, it had m. p. 175°. A further crop (0·3 g.), m. p. 174°, α ± 0·01° in acetic acid (*c*, 1·0; *l*, 2) and in acetone (*c*, 1·1; *l*, 2), was obtained on cooling and dilution with water.

The mother-liquors from this preparation were heavily salted with potassium carbonate and twice extracted with ether; the dried ethereal extract, concentrated to 5 c.c., had $\alpha_{5461}^{18°}$ + 0·04° (*l*, 0·25).

The phenyl αβ-dideuterethyl ketone recovered by hydrolysis of the semicarbazone with hot dilute sulphuric acid, followed by steam-distillation, had zero optical rotation, α ± 0·01° (*l*, 0·25; *t*, 18°), m. p. 19·5°.

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BATTERSEA POLYTECHNIC, LONDON, S.W. 11. [*Received, May* 23*rd*, 1938.]