"undecomposed fraction" of propene-3-*d* was found to have the same deuterium content as the original propene-3-*d*. These results indicated that the parent hydrocarbon which is recovered after pyrolysis is not exclusively the original unchanged material but includes substantial amounts of synthetic material. The free radical mechanism explains these results satisfactorily. The data confirm previous findings that *n*-butyl participates more actively in butane production than *s*-butyl.

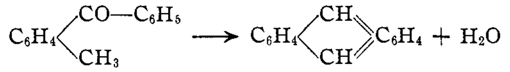
EVANSTON, ILLINOIS RECEIVED APRIL 10, 1950

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY]

Deuterium Tracers in the Elbs Reaction

BY CHARLES D. HURD AND JULIAN AZORLOSA

Two groups of workers[1] preceded Elbs in studying the thermal decomposition of *o*-methylbenzophenones, but it was Elbs[2] who made the first extensive study, in consequence of which the behavior is known as the Elbs reaction. In the simplest example, *o*-methylbenzophenone changes on refluxing into anthracene and water

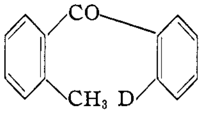


$$C_6H_4{<}\begin{matrix}CO-C_6H_5\\CH_3\end{matrix} \longrightarrow C_6H_4{<}\begin{matrix}CH\\CH\end{matrix}{>}C_6H_4 + H_2O$$

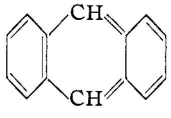
No further important study of this reaction was made for four decades, but between 1929–1935 several investigators made important contributions.

Morgan and Coulson[3] found that the low yields reported by Elbs could be increased considerably by removing the anthracene derivative at intervals from the reaction zone. Many polynuclear hydrocarbons containing the anthracene skeleton have been synthesized[4] by means of the Elbs reaction.

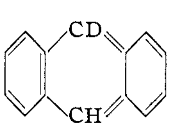
Any mechanism of the Elbs reaction must explain the disappearance of the carbonyl oxygen and the appearance of a hydrogen atom at the 9-position in anthracene. Obviously, the hydrogen must have come either from the ortho nuclear position or from the methyl group, since these were the only locations involving any loss of hydrogen. To gain insight into this question, benzophenones were synthesized in the present investigation which contained deuterium in an ortho nuclear position. 2-Methylbenzophenone-2'*d* (I) would conceivably give rise to anthracene itself (II), anthracene-9*d* (III) or anthracene-1*d* (IV).



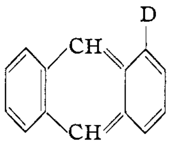
I



II



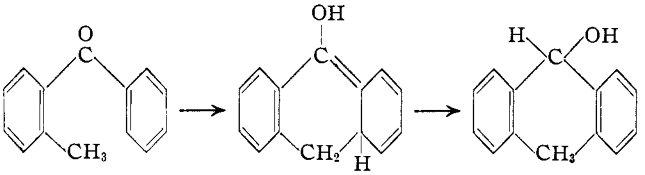
III



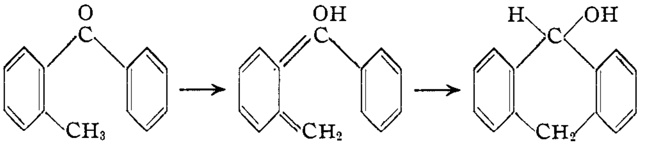
IV

Since heavy water would be formed in the production of II but not of III or IV, analysis of the evolved water for presence or absence of deuterium would provide a clue as to the course of reaction. Only one of the three possible reaction products shows deuterium at position 9. Hence oxidation of the anthracene to anthraquinone would serve as check on the previous observation, since if this operation caused loss of deuterium content in the quinone and formation of heavy water, it would prove that deuterium was at position 9 in the hydrocarbon molecule.

Three courses have been suggested for the route of the Elbs reaction. Fieser's[5] proposal involves an intramolecular 1,4-addition of the aliphatic (methyl) group to the opposite conjugated system of the ketone, thus making the first step one of cyclization. A tautomeric shift gives rise to dihydroanthrol, from which anthracene results by dehydration or anthrone by dehydrogenation.



Cook[6] also proposed dihydroanthrol as intermediate but he favored tautomerism as the initial step followed by 1,4-addition of the aromatic (phenyl) group to the opposite conjugated enolic system.



Use of an ortho deuterium atom in the ketone would not distinguish between these two mechanisms, since the same dihydroanthranol-*d* would arise from either one. Anthracene-9*d* would result by dehydration of this compound.

Morgan[7] made a third proposal to account not

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[1] Behr and Van Dorp, *Ber.*, **6**, 753 (1873); **7**, 16 (1874); Ador and Rilliet, *ibid.*, **11**, 399 (1878).

[2] Elbs and co-workers, *ibid.*, **17**, 2847 (1884); **18**, 1797 (1885); **19**, 408 (1886); *J. prakt. Chem.*, **33**, 180 (1886); **35**, 465 (1887); **41**, 1, 121 (1890).

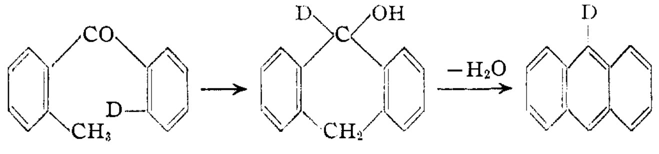
[3] Morgan and Coulson, *J. Chem. Soc.*, 2203, 2551 (1929).

[4] Clar, *Ber.*, **62**, 350, 1378, 3021 (1929); **63**, 2967 (1930); Cook, *J. Chem. Soc.*, 456 (1932); Fieser and Seligman, THIS JOURNAL, **57**, 228, 942 (1935).

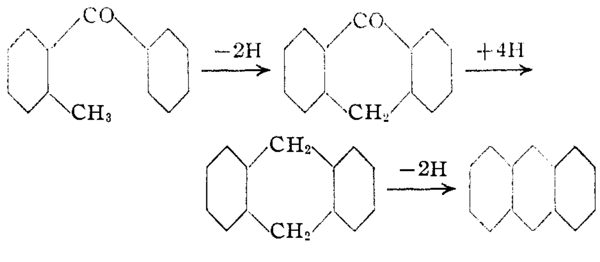
[5] Fieser and Dietz, *Ber.*, **62**, 1827 (1929).

[6] Cook, *J. Chem. Soc.*, 487 (1931).

[7] Morgan and Coulson, *ibid.*, 2328 (1931).



only for the anthracenes formed but also for the anthrones which he discovered. He regarded dehydrogenation to anthrone as the first step, then hydrogenation to anthracene dihydride, and finally dehydrogenation to anthracene. In support of this proposal, he found a small yield of tetramethylanthrone and none of the corresponding anthracene on refluxing 2,4,5-trimethylphenyl 3,4-dimethylphenyl ketone. Clar's[4] synthesis of pentacene dihydride by pyrolysis of 2,4-dimethyl-5-benzoylbenzophenone was cited in support of the anthracene dihydride as intermediate. Morgan's assumption that the anthrone is the precursor of the anthracene may be tested by the deuterium approach, since it is obvious that on this basis the deuterium would be separated from the molecule during pyrolysis.



2,5,4′-Trimethylbenzophenone-2′*d* and 2,5-dimethylbenzophenone-2′*d* were selected for study, since the non-deuterium analog of the former gave good yields[3] of dimethylanthracene on pyrolysis. Two methods were tested for inserting deuterium, one involving the Friedel–Crafts reaction on toluene-*d* and the other involving decarboxylation of a —COOD group.

The best of several methods tried for the conversion of *m*-tolylmagnesium bromide into toluene-3*d* was by reaction with sulfuric acid-d_2: $2ArMgBr + D_2SO_4 \rightarrow 2ArD + MgBr_2 + MgSO_4$. Yields were about 50% of theoretical, but an 85% yield of toluene-2*d* was realized starting with the *o*-tolyl isomer. For experience ordinary sulfuric acid was used first. It should be appreciated that this decomposition differs from conventional hydrolyses wherein an excess of water is used, since here the Grignard reagent was necessarily in excess so as to consume the deuterium compound completely. The use of water or hydrogen chloride (models for D_2O or DCl) was less satisfactory, yields being 12–35%. The deuterium content of the toluene-3*d* was only 0.360 atom per molecule instead of the expected 0.995. The water-d_2 taken for the synthesis of the sulfuric acid-d_2 was 99.5% purity. The only source of hydrogen atoms, other than from the *m*-tolyl radical, was the butyl ether taken as solvent.

Conversion of the toluene-3*d* into 2,5,4′-trimethylbenzophenone-2′*d* by reaction with 2,5-dimethylbenzoyl chloride and aluminum chloride resulted in almost complete retention of the deuterium, since 0.355 deuterium atom was found per molecule of ketone. This retention is in contrast to the loss reported[8] in the formation of benzoic-d_3 acid from benzene-d_6, carbamyl chloride and aluminum chloride. In the present study another ketone containing deuterium also was prepared, namely, 1-naphthyl phenyl-2*d* ketone starting with toluene-2*d*. Presumably the same deuterium loss occurs in the Grignard synthesis of toluene-2*d*, since after it was oxidized by permanganate to benzoic-2*d* acid and the latter converted first to benzoyl-2*d* chloride and then to 1-naphthyl phenyl-2*d* ketone by reaction with naphthalene, only 0.324 deuterium atom per molecule was found.

Deuterium loss was suffered also when the ketone was made by the decarboxylation approach, but the loss was much less. 2-(2,5-Dimethylbenzoyl)-benzoyl chloride was hydrolyzed with water-d_2. The acid-*d* thus formed showed 0.630 deuterium atom per molecule by analysis. The anhydrous acid was decarboxylated by heating at 260–270° in the presence of a little of the copper salt of the same acid and the 2,5-dimethylbenzophenone-2′*d* formed revealed a deuterium content of 0.651. No explanation is at hand for the anomalous, slightly higher deuterium content in the last compound.

Several preliminary experiments with 2,5-dimethylbenzophenone and 1-naphthyl 2,5-dimethylphenyl ketone showed that whereas the yield of water obtained in the Elbs reaction was 50–90%, the corresponding yield of the anthracene compound was only 16–21%. Also, from 0.062 mole of the latter ketone there was formed 0.004 mole of an acid showing some hydrolytic cleavage of the ketone at the high reaction temperature: $RCOR' + H_2O \rightarrow RCOOH + R'H$. This type of hydrolysis was noted also by Fieser and Dietz.[5] In all experiments the reaction produces colored by-products, ranging in color from blood red to dark brown.

Following pyrolysis of the deuterium-containing ketones, the water and anthracene derivatives were isolated and purified and some of the anthracene was oxidized to the corresponding quinone. Samples of the hydrocarbon and its quinone were burned and the water collected. Analysis of the latter by the density method made it possible to calculate the relative number of deuterium atoms per molecule in the several products. Results were as follows. The sequence of compounds: 2,5,4′-trimethylbenzophenone-2′*d*, 2,6-dimethylanthracene-*d*, 2,6-dimethylanthraquinone-*d*, and the water produced in pyrolysis of the ketone showed these D atoms per molecule: 0.355, 0.240, 0.184 and 0.0036. On a relative basis, these values become 1.000, 0.676, 0.518 and 0.010.

Similarly, this sequence was observed: 2,5-dimethylbenzophenone-2′*d*, 2-methylanthracene-*d*, 2-methylanthraquinone-*d*: 0.651, 0.514 and 0.399 D atom per molecule, or in relative terms, 1.000, 0.790 and 0.613.

The above data show that only one per cent. of

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(8) Erlenmeyer and co-workers, *Helv. Chim. Acta*, **19**, 336, 546 (1936).

the deuterium atoms in the original ketone appears in the water formed in the Elbs reaction. Evidently, therefore, the source of the hydrogens in this water must be the ortho methyl group and not the ortho nuclear position. Since the latter position is displaced in the formation of the anthracene, this H or D atom must have wandered to the 9-position of the anthracene.

The fact that less deuterium per molecule was found in the anthracene than in the original ketone suggests deuterium–hydrogen exchange reactions between the anthracene-9*d* and the by-products of the Elbs reaction other than water. This suggestion is supported by the relatively low yields of anthracene and the known reactivity of the 9,10-positions of anthracene. In the formation of the anthracene the wandering ortho nuclear atom may be either deuterium or hydrogen. Thus part of the deuterium should persist in the anthraquinone, which was observed. The fact that considerably more than half of it persisted is evidence for the greater reactivity of ortho hydrogen over ortho deuterium, showing the more facile formation of IV than III.

These results are compatible with either Cook's or Fieser's mechanisms, but do appear to eliminate Morgan's representation at least as a generality, since by his proposal, water rich in deuterium content would have been produced.

A final experiment was performed showing that no intermolecular process was observable for this reaction. Ordinary 2,5-dimethylbenzophenone was pyrolyzed in the presence of 1-naphthyl phenyl-2*d* ketone at a temperature of 330–340°; 2-methylanthracene was isolated in 20% yield. A sample of the latter was burned to water and its deuterium content determined; it was the same as the standard water within experimental error. This showed that the hydrogen atom ortho to the keto group in a diaryl ketone was not active enough under the conditions of the Elbs reaction to add to the conjugated system of the enolized 2,5-dimethylbenzophenone (Cook's mechanism), if the latter actually existed. Furthermore, this result demonstrates that the ring hydrogen atoms of diaryl ketones will not exchange at temperatures up to 340°.

Experimental Part

Preparation of Arenes from Arylmagnesium Bromide. Sulfuric Acid.—To the stirred Grignard solution made from 96 g. of *m*-bromotoluene, 14 g. of magnesium and 200 g. of butyl ether was added slowly 24 g. of 98% sulfuric acid. Stirring was continued for half an hour after addition. Distillation of the product at 50 mm. into a receiver at −15° and redistillation (b.p. 109–119°) through an efficient column gave 24.0 g. of toluene, or 53% based on the total hydrogen of the sulfuric acid.

Similarly, the Grignard solution from 100.7 g. of bromobenzene when decomposed by 24 g. of sulfuric acid yielded 25.2 g. (64%) of benzene.

Sulfuric Acid-d_2.—About 35 g. of sulfur trioxide was distilled from fuming sulfuric acid into a 50-ml. flask equipped by a standard taper connection to a 20-cm. column packed with glass helices. This column was attached, also by glass connections, to a 40-ml. receiver whose outlet tube was attached to a calcium chloride tube. The receiver with two glass plugs was tared for weighing, then 28.83 g. of sulfur trioxide was distilled into it. The outlet tube of the receiver was then connected by glass joints to another 40-ml. flask containing 7.21 g. of deuterium oxide (99.5%, sp. gr. 1.1074, supplied by the Ohio Chem. and Mfg. Co., Cleveland, Ohio). The trioxide was poured drop by drop into the water-d_2 with cooling after each addition, finally making 36.04 g. of sulfuric acid-d_2.

Toluene-3*d* was prepared by adding 22 g. of this acid during two hours to the Grignard solution prepared from 90 g. of *m*-bromotoluene, 13 g. of magnesium and 250 g. of butyl ether as described above. The distilled toluene–ether mixture was washed with dilute sodium hydroxide, dried over calcium chloride, and distilled through a 60-cm. column packed with glass helices. To give a sharper boiling fraction the 21 g. of toluene-3*d* was mixed with 50 ml. of *n*-pentyl ether and refractionated, the reflux ratio being about 25 to 1. The final yield of toluene-3*d*, b.p. 109–110.5°, was 19.7 g. or 49% of the theoretical based on the total deuterium.

Toluene-2*d* was prepared similarly but the 12.4 g. of sulfuric acid-d_2 was added during 2.5 hours. The Grignard was made in butyl ether from 60 g. of *o*-bromotoluene. Only one fractionation was required to yield a sharp boiling fraction, b.p. 110–111°. This represents an 85% yield.

Preparation of Ketones. 2,5,4′-Trimethylbenzophenone-2′*d*.—2,5-Dimethylbenzoyl chloride, b.p. 126–128° (28 mm.), was prepared starting with *p*-xylene of m.p. 12.5–13.0°. Xylene was converted into 2,5-dimethylacetophenone, which in turn was changed into 2,5-dimethylbenzoic acid by use of sodium hypochlorite. Reaction of the acid with thionyl chloride completed the synthesis.

Twenty-seven grams of anhydrous aluminum chloride and 60 ml. of carbon disulfide were placed in a 3-neck, 500-ml. flask equipped with stirrer, dropping funnel and condenser. A solution of 27.1 g. of 2,5-dimethylbenzoyl chloride and 15.0 g. of toluene-3*d* in 40 ml. of carbon disulfide was slowly added to the stirred suspension of aluminum chloride over a period of two hours. The mixture was then refluxed for another two hours. On cooling, it was poured slowly into 75 ml. of concd. hydrochloric acid and 100 g. of ice. Twenty ml. of ether was added and the two phases were separated, the water layer being extracted twice with 60-ml. portions of ether. The solution of ether and carbon disulfide was washed with dilute sodium hydroxide and dried over calcium chloride. After removal of the solvent, the remainder was distilled. The yield of product boiling at 148–160° (3 mm.) was 28 g. This was redistilled to give 26.2 g. of 2,5,4′-trimethylbenzophenone-2′*d* (b.p. 157–160° at 3 mm.) or 72%. All attempts to make this liquid product crystallize were unsuccessful.

2,5-Dimethylbenzophenone-2′*d*.—*p*-Xylene and phthalic anhydride were condensed in the presence of aluminum chloride. 2-(2,5-Dimethylbenzoyl)-benzoic acid, m.p. 148–149°, was obtained in 80–81% yield.

The acid (47.4 g.) was placed in a 250-ml. Claisen flask which was attached to a condenser and receiver. Then 80 ml. of redistilled thionyl chloride (b.p. 77–78°) was added and the mixture was refluxed for two hours. Excess thionyl chloride was removed first by heating at 60° under reduced pressure, then twice adding 30–40 ml. of dry toluene and distilling it off under diminished pressure on a steam-bath. Then the cream colored product was dissolved in 150 ml. of toluene and 4 ml. of water-d_2 (99.5% pure) was added. The mixture was stirred and heated on a steam-bath for one hour. Evolved deuterium chloride was dissolved in sodium hydroxide solution. The 2-(2,5-dimethylbenzoyl)-benzoic acid-*d* which separated on cooling was collected and recrystallized from ligroin–toluene (1:1), the flask being protected with a drying tube. Additional material was obtained by concentrating the filtrate. In all 41.6 g. (88%) of the acid-*d* was obtained.

For the decarboxylation, Daugherty's general procedure[9] was used, a 67% yield of 2,5-dimethylbenzophenone (b.p. 135–138° (3 mm.)) being obtained from ordinary 2-(2,5-dimethylbenzoyl)-benzoic acid. A 67% yield was realized also for the deuterium analog, as follows.

Forty grams of 2-(2,5-dimethylbenzoyl)-benzoic acid-*d* was placed in a 125-ml. distilling flask connected in series to a trap, a gas bubbler containing a little sulfuric acid and an aspirator pump. Any moisture was expelled by heating to 200°, and flaming the walls of the apparatus. Then 1.7 g. of the dry cupric salt of this acid was added and the mixture heated rapidly to 260–270° and maintained there for one hour. When carbon dioxide evolution ceased, the contents

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(9) Daugherty, THIS JOURNAL, **50**, 571 (1928).

were cooled and dissolved in 50 ml. of ether. The solution was washed twice with 20-ml. portions of 10% sodium hydroxide solution, then with water, dried over calcium chloride, and the ether distilled off. Distillation then yielded 22.1 g. of 2,5-dimethylbenzophenone-2′*d*, b.p. 126–129° at 2 mm. It was a liquid of light yellowish cast and did not solidify on standing.

1-Naphthyl Phenyl-2*d* Ketone.—Benzoyl-2*d* chloride was prepared by first refluxing for six hours with stirring a mixture of 19.5 g. of toluene-2*d*, 100 ml. of 10% sodium hydroxide solution, and 68 g. of potassium permanganate in 700 ml. of water. By conventional processing operations, 14.3 g. of benzoic-2*d* acid was obtained. By refluxing 14 g. of the latter with 26 ml. of thionyl chloride, a yield of 14.5 g. of benzoyl-2*d* chloride, b.p. 87–88° (22 mm.), was realized.

The 14.5 g. of acid chloride was treated in the customary manner with 13.2 g. of naphthalene and 18 g. of aluminum chloride to form 17.6 g. (73% yield) of 1-naphthyl phenyl-2*d* ketone, b.p. 207–208° (6 mm.), m.p. 70–71°. Its color was straw yellow even after redistillation.

Pyrolysis of the Ketones.—A dry, 50-ml., 2-necked reaction flask was equipped with a thermometer dipping into the reaction mass, and a column. The latter was maintained at 115–135° by an electrical heating jacket, thus preventing condensation of any water but retaining the higher boiling components. Connected to the column was a small ice-cooled trap and a calcium chloride tube was attached to the exit of the trap. The reaction mixture itself was heated by a fused salt bath of sodium nitrite and potassium nitrate.

Results are collected in Table I. The water of the reaction was freed from entrained organic matter by shaking with ether. It was established, for example, that after mixing 0.80 ml. of water and 4 ml. of ether in this manner, the volume of the water layer was still 0.80. In the deuterium experiments the water (about 0.5 ml.) was transferred into a micro distilling flask of 2-ml. capacity with 2 ml. of absolute ether, the latter being largely sucked off through a long capillary tube. After a second ether extraction, the dissolved ether was removed by boiling the water gently.

TABLE I

DATA REGARDING ELBS REACTION

Ketone[d]	G.	Reaction °C.	hr.	Water, ml.	Crude anthracenes, g.	Purified anthracenes G.	Purified anthracenes M.p., °C.
I	10.9	310–315	27	0.75	3–4	2.1	203–205
II	16.0	372–380[a]	2	.80[b]	Resinous	...	.....
III	16.4	350	8 5[c]	.5	5.0	4.0	235–238
IV	20.0	325–334	48 15[c]	.5	3.3 4.5	2.1	204–205

[a] No heating jacket on condenser and the water refluxed back. [b] Also 1.0 ml. of an acidic oil in the trap, requiring 9.5 ml. of 0.445 *N* alkali to neutralize it. Both xylene and naphthalene were identified also. [c] Heating continued on the extracted ketone. [d] I, 2,5-dimethylbenzophenone; II, 1-naphthyl 2,5-dimethylphenyl ketone; III, 2,5,4′-trimethylbenzophenone-2′*d*; IV, 2,5-dimethylbenzophenone-2′*d*.

Finally, a crystal of potassium permanganate was added and the water was distilled over into a small glass bulb and sealed off. It amounted to about 0.3 g.

The residue after heating was dark red or brown in color if reaction occurred. Such was the case with ketone III, for example, at 350°, whereas if the same compound was heated at 325° for nine hours, the light color of the product indicated very little change. The original ketones were either liquids or low-melting solids and quite soluble in ether. The anthracenes formed were high-melting and insoluble. Hence if reaction occurred, the melt solidified on cooling. In the deuterium experiments the unused ketone was extracted from the reaction mass at some point in the heating period to lessen the effect of any thermal reactions on the anthracene after its formation. The "crude anthracene" in Table I represents the ether-insoluble material, and the "purified anthracene" the material crystallized from carbon disulfide and benzene.

Pyrolysis of Ketone Mixtures.—A mixture of 8.6 g. of 2,5-dimethylbenzophenone and 16.5 g. of 1-naphthyl phenyl ketone was refluxed (345–350°) for 13 hours in the apparatus described above. The water formed was 0.50 ml. The residue was distilled at 3 mm. yielding 22 g. of distillate. All except 1.25 g. of the latter dissolved in 20 ml. of ether. The 1.25 g. was methylanthracene. In a separate test it was found that 4.35 g. of the 5.2 g. of anthracene in a mixture of it with 4.8 g. of benzophenone was not dissolved when warmed with 50 ml. of ether.

A mixture of 20 g. of 2,5-dimethylbenzophenone and 7.0 g. of 1-naphthyl phenyl-2*d* ketone was refluxed (330–344°) for thirty-two hours. The dark brown solid obtained was processed as above to yield 4.1 g. of tan solid. The latter was crystallized from carbon disulfide and once more from toluene and ligroin. Two grams of light yellow 2-methylanthracene resulted. It was essentially free of deuterium.

The Anthraquinones.—Two grams of 2,6-dimethylanthracene-*d* was dissolved in 15 ml. of hot acetic acid into which was slowly added a solution of 3.0 g. of chromic anhydride in 5 ml. of water. The mixture was refluxed 30 minutes, and poured into 50 ml. of water. The insoluble 2,6-dimethylanthraquinone-*d* was crystallized from ethanol; m.p. 239–240°.

Similarly, 3 g. of recrystallized 2-methylanthracene-*d* gave rise to 1.9 g. of 2-methylanthraquinone-*d* of m.p. 172–174°.

Combustion of the Deuterium Compounds.—The samples were burned in an oxygen atmosphere in a tube packed with copper oxide, essentially as ordinary combustions for hydrogen in an organic compound are performed. The oxygen was first passed through a copper oxide furnace to ensure absence of organic matter. Then it passed through a calcium chloride drying tube into the combustion tube. Water escaping from the furnace was condensed in two U-tube traps separated by a copper oxide furnace. A calcium chloride tube protected the second trap from atmospheric moisture. The first trap at 0° caught most of the water. A T-tube connection to an ampoule was present at the bottom of the second trap, held at −80°. At the conclusion of the combustion all the water was heated from the first trap through the hot copper oxide into the second trap, where it solidified as ice. This was finally melted to drain into the ampoule which was then sealed off. The water in these ampoules

TABLE II

ANALYSES OF COMBUSTION WATER SAMPLES

Water from combustion of	W_0, g.	W', g.	ΔR, ohms	D, p.p.m.	$N'_{D_2O} \times 10^4$	$n°_{D_2O} \times 10^3$	$N°_{D_2O}$
2,5,4′-Trimethylbenzophenone-2′*d* (A)	0.8849	28.239	0.0227	72.4	6.70	1.08	0.0221
2,6-Dimethylanthracene-*d*	.9399	28.940	.0182	58.1	5.39	0.892	.0171
2,6-Dimethylanthraquinone-*d*	.2591	29.136	.00457	14.6	1.35	.237	.0153
Water from pyrolysis of (A)	.1201	30.375	.00027	0.8	0.07	.012	.0018
[a]Toluene-3*d*	.5586	29.938	.0274	88.4	8.20	1.39	.0450
[a]1-Naphthyl phenyl-2*d* ketone	.7381	29.284	.0221	71.5	6.62	1.11	.0270
[a]2-(2,5-Dimethylbenzoyl)benzoic acid-*d*	.4546	30.283	.0221	71.5	6.62	1.13	.0450
[a]2,5-Dimethylbenzophenone-2′*d*	.7672	30.136	.0384	124.2	11.49	1.97	.0465
[a]2-Methylanthracene-*d*	.4435	30.421	.0205	66.1	6.12	1.05	.0428
[a]2-Methylanthraquinone-*d*	.5565	30.654	.0237	76.5	7.09	1.35	.0399

[a] The equation $D = 2.54\ \Delta R/0.000786$ was used. In the other four runs (with a different float) 2.51 was used instead of 2.54.

was analyzed for deuterium by the float method for determining the density of a mixture of the combustion water diluted with 30–250 volumes of purified "standard water." The resistance (R_s) of a platinum thermometer is read at the balancing temperature where the float neither sinks nor rises. Details for the method have been described.[10] Results are summarized in Table II. W_0 is the weight of the combustion water, and W' the weight of the standard water used as diluent. ΔR represents $R_s - R_0$, R_0 being the resistance for the standard water. D is the density difference between the diluted and standard samples in parts per million. $n°_{D_2O}$ is the number of moles of D_2O in the undiluted sample, and N'_{D_2O} and $N°_{D_2O}$ represent mole fractions, respectively, of D_2O in the diluted and undiluted samples.

Summary

By use in the Elbs reaction of *o*-methylbenzophenones with an ortho deuterium substituent, it has been possible to demonstrate that the hydrogen atom appearing at the 9-position in anthracene comes from the ortho nuclear position, not from the methyl group.

EVANSTON, ILLINOIS

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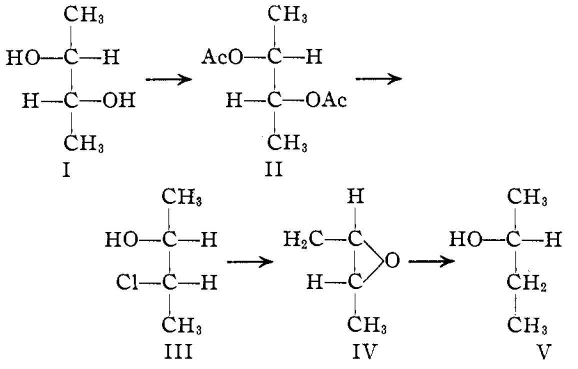
[10] Hurd and Azorlosa, THIS JOURNAL, **72**, 33 (1950).

[CONTRIBUTION NO. 1425 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

L(−)-2-Butanol from D(−)-2,3-Butanediol

BY P. J. LEROUX AND H. J. LUCAS

The ready availability of D(−)-2,3-butanediol, I, through fermentation methods[1] and the satisfactory yields realized in former work with active and inactive compounds[2,3] have led to the preparation of L(−)-2-butanol, 99% optically pure, from the active glycol in 49% yield through the steps: D-(−)-2,3-butanediol[4] (I), D(+)-2,3-diacetoxybutane[3] (II), L(+)-*erythro*-3-chloro-2-butanol[2,3b] (III), D(+)-2,3-epoxybutane[2] (IV), and L(−)-2-butanol (V). The last step, the reduction of the oxide to the alcohol, has been accomplished with lithium aluminum hydride, following the procedure of W. G. Brown and co-workers.[5] As solvent absolute ethyl ether gave the best results; the yield was 80%. Tetrahydrofuran is less satisfactory, largely because separation by distillation is more difficult. Reduction of L(+)-*erythro*-3-chloro-2-butanol was attempted but the yield was low with either tetrahydrofuran or ethyl ether as solvent.



The conversion of D(+)-2,3-epoxybutane to L-(−)-2-butanol is a confirmation of the configuration of the oxide.[2] The over-all conversion from D(−)-2,3-butanediol requires more steps than were involved in the original determination of the glycol configuration by Morell and Auernheimer,[6] but the high temperature required in the decomposition of the glycol diacetate caused some racemization. Moreover the intermediate methylvinylcarbinol that they reduced to 2-butanol was a byproduct, not the main reaction product.

An over-all yield of 45 to 48% would be expected by way of the oxide, in view of the yield at the last step and previous results, some with active compounds,[2] others with inactive compounds.[3] By raising the yield of chlorohydrin from 70 to 77%, an over-all yield of 49% has been obtained. The yield at the last step probably can be increased to 90% to bring the over-all yield to over 50%.

The active alcohol has d^{25}_4 0.8042, n^{20}_D 1.3970, n^{25}_D 1.3949, α^{25}_D −10.67°, $[\alpha]^{25}_D$ −13.51°. This compares with d^{27}_4 0.8025 (d^{25}_4 0.8041, interpolated) n^{20}_D 1.3954, $[\alpha]^{27}_D$ +13.52 ($[\alpha]^{25}_D$ + 13.63, interpolated) for the purest dextro alcohol described.[7] If the active alcohol of Pickard and Kenyon is taken as 100%, the product from 2,3-butanediol has about 1% impurity (including any DL-alcohol), calculated from the specific rotation. The density of our alcohol checks that of theirs, but the refractive index is not in good agreement.[8]

The advantages of the method are convenience, reasonably good yield and high optical purity. The preparations are easy and with the exception of 3-chloro-2-butanol can be carried out with reasonable rapidity. Although the chlorohydrin requires a standing time of two to three weeks, the actual preparation is not laborious. The standard method of resolution of the acid phthalate of 2-butanol with brucine[9] gives about a 40% yield of (+)-alcohol after five to seven crystalliza-

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[1] (a) G. E. Ward, O. G. Pettijohn, L. B. Lockwood and R. D. Coghill, THIS JOURNAL, **66**, 541 (1944); (b) A. C. Neish, *Can. J. Research*, **23B**, 10 (1945); (c) J. W. Knowlton, N. C. Schieltz and D. Macmillan, THIS JOURNAL, **68**, 208 (1946).

[2] H. J. Lucas and H. K. Garner, *ibid.*, **70**, 990 (1948).

[3] (a) C. E. Wilson and H. J. Lucas, *ibid.*, **58**, 2396 (1936); (b) H. J. Lucas and C. W. Gould, Jr., *ibid.*, **63**, 2541 (1941).

[4] Since the configuration of the higher numbered asymmetric carbon atom determines the family, the glycol is called D, in conformity with the Report of the Committee on Nomenclature, *Chem. Eng. News*, **26**, 1623 (1948). The glycol should be assigned to the family to which the threitol of the same configuration belongs.

[5] R. Nystrom and W. G. Brown, THIS JOURNAL, **70**, 3738 (1948); L. W. Trevoy and W. G. Brown, *ibid.*, **71**, 1675 (1949).

[6] S. A. Morell and A. H. Auernheimer, *ibid.*, **66**, 792 (1944).

[7] R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, **99**, 45 (1911); **103**, 1923 (1913).

[8] We obtain for redistilled DL-2-butanol, also dried with potassium carbonate, n^{20}_D 1.3969, n^{25}_D 1.3949, in good agreement with our values for the active alcohol, and with n^{25}_D 1.39495, obtained with thoroughly dried DL-2-butanol, b. p. (760 mm.) 99.259°; R. Brunel, THIS JOURNAL, **45**, 1337 (1923).

[9] A. W. Ingersoll, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 376.