On the Catalytic Action of Japanese Acid Earth. XIII*. The Catalytic Action on Some Alkyl Aryl Acetaldehydes.

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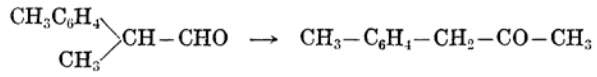
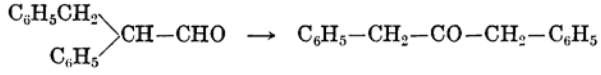
In the previous papers it was reported that some diarylacetaldehydes were converted into the corresponding ketones when heated at about 300°C. in the presence of Japanese acid earth. When this rearrangement occurs there is a possibility of the formation of either one ketone or other as the result of the migration of one of the radicals, and the author has postulated that it separates as an anion and that the more electron-attracting radical always migrates in preference to the other less electron-attracting. When the migrating tendencies of the two radicals are not greatly different, both of the radicals migrate simultaneously, giving a mixture of two isomeric ketones. The yields in the two ketones depend upon the migrating tendencies of the two radicals, which are determined by their capacities for electron-attraction.

Now the methyl group is generally accepted as less electron-repelling than the *p*-tolyl group[1], therefore the methyl group will migrate in preference to the *p*-tolyl if methyl p-tolyl acetaldehyde is subjected to the above-mentioned rearrangement as shown below:—



Similarly, the benzyl group will be expected to migrate in preference to the phenyl group in the case of benzyl phenyl acetaldehyde. The facility of the separation of the benzyl anion must be increased, moreover, by the enhanced stability of this anion relative to phenyl.



It has been found, however, that the above mentioned two aldehydes are converted chiefly into hydrocarbons at 300°C. in the presence of the earth and the corresponding ketones have not been confirmed to exist in the reaction products. They must, therefore, be considerably more unstable than diarylacetaldehydes, described in the previous papers, and the condition of the present experiment is probably too drastic for them to undergo smoothly the usual rearrangement.

The reaction product from methyl *p*-tolyl acetaldehyde has been found to contain only about 3% of oxygen, but the aldehyde or ketones isomeric to it should contain 10.8%. Benzyl phenyl acetaldehyde gave products containing a still less quantity of oxygen. The reaction products

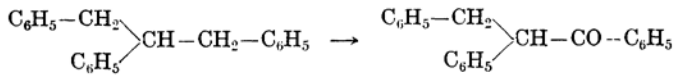
* This Bulletin **16** (1941), 349.

(1) H. Burton and C. K. Ingold: *J. Chem. Soc.* **1928**, 907.

from both of the aldehydes showed no colour reaction, characteristic to aldehyde. All attempts to obtain definite forms of oximes or semicarbazones of ketones from the reaction products failed. The main products were accordingly treated with metallic sodium in order to remove the oxygen-containing substances, and then fractionated, when a mixture of almost pure hydrocarbons was obtained.

Among the reaction products from methyl *p*-tolyl acetaldehyde, toluene and a compound $C_{10}H_{12}$, possibly $CH_3-C_6H_4-CH=CH-CH_3$ were confirmed to exist, while in the reaction products from benzyl phenyl acetaldehyde a solid crystalline substance of the composition $C_{15}H_{12}$[2] with a melting point 165–166°C. was found.

It has been found that 1,2,3-triphenylpropane (I) is produced together with benzyl phenyl acetaldehyde when *α*-benzyl *α*-phenyl ethylene glycol is heated with a mixture of oxalic acid and water at 113°C. 1,2,3-Triphenylpropane gave benzyl deoxybenzoin (II) on oxidation with chromic oxide. From this fact its constitution has been confirmed.



(I) (II)

Experimental. *α-Benzyl α-phenyl ethylene glycol.* When magnesium is allowed to react with the calculated quantity of benzyl bromide, dissolved in dry ether, as has J. Marshall[3] noticed, a large proportion of magnesium remains undissolved with the formation of a considerable quantity of dibenzyl. Pulverised benzoyl carbinol (20 g.) was added by portions to the solution of magnesium (16.4 g.) in benzyl bromide (193 g.) dissolved in ether, and the Grignard reagent thus formed was boiled for 30 hours. It was poured into acetic acid (50 g. glacial acetic acid in 300 c.c. ice water) and the upper layer of the reaction mixture was treated as usual, giving a yellowish liquid (ca. 300 c.c.), from which separated a large amount of dibenzyl. It was filtered and the filtrate was distilled in steam and further amount of dibenzyl (ca. 40 g. in total) passed over. The contents of the distilling flask were cooled and a part of *α*-benzyl *α*-phenyl ethylene glycol separated out in flocky precipitate while the main part of the glycol settled down at the bottom in viscous oily mass (30 g.).

The precipitate was recrystallised from ligroin into fine needles, m.p. 79–80°C. (Found: C, 78.9; H, 7.3. $C_{15}H_{16}O_2$ requires C, 78.9; H, 7.0%). The viscous oil solidified only when innoculated with crystals of the glycol. The monobenzoyl drivative of the glycol was obtained by Schotten-Baumann's method. It formed a viscous matter, which solidified when rubbed with a glass rod with the addition of a small quantity of alcohol. It was recrystallised from dilute alcohhol into fine needles, m.p. 100.5–

(2) Ramart and F. Salmon-Legagneur (*Bull. soc. chim.*, **45** (1929), 478) obtained a substance of the composition $C_{15}H_{12}$ by passing *α*-benzyl *α*-phenyl ethylene glycol over diatomaceous earth heated at 500°C. Though its chemical and physical properties are not described at all, it may probably be identical with the substance obtained by the present author.

(3) *J. Chem. Soc.*, **107** (1915), 520.

101.5°C. (Found: C, 79.6; H, 5.9%; Mol. wt. (Rast), 335.1. $C_{22}H_{20}O_3$ requires C, 79.5; H, 6.0%: Mol. wt., 332).

Oxidation of α-benzyl α-phenyl ethylene glycol to desoxybenzoin. Chromic oxide (0.31 g.) was added to the solution of the glycol (0.3 g.) dissolved in 70% acetic acid (50 c.c.) and the solution was heated on the water bath for 4 hours and poured into a large amount of water. White crystals separated out, which formed colourless scales (0.15 g.) from dilute alcohol. It melts at 57–58°C. alone or mixed with the authentic specimen of desoxybenzoin.

Benzyl phenyl acetaldehyde. A mixture of α-benzyl α-phenyl ethylene glycol (60 g.), crystalline oxalic acid (150 g.) and water (60 c.c.) was heated in an oil bath for 4 hours at 113°C. The reaction mixture was treated as usual and distilled under the reduced pressure of 4 mm., giving the following fractions:—

Table 1.

Fraction	B. p. (°C.)	Yields (in g.)	Remarks
(1)	Below 172	1.0	—
(2)	172–175	7.5	—
(3)	175–205	13.8	Boiling mainly at 202–205°C.
(4)	Residue	—	—

The fraction (2) in Table 1 consisted of the required aldehyde, d_4^{22} 1.0684; n_D^{22} 1.5861; M. R. found, 65.96; calc. (Eisenlohr), 64.28. The semicarbazone was produced with difficulty; after standing for 5 days the mixture of the aldehyde (1.0 g.), semicarbazide hydrochloride (1.0 g.) and potassium acetate (1.0 g.) dissolved in dilute alcohol, a large amount of water was added to the solution. The oil drops separated thereby solidified to the yellow powder (0.95 g.), which was recrystallised several times from dilute alcohol forming colourless fine needles, m.p. 123.4–124.4°C. (corr.). H. Burton and C. W. Shoppee[4] obtained the same aldehyde by reducing the corresponding iminochloride with stannous chloride and then hydrolysing the resulting aldimine. It boiled, according to them, at 170°C./11 mm., and solidified after several weeks, and on recrystallisation formed colourless plates, m.p. 54°C. and its semicarbazone melted at 124–125°C. R. Stoermer, Cl. Thier and E. Laage[5] described it as the monohydrate, m.p. 116°C., characterised by a semicarbazone, m.p. 189°C. (decomp.), which however was confirmed by H. Burton and C. W. Shoppee to be phenyl acetylphenyl carbinol. F. Kayser[6] synthesised the aldehyde by treating 1,3-diphenylpropane-(1) with mercury oxide and iodine and gave the boiling point 179–180°C./18 mm.

(4) *J. Chem. Soc.*, **1937**, 546.
(5) *Ber.*, **58** (1925), 2607.
(6) *Ann. chim.*, [11] **6** (1936), 145.

1,2,3,-Triphenylpropane. The fraction (3) in Table 1 tinged concentrated sulphuric acid with a deep red colour and contained a small proportion of oxygen. (Found: C, 91.3; H, 7.2%). It was treated with metallic sodium to remove the oxygen-containing substances, and a hydrocarbon $C_{21}H_{20}$ was obtained in colourless viscous oil, b.p. 204–205°C./8 mm.; $d_4^{30.4}$ 1.0254; $n_D^{30.4}$ 1.5864; M. R. found, 89.07, calc. (Eisenlohr), 88.38. (Found: C, 92.5; H, 7.5. $C_{21}H_{20}$ requires C, 92.7; H, 7.3%). It dissolves in concentrated sulphuric acid, developing brownish yellow colour with faint cobalt fluorescence. Its identity with 1,2,3-triphenylpropane was revealed by the formation of benzyl desoxybenzoin when oxidised with chromic oxide. E. Späth[7] obtained the hydrocarbon by allowing benzyl halide to react with methyl- or ethylmagnesium halide and gave b.p. 225–230°C./10 mm. The hydrocarbon (1.1 g.) was dissolved in glacial acetic acid (30 c.c.), and chromic oxide (3.3 g. dissolved in 3 c.c. water) was added to the solution. After completing the reaction by heating the solution on the water bath for 1 hour, a small quantity of formic acid was added in order to decompose the excess chromic acid and the acetic acid was distilled off under the reduced pressure on the water bath. The residue was a deep green mud. It turned white on washing with water, and crystallised from dilute alcohol forming pure *ms*-benzyl desoxybenzoin in fine needles (0.25 g.), m.p. 120–121°C. (Found: C, 87.7; H. 6.5%; Mol. wt. (Rast), 289 295. $C_{21}H_{18}O$ requires C, 88.1; H, 6.3%; Mol. wt., 286). The oxime obtained by Auers' method formed colourless needles, apparently a pure substance, which however melted at 116–127°C. after recrystallisation 10 times from dilute alcohol and most probably consisted of a mixture of stereo-isomers. F. Klingemann[8] obtained *ms*-benzyl desoxybenzoin by reducing *ms*-benzal desoxybenzoin and gave m.p. 120–122°C. A. Mckenzie and E. R. Winton[9] obtained it by interacting methyltropate with phenyl magnesium iodide, which melted at 120–121°C.

Attempted isomerisation of benzyl phenyl acetaldehyde. By passing 7.0 g. of the aldehyde on the Japanese acid earth (25 g.), heated at 300°C. at a rate of 3.2 g. per hour, accompanied by a slow current of carbon dioxide the following products were obtained: (a) 0.6 g. of easily-flowing oil with faint fluorescence and (b) 3.5 g. of a yellow solid mass moistened with oily substance. The product (a) consisted chiefly of toluene and benzene. The product (b) was separated into two parts, i.e., (i) crystalline mass (0.6 g.) and (ii) oily substance (2.3 g.), when it was pressed with a filter paper and the paper was extracted with ether. The product (i) crystallised from alcohol in colourless scales, m.p. 165–166°C. (Found: C,93.5; H, 6.3%; Mol. wt. (Rast), 197, 206. $C_{15}H_{12}$ requires C, 93.8; H, 6.2%; Mol. wt., 192). Attempts to obtain any compound of a definite constitution by oxidising the foregoing hydrocarbon with chromic oxide failed and its constitution was for the time left open. Ramart and F. Salmon-Legagneur[10] obtained a compound $C_{15}H_{13}$ by passing α-benzyl α-phenyl ethylene glycol on the diatomaceous earth heated at 500°C. How-

(7) *Monatschaft.*, **34** (1913), 1992.
(8) *Ann.*, **275** (1893), 65.
(9) *J. Chem. Soc.*, **1940**, 840.
(10) *Bull. soc. chim.*, **45** (1929), 478.

ever, no detailed description of properties of the compound has been given by them.

The portion (ii) was distilled under the reduced pressure of 10 mm. and 1.7 g. out of 2.3 g. passed over between 150–200°C, which contained 91.7% of carbon and 7.2% of hydrogen and may be considered to consist of 74% of $C_{15}H_{12}$ and 26% of $C_{15}H_{14}O$. It showed no colour reaction characteristic to aldehydes and formed neither semicarbazone nor oxime.

α-Methyl α-p-tolyl ethylene glycol. *p*-Methyl benzoyl carbinol (45 g.) was added by portions to the Grignard reagent prepared from methyl iodide (150 g.) and magnesium (24 g.) and left to stand for 2 days. It was treated with acetic acid (120 g. glacial acetic acid in 300 c.c. ice water), the ethereal layer was separated and combined with the ether extract of the water layer, the combined ethereal extract dried with anhydrous sodium bicarbonate, the ether removed and the residue was distilled in vacuo. 33 g. of the raw α-methyl α-*p*-tolyl ethylene glycol passed over between 150 and 158° under 33 mm. M. Tiffeneau[11] obtained the glycol by the same method and found that it melted at 36°C. and boiled at 175–180°C/15 mm. These data widely deviated from the present author's values.

p-*Tolyl propionaldehyde.* A mixture of raw α-methyl α-*p*-tolyl ethylene glycol (30 g.), crystalline oxalic acid (75 g.) and water (30 c.c.) was boiled gently in an oil bath for 3 hours, meanwhile a slow current of carbon dioxide was passed into the reaction flask. The reaction product was extracted with ether, washed with aqueous potassium carbonate and with water, dried over anhydrous sodium sulphate, the ether removed and the residue was distilled. 14 g. of the required aldehyde were obtained, b.p. 222–225°C.; d_4^{23} 0.9928; n_D^{23} 1.5173; M. R. found 45.12. $C_{10}H_{12}O$ 3 (Eisenlohr) requires 44.79. W. v. Miller and G. Rohde[12] gave b.p. 222–224°C./760 mm. (corr.), G. G. Henderson and W. Cameron[13] b.p. 221–222°C./755 mm.; d_{20}^{20} 0.984; n_D^{20} 1.51436, and M. Tiffeneau,[14] b.p. 219–221°C. The semicarbazone was synthesised by the usual way forming silky needles from dilute alcohol, m.p. 155.5–156.5°C. (uncorr.). G. Darzens[15] gave m.p. 159–160°C. and G. G. Henderson[16] m.p. 156–157°C., while M. Tiffeneau[17] m.p. 152°C.

Attempted isomerisation of methyl p-*tolyl acetaldehyde.* The aldehyde (12 g.) was passed on the Japanese acid earth (25 g.) heated at 300°C. at a rate of 3.6 per hour, accompanied by a slow current of carbon dioxide and gave (a) a yellow oil (5.9 g.) mixed with a small amount of crystals and water (1.1 g.) which came out until the passing of the aldehyde ended and (b) a faint yellow resinous matter (0.5 g.). The product (a) was separated from water and distilled, giving the following fractions:—

(11) *Compt. rend.* **137** (1903), 1261; *Ann chim.*, [8] **10** (1907), 343.
(12) *Ber.*, **23** (1890), 1075.
(13) *J. Chem. Soc.*, **95** (1909), 969.
(14) *Compt. rend.*, **137** (1903), 126.
(15) *ibid.*, **139** (1904), 1216.
(16) *J. Chem. Soc.*, **91** (1907), 1874.
(17) *Loc. cit.*

Table 2.

Fraction	B. p. (°C.)	Yield (in g.)	Remarks
(1)	Below 200	2.1	Main part passed over above 180°C.
(2)	200–205	0.7	
(3)	205–230	0.9	The last 2 or 3 drops changed to mush on cooling.
(4)	Residue	1.1	Redish viscous oil containing crystals.

The fractions (1), (2) and (3) in Table 2 gave the following analytical data; C, 89.3, 88.0 and 86.7; H, 9.3, 9.2 and 8.2% respectively, suggesting that the higher the boiling point the richer in compounds which contain oxygen. The fractions (1) and (2) were combined and treated with metallic sodium in order to remove oxygen-containing substances and again fractionated as follows:—

Table 3.

Fraction	B. p. (°C.)	Yield (in g.)	Remarks
(1)	Below 110	0.6	Boiled almost constantly at 110°C.
(2)	110–180	0.4	Main part passed over above 150°C.
(3)	180–185	0.5	—
(4)	Residue	0.5	—

The fraction (1) in Table 3 consisted of almost pure toluene and the fraction (2) was found to be a compound $C_{10}H_{12}$; d_4^{26} 0.8615; n_D^{26} 1.4940; M. R. found, 44.61, calc. (Einsenlohr) for $C_{10}H_{12}$, 44.31. (Found: C, 90.4; H, 9.4. $C_{10}H_{12}$ requires C, 90.9; H, 9.1%).

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