On the Catalytic Action of Japanese Acid Earth. XI. The Isomerisation of Aldehydes to Ketones and the Explanation of the Migration of the Radicals from the Standpoint of the Electronic Theory (*Continued*).

By **Koshiro ISHIMURA.**

(Received May 14, 1941.)

Experimental. *Benzoyl carbinol.* Various methods of obtaining benzoyl carbinol have been tried by the author. Acetophenone was brominated by R. Möhlaus'(38) method in glacial acetic acid. Interaction of the resulting ω-bromacetophenone with potassium acetate was carried out more smoothly by R. Stroemer's(39) method than by W. L. Evans'(40) method, while the hydrolysis of the acetate according to the latter's information gave a better result. But I. Fischer and M. Busch's(41) method of hydrolysing it by boiling with the excess of barium carbonate in hot water about fifty times as much as the amount of the acetate gave the best. Benzoyl carbinol thus obtained has one molecule of water of crystallisation when recrytallised from hot water, m.p. 73–74°C. On standing it in a desiccator under the reduced pressure for about five hours the water of crystallisation was set free, giving anhydrous crystal, m.p. 86–87°C. Evans gave the m.p. 85–86°C., while J. Plöchl and F. Blümlein(42) 86–87°C.

α-Phenyl α-p-tolyl ethylene glycol. Anhydrous benzoyl carbinol (27 g.) dissolved in ether was added into the Grignard reagent prepared from *p*-tolyl iodide (110 g.) and magnesium ribbon (10 g.). As the solubility of the carbinol in ether is not so great, it was put in Soxlet's apparatus connected with the flask containing the reagent. The content of the flask was gently boiled so that the carbinol was gradually extracted by hot ether and the solution flowed down into the flask. When all the carbinol was dissolved the reaction mixture was left to stand overnight. It was treatd with a mixture of ice water (500 g.) and glacial acetic acid (25 c.c.). The ethereal layer was separated from the water layer which was extracted with ether several times. The combined ethereal solution was washed with dilute solution of sodium hydroxide, with water and then with a saturated solution of sodium bisulphite in order to remove the remaining carbinol. It was again washed with dilute solution of sodium hydroxide and water, concentrated by distillation till about 100 c.c. of the solution remained. On cooling a large amount of *pp'*-ditolyl produced by the side reaction crystallised out. The solution freed from the solid matter was distilled in steam and a considerable quantity of *pp'*-ditolyl, iodotoluene and toluene came over thereby. Without the previous

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(38) *Ber.*, **15** (1882), 2465.
(39) *Ber.*, **39** (1906), 2294.
(40) *Am. Chem. J.*, **35** (1906), 120.
(41) *Ber.*, **24** (1894), 2680.
(42) *Ber.*, **16** (1883), 1292.

removal of these impurities, the purification of the required glycol often became very difficult. The contents of the distilling flask were extracted with ether. The ethereal solution was dried over anhydrous sodium sulphate and the solvent was removed. The required glycol was solidified on cooling. Yield about 26 g. It was recrystallised from petroleum benzine in colourless fine needles, m.p. 84.5–85.5°C. (Found: C, 78.9; H, 7.3. $C_{15}H_{16}O_2$ requires C, 78.9; H, 7.0%).

The benzoyl derivative was obtained by dissolving the glycol (0.8 g.) in ether (10 c.c.) and adding benzoyl chloride (3 g.) and sodium hydroxide (3 g.) dissolved in water (20 c.c.) and by shaking the mixture vigorously. The reaction heat evolved thereby was removed away by cooling with water intermittently. The ethereal layer was washed with water, dried over anhydrous sodium sulphate and the ether removed, leaving colourless sylup which on the addition of a small quantity of alcohol solidified immediately. It did not tend to crystallise for several days, if not treated as stated above. It formed colourless plates from dilute alcohol, m.p. 136°C. (corr.). (Found: C, 79.0; H, 6.2. $C_{22}H_{20}O_3$, monobenzoyl derivative requires C, 79.5; H, 6.0; $C_{29}H_{24}O_4$, dibenzoyl derivative, C, 79.8; H, 5.5%). Mol. wt., found (Rast), 344. $C_{22}H_{20}O_3$ requires 332 whereas $C_{29}H_{24}O_4$ 436. The substance was therefore the monobenzoyl derivative.

*Oxidation of α-phenyl α-*p*-tolyl ethylene glycol to phenyl* p*-tolyl ketone.* The glycol (0.5 g.) was added by portions into the solution of chromic oxide (0.55 g.) dissolved in 80% acetic acid (30 c.c.), and the mixture was left to stand overnight. It was heated for 30 minutes on the water bath, cooled and poured into water (400 c.c.) and then cooled with ice and salt. White crystals (0.37 g.) were thrown down which when washed with water and recrystallised from dilute alcohol melted at 57–57.5°C. (uncorr.) alone or mixed with the specimen of phenyl *p*-tolyl ketone which was obtained from toluene and benzoyl chloride and melted at the same temperature. (Found: C, 85.9; H, 6.7. $C_{14}H_{12}O$ requires C, 85.7; H, 6.1%). According to Th. Zinke(43) the stable modification of the ketone melted at 59–60°C. and the metastable at 55°C, while K. Schaum, K. Schäling and F. Klausing(44) gave the m.p. 55 and 52°C. respectively.

Phenyl p*-tolyl acetaldehyde.* The mixture of α-phenyl α-*p*-tolyl ethylene glycol (16 g.), water (40 c.c.) and 9 drops of concentrated sulphuric acid was heated in a sealed tube at 180–185°C. for 3 hours. When cooled down the contents were extracted with ether, washed with dilute solution of sodium carbonate, shaken with saturated solution of sodium bisulphite, the addition compound of which with the required aldehyde, white crystalline powder, was collected. Yield, 19 g. The addition compound (15 g.) was decomposed by 15% sodium hydroxide solution (50 c.c.), the aldehyde set free was extracted with ether and distilled under reduced pressure after separated from the solvent. The pure aldehyde (6.7 g.) thus obtained boiled at 176°C. (corr.) under 7 mm. It formed a colourless and almost odourless oil, tinged fuchsin sulphurous acid with pink colour when pure, while the specimen mixed with a trace of impurity prussian blue. d_4^{25}, 1.0785; n_D^{25}, 1.5844; M. R., 65.20; calculated (Eisen-

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(43) Cited by C. Bodewig, *Ann. d. Physik*, **158** (1876), 234.

(44) *Ann.*, **411** (1911), 188.

lohr), 64.28. (Found: C, 85.9; H, 6,7. $C_{15}H_{14}O$ requires C, 85.7; H, 6.6%). On long standing its analytical data showed gradual decreases in the contents of both carbon and hydrogen suggesting the autoxidation of the aldehyde with atmospheric oxygen. The oxime of the aldehyde formed oil at the ordinary temperature. The semicarbazone was obtained by standing overnight a mixture of the aldehyde (2 g.), potassium acetate (2 g.), semicarbazide hydrochloride (2 g.), dissolved in hot 95% alcohol (20 c.c.) diluted with water (10 c.c.). It crystallised from dilute alcohol in colourless columns (3.0 g.) m.p. 158–159°C. (corr.) (Found: N, 16.0. $C_{16}H_{17}ON_3$ requires N, 15.7%). M. Tiffeneau and J. Lévy(45) obtained the same aldehyde by the isomerisation of α-phenyl β-tolyl ethylene oxide and gave the following data: b.p., 180–185°C./10 mm.; n_D^{16}, 1.582; m.p. of the semi-carbazone, 157–158°C.

Oxidation of phenyl p-*tolyl acetaldehyde.* Silver nitrate (1.2 g. in 1 c.c. water) was added to the alcoholic solution of the aldehyde (0.8 g. in 15 c.c.) and then potassium hydroxide (0.9 g. in 10 c.c. water) was added gradually, the mixture was shaken for 3 hours and left to stand overnight. It was filtered, the filtrate was concentrated on the water bath, and acidified with dilute sulphuric acid. An oily substance separated out which solidified on cooling. Yield, 0.5 g. Phenyl *p*-tolyl acetic acid thus obtained was recrystallised from dilute alcohol with the addition of active charcoal forming colourless plates, m.p. 115° (Found: C, 79.1; H, 6.6. $C_{15}H_{14}O_2$ requires C, 79.6, H, 6.2%). M. Tiffeneau and J. Lévy(45) gave the m.p. 112–115°C.

Isomerisation of phenyl p-*tolyl acetaldehyde.* The isomerisation was carried out as stated above (p. 199*). The aldehyde (12.0 g.) was passed over Japanese acid earth (25 g) drop by drop with a rate of 3.5 g. per hour. The reaction products consisted of (i) colourless easily-flowing liquid (2.0 g.) with a faint fluorescence mixed with water drops, (ii) colourless fragrant viscous oil (5.0 g.) which flowed out of the tube when the temperature of the furnace was raised to 350°C. after the total aldehyde was passed into it, and solidified to colourless crystalline mass, and (iii) a reddish brown viscous liquid (2.0 g.) mixed with a small quantity of crystals, obtained when the temperature was raised to 450°C.

The product (i) was separated from water drops and distilled over metallic sodium giving colourless liquid (1.0 g.), b.p. 80–112°C, d_4^{24} 0.8690, n_D^{18} 1.4997. It proved to be a mixture of about 20% benzene and about 80% toluene, when calculated from the specific gravity or from the refractive index. The product (ii) consisted of almost pure phenyl *p*-methylbenzyl ketone. (Found: C, 85.9; H, 6.7. $C_{15}H_{14}O$ requires C, 85.7; H, 6.6%). After recrystallised from dilute alcohol several times it melted at 97°C. alone or mixed with the authentic specimen synthesised from ω-bromacetophenone and toluene by Friedel-Crafts' reaction. A. Mckenzie, A. K. Mill and J. R. Myles(46) gave the m.p. 95–96°C., while M. Tiffeneau(47)

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(45) *Bull. soc. chim.*, **49** (1931), 1744.

* All the samples of the acid earth used throughout this series of experiments were taken from one and the same stock, and the electric furnace as well as the reaction tube were also the same ones. This Bulletin, **16** (1941), 199.

(46) *Ber.*, **63** (1930), 908.

(47) *Compt. rend.*, **139** (1904), 1507.

94–95°C. The oxime of the ketone obtained by K. Auers'(48) method formed colourless needles melting sharply at 101°C. after recrystallisation several times from either dilute alcohol or from ligroin. H. Strassmann(49) gave the m.p. 109°C. and A. Mckenzie, A. K. Mill and J. R. Myles(50) 108–109°C. (Found: N, 6.7. $C_{15}H_{15}ON$ requires N, 6.2%).

p-Tolyl benzyl ketone, isomeric to the above one, was not found to be present in the reaction product of the present experiment. The specimen synthesised from acetyl chloride and toluene melted at 110–110.5°C. H. Strassmann(51) gave the m.p. 109°C., while M. Tiffeneau(52) 108–109°C. Its semicarbazone was obtained by heating a mixture of the ketone (0.2 g.), semicarbazide hydrochloride (0.2 g.) and potassium acetate (0.2 g.), dissolved in dilute alcohol (3 c.c.). After three day's standing long glittering needles (0.3 g.) crystallised out, which melted at 166.5°C. (corr.) after recrystallised from dilute alcohol. (Found: N, 15.4. $C_{16}H_{17}ON_3$ requires N, 15.7%). Kipping(53) obtained only azine melting at 170–173°C. by prolonged heating of the ketone with semicarbazide hydrochloride and sodium acetate and E. E. Turner(54) obtained the same product melting at 181°C. by heating the ketone with semicarbazide hydrochloride dissolved in dilute alcohol, in a sealed tube heated at 180°C. for three hours. Both the English authors reported that they could not obtain the semicarbazone. The oxime melts at 131°C. H. Strassmann(49) gave the same melting point.

Phenyl *p*-methylbenzyl ketone dissolves in concentrated sulphuric acid with a tint of canary yellow while *p*-tolyl benzyl ketone thereby develops at first dirty green which gradually changes into greenish yellow colour.

α,β-Dibenzoyl ethane. When phenyl *p*-methylbenzyl ketone was synthesised from ω-bromacetophenone and toluene by the Friedel and Crafts' reaction, a small quantity of colourless microcrystalline columns, m.p. 145–146°C. (uncorr.), was also obtained. It was confirmed to be α, β-dibenzoyl ethane produced undoubtedly by the condensation of two molecules of ω-bromacetophenone. (Found: C, 81.0; H, 5.8; Mol. wt., (Rast), 289. $C_{16}H_{14}O_2$ requires C, 80.7; H, 5.9%; Mol. wt., 238). S. Kape and C. Paal(55) gave it a melting point 144–145°C. and G. Dupont(56) 144°C.

p-*Methylbenzoyl carbinol.* p-Methylbenzoyl methyl acetate (30 g.) was hydrolysed by boiling with barium carbonate (30 g.) in hot water (1500 c.c.) for two hours. The solution was filtered hot. On cooling *p*-methylbenzoyl carbinol (15 g.) crystallised out, which was recrystallised from ligroin in colourless prisms, m.p. 89–90°C. (Found: C, 75.9; H, 5.4. $C_{16}H_{14}O_3$ requires C, 75.6; H, 5.5%). K. Auers(57) described it as light yellow prisms melting at 89–89.5°C., and J. Boëseken, L. W. Hansen and S. H. Bertram(58) gave a melting point 90°C. It dissolved in concentrated

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(48) *Ber.*, **22** (1889), 604.
(49) *Ber.*, **22** (1889), 1231.
(50) *Loc. cit.*
(51) *Loc. cit.*
(52) *Compt. rend.*, **134** (1902), 1507.
(53) Proceeding of the Chemical Society, No. 220.
(54) *J. Chem. Soc.*, **107** (1915), 1462.
(55) *Ber.*, **21** (1888), 3056.
(56) *Compt. rend.*, **158** (1914), 1350; *Bull. soc. chim.*, (4) **15** (1914), 606.
(57) *Ber.*, **39** (1906), 3761.
(58) *Rec. trav. chim. Pays-Bas*, **35** (1916), 311.

sulphuric acid with canary yellow colour which faded away on dilution with water.

α-m-*Tolyl α*-p-*tolyl ethylene glycol.* *p*-Methylbenzoyl carbinol (28 g.) dissolved in ether was gradually added to the Grignard reagent prepared from *m*-iodotoluene (140 g.) and magnesium ribbon (14 g.) and the solution was boiled for 5 hours. As the solubility of the carbinol in ether is relatively small, a Soxlet's flask was very useful to carry out the reaction as in the case of the preparation of *α*-phenyl *α*-*p*-tolyl ethylene glycol. The contents of the reaction flask formed two layers which became one on concentration on the water bath. It was treated with a solution of glacial acetic acid (28 g.) in ice water (800 c.c.). Two layers again appeared, the upper layer was combined with the ethereal extract of the lower one, washed with dilute sodium carbonate solution and with water, shaken mechanically with saturated solution of sodium bisulphite for 10 hours to remove the remaining *p*-methylbenzoyl carbinol. It was washed with dilute aqueous sodium hydroxide and with water, the ether was removed by distillation and the residue was subjected to steam distillation for about 35 hours until no more oily substance came over. The contents of the distilling flask turned turbid white with amber coloured oil at the bottom. On cooling to −15°C. white powder was thrown down from the solution and the amber coloured oil became viscous mass (39 g.). Both were recrystallised from a large amount of hot water and then from petroleum ether giving colourless powder of *α*-*m*-tolyl *α*-*p*-tolyl ethylene glycol, m.p. 59–60°C. (Found: C, 79.0, 79.6; H, 7.2, 7.5. $C_{16}H_{18}O_2$ requires C, 79.3, H, 7.4%). Monobenzoyl derivative was obtained by Schotten-Baumann's method. It crystallised from 95% alcohol in colourless columns with one molecule of water of crystallisation, m.p. 173–174°C. (corr.) (decomp.). (Found: C, 75.6, 75.9; H, 6.7, 6.2%; Mol. wt. (Rast), 370. $C_{23}H_{22}O_3 \cdot H_2O$ requires C, 75.8; H, 6.6%; Mol. wt., 364). The water of crystallisation was not set free by heating at 57°C. under the reduced pressure of 7 mm. for 1 hour or at 120°C. under 760 mm. for 2 hours.

Oxidation of α-m-*tolyl α*-p-*tolyl ethylene glycol.* The glycol (0.14 g.) was dissolved in 80% acetic acid (10 c.c.) and chromic oxide (0.15 g) was added by portons into the solution, the solution was heated on the water bath for 20 minutes, diluted with water and cooled to −5°C. when white granules of *m*-tolyl *p*-tolyl ketone were obtained. It crystallised from dilute alcohol in long blades or prisms, m.p. 72°C. Yield 0.1 g.

m-*Tolyl* p-*tolyl acetaldehyde.* *α*-*m*-Tolyl *α*-*p*-tolyl ethylene glycol (50 g.) was boiled gently with a mixture of crystalline oxalic acid (125 g.) and water (50 c.c.) in an oil bath for 3 hours. The temperature of the boiling mixture was maintained at 115–120°C. while that of the bath showed 150–160°C. After cooling, it was extracted with ether, the ethereal extract was washed with dilute aqueous solution of potassium hydroxide and with water, dried over anhydrous sodium sulphate. The ether was removed and the residue was distilled in vacuo. 29.1 g. of the raw aldehyde came over boiling between 160°C. and 180°C. under 5 mm. It was purified through the addition compound with sodium bisulphite. *m*-Tolyl *p*-tolyl acetalydehyde thus obtained boiled at 182°C. (corr.) under 7 mm., d_4^{20}, 1.0684; n_D^{20}, 1.5803; M.R., 69.81; calculated (Eisenlohr), 68.90. (Found: C, 85.2; H, 7.6. $C_{16}H_{16}O$ requires C, 85.7; H, 7.1%). The semicarbazone was produced by adding the aldehyde (1 g.) to a mixture of potassium acetate (1 g.) and semicarbazide hydrochloride (1 g.) dissolved in dilute alcohol (10 c.c. of 95% alcohol and 6 c.c. of water) and heating to make a clear solution. On cooling white crystals (1.1 g.) were formed. It was recrystallised from dilute alcohol in long prisms, m.p. 179–180°C. (corr.) (decomp.) (Found: N, 15.0. $C_{17}H_{19}ON_3$ requires N, 14.9%).

m-*Tolyl* p-*tolyl acetic acid.* Silver nitrate (10 g. in 10 c.c. water) was added to *m*-tolyl *p*-tolyl acetaldehyde (5 g.) dissolved in 95% alcohol (100 c.c.), followed by potassium hydroxide (7.5 g. in 70 c.c. water). 5 c.c. of the potash solution were added at a time every 10 minutes and the vessel was well shaken after each addition. After all the potash was added shaking was continued for further 3 hours, the reaction mixture was filtered and the filtrate was saturated with carbon dioxide and concentrated on the water bath. An oily substance separated out and floated on the surface, which solidified on cooling and confirmed to be *m*-tolyl *p*-tolyl ketone. The solution removed from the above ketone was neutralised with dilute sulphuric acid. Impure *m*-tolyl *p*-tolyl acetic acid separated thereby as an oily substance which on cooling turned to semi-solid mass. It was dissolved in alkali leaving a small quantity of *m*-tolyl *p*-tolyl ketone as an insoluble oil, and the solution again neutralised by the mineral acid. These steps of purification were repeated several times and finally *m*-tolyl *p*-tolyl acetic acid (0.2 g.) was recrystallised from hot water in pure state. It formed long prisms, m.p. 93–94°C. (Found: C, 79.5; H, 7.3%. Equiv. wt. (by titrating with 1/20 N NaOH), 240.1. $C_{16}H_{16}O_2$ requires C, 80.0; H, 6.7%; Equiv. wt., 240.1).

m-*Tolyl* p-*tolyl ketone.* As stated above, a considerable quantity of this ketone was produced when *m*-tolyl *p*-tolyl acetaldehyde was oxidized by moist silver oxide. It was also found to be present as less reactive substance with sodium bisulphite than *m*-tolyl *p*-tolyl acetaldehyde when the latter was purified through the addition product, and likewise obtained by the oxidation of *α*-*m*-tolyl *α*-*p*-tolyl ethylene glycol by chromic acid in acetic acid as mentioned above. The Friedel Crafts' reaction between *m*-toluyl chloride and toluene also gave the same ketone. All these specimens melted at 72°C. alone or mixed with one another, and gave the analytical data conforming with the formula. (Found: C, 85.2; H, 7.2%. Mol. wt. (Rast), 226, (cryoscopic in benzene), 218. $C_{15}H_{14}O$ requires C, 85.7; H, 6.6%. Mol. wt., 210). J. Lavaux(59) obtained the ketone by the oxidation of *m,p*-ditolylmethane finding the melting point 70.5°C, while W. Scharivin and Schorygin(60) gave 82°C., probably a typographical error for 72°C. The semicarbazone was obtained by standing the hot solution of the ketone (0.2 g.), semicarbazide hydrochloride (0.2 g.) and potassium acetate (0.2 g.) dissolved in dilute alcohol (2 c.c.) for 22 days. The solution of the mixture had been heated and shaken every morning and on the 22nd day the content of the flask was first found solidifing to a semi-solid mass. It crystallised from dilute alcohol in flat prisms, m.p. 177–179°C. (corr.). Lavaux(59) gave the melting point 180°C. The oxime of the ketone was obtained by adding aqueous sodium hydroxide (0.7 g. in 2 c.c.

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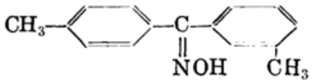
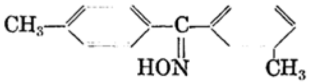
(59) *Chem. Zentr.*, **1910 II**, 1386.

(60) *Ber.*, **36** (1903), 2027.

water) into the alcoholic solution of the ketone (0.4 g. in 7 c.c. alcohol) mixed with hydroxylamine hydrochloride (0.4 g. in 2 c.c. water) and by the subsequent heating of the mixture for a while. The reaction mixture was left to stand overnight and neutralised with dilute hydrochloric acid. An oil separated which soon solidified. It melted at 119–129° when recrystallised once from dilute alcohol. By the fractional crystallisation over twenty times from dilute alcohol two fractions melting at 119–121°C. (A) and 133–134°C. (B) were obtained. J. Lavaux(59) obtained the oxime melting at 128–129°C. and W. Scharivin and Schorygin(60) two isomers melting at 118–119°C. and 143°C. respectively. Both (A) and (B) were sujbected to the Beckmann rearrangement by the action of phosphorus pentachloride in ether solution giving two isomeric toluyl toluidides melting at 104°C. (glittering scales from dilute alcohol) and 111–112°C. (silky needles from the same solvent) respectively. (Found: N, 6.8 for the former, 6.1 for the latter. $C_{15}H_{15}ON$ requires N, 6.2%). The former (m.p. 104°C.) was confirmed to be *p*-toluyl *m*-toluidide by the mixed melting point with the specimen synthesised form *p*-toluic acid and *m*-toluidine, while the latter (m.p. 111–112°C.) *m*-toluyl *p*-toluidide, the same product as that from *m*-toluic acid and *p*-toluidine. The configurations of the oximes, therefore, are as follows:—



(A) (m.p. 119-121°C.)



(B) (m.p. 133–134°C.)

p-*Tolyl* m-*methylbenzyl ketone.* As one of the starting materials for the preparation of the above ketone *m*-xylene was taken. It was first brominated and then interacted with potassium cyanide following the informations given by E. F. J. Atkinson and J. F. Thorpe(61) and A. F. Titley(62) respectively. *m*-Xylyl cyanide thus obtained was converted to *m*-tolyl acetamide by Br. Radziszewski and P. Wispek's method,(63) which (5 g.) on boiling with concentrated hydrochloric acid (15 c.c.) gave m-tolyl acetic acid (3.5 g.). The acid (5 g.) was boiled with thionyl chloride (20 c.c.) on the water bath for 2 hours, the excess thionyl chloride was driven by evacuation and the residue distilled in vacuo giving pure *m*-tolyl acetyl chloride (5 g.). At every step of the above preparation the fractional distillation or fractional crystallization was carried out in order to remove the isomeric impurities as far as possible. The most effective separation from isomers was now found to be performed by the fractional crystallization of the acid amides from hot water. P. Hill and W. F. Short(64) reported the inseparability of the mixture of ortho and para isomers of xylyl bromides, chlorides, cyanides, acetates or alcohols and tolyl acetic acids by fractionations as already stated.

m-Tolyl acetyl chloride (5 g.) thus obtained was added drop by drop to toluene (30 c.c.) mixed with anhydrous aluminium chloride (5 g.). After 4 hour's standing all the aluminium chloride was dissolved. The

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(61) *J. Chem. Soc.*, **91** (1907), 1699.
(62) *J. Chem. Soc.*, **1926**, 514.
(63) *Ber.*, **18** (1885), 1282.
(64) *J. Chem. Soc.*, **1935**, 1126.

reaction mixture was poured into ice water (150 c.c.), the upper layer was separated, combined with the toluene extract of the lower layer, washed with dilute caustic potash and with water, dried over anhydrous sodium sulphate. On distilling off the toluene a blackish brown mass (8 g.) was obtained, which was recrystallised from dilute alcohol several times with the addition of active charcoal and gave the required ketone which formed colourless long flat needles (3.1 g.), m.p. 68°C. (Found: C, 85.8; H, 7.4 . $C_{16}H_{16}O$ requires C, 85.7; H, 7.1%). The ketone dissolves in concentrated sulphuric acid tinging it with a canary yellow colour. The semicarbazone crystallised in colourless needles from dilute alcohol, m.p. 192–194°C. (uncorr.) (with slight decomp.). (Found: N, 14.8. $C_{17}H_{19}ON_3$ requires N, 14.9%).

The oxime formed also colourless needles when recrystallised from dilute alcohol, m.p. 108–109°C. (Found: N, 6.3. $C_{16}H_{17}ON$ requires 5.9%).

m-*Tolyl* p-*methylbenzyl ketone.* The ketone was synthesised in two ways.

(a) *p*-Tolyl acetonitrile (6 g.) dissolved in ether (50 c.c.) was added to the Grignard reagent prepared from *m*-iodotoluene (40 g.) and magnesium ribbon (4.4 g.), the reaction mixture was boiled for 10 hours, treated with cold dilute sulphuric acid (20 g. conc. acid in 800 c.c. ice water). The required ketone was produced as ketimine sulphate dissolved in the water layer, which was separated, washed with ether and heated gently on the water bath. The ketone was liberated as a reddish oil floating on the surface. It was extracted with ether, washed with water, dried over anhydrous sodium sulphate and the ether was driven off. A brownish oil (1.4 g.) thus obtained solidified on cooling to −15°C., which crystallised from dilute alcohol in colourless fine needless, m.p. 40–41°C. (Found: C, 85.4; H, 7.4. $C_{16}H_{16}O$ requires C, 85.7; H, 7.1%).

(b) The ketone was obtained by the oxidation of the corresponding alcohol, which was in its turn obtained by the interaction of p-tolyl acetaldehyde with *m*-tolyl magnesium iodide. The *p*-tolyl acetaldehyde was prepared by dehydration of *p*-tolyl ethylene glycol produced by the catalytic hydrogenation of *p*-methylbenzoyl carbinol in the following way.

A colloidal solution of platinum was obtained by passing hydrogen into the solution of chloroplatinic acid (1.5 g., calc. as Pt) and gum arabic (1 g.) in dilute acetic acid (50 c.c. acid in 120 c.c. water) with platinum black (0.03 g.) suspended in the solution. *p*-Methylbenzoyl carbinol (13.1 g. dissolved in 80 c.c. glacial acetic acid) was added to the above colloidal solution and the mixture was shaken in the atmosphere of hydrogen at the ordinary temperature and pressure. 1800 c.c. (22°C, 761 mm.) of hydrogen were absorbed in 60 minutes. Caustic soda (85 g. dissolved in a small quantity of water) was added to the solution. Care must be taken not to make the solution alkaline, as otherwise the next step i.e. the extraction with ether would become difficult. It was extracted with a large amount of ether, the ethereal extract washed with dilute alkali and with water, dried over anhydrous sodium sulphate and the ether was removed by distillation. The residue (11 g.) solidified on standing. The raw p-tolyl ethylene glycol thus obtained crystallised from petroleum benzine in glittering scales, m.p. 76.5–77.5°C. (Found: C, 70.5; H, 8.0. $C_9H_{12}O_2$ requires C, 71.1; H, 7.9%). The remaining *p*-methylbenzoyl carbinol could thereby be easily removed, as it is more soluble in the solvent than the glycol though its melting point is higher than that of the glycol by about 15°. E. Späth(65) obtained diethyl ether of the glycol. No description of the free glycol was however given by him.

The raw product of *p*-tolyl ethylene glycol (8 g.) was sealed in a glass tube mixed with water (20 c.c.) and 4 drops of concentrated hydrochloric acid, heated at 180–185°C. for 4 hours. The contents of the tube were then extracted with ether, washed with water, dried over anhydrous sodium sulphate and distilled in vacuo. *p*-Tolyl acetaldehyde (2 g.) thus obtained passed over at 92–93°C. under the reduced pressure of 8 mm. which on further purification boiled at 97°C. under 10 mm., d_4^{20}, 1.0052; n_D^{20}, 1.5255; M. R. found: 40.86; calc. (Eisenlohr) 40.17. K. Kling(66) gave the boiling point 109°C./17 mm. while E. Späth(67) 96°C./10 mm.

p-Tolyl acetaldehyde (2 g. dissolved in 2 c.c. ether), synthesised as stated above, was added to the Grignard reagent prepared from *m*-iodotoluene (3.5 g.) and magnesium ribbon (0.36 g.). The reaction mixture was boiled for 2 hours and left to stand overnight. It was decomposed by dilute hydrochloric acid (1.2 c.c. conc. acid in 50 c.c. ice water) and extracted withe ether, the ethereal extract was washed with dilute solution of potassium carbonate, dried over anhydrous sodium sulphate and the ether was removed by distillation. The residue was distilled in steam leaving in the flask a thick oil (0.85 g.), the raw *p*-methylbenzyl m-tolyl carbinol, which without further purification was oxidized to the corresponding ketone; the oil was dissolved in 80% acetic acid (60 c.c.) and chromic oxide (0.28 g. in 1 c.c. water) was added to it. The mixture turned at once blackish, and then green when heated on the water bath for 30 minutes. It was poured into ice water (600 c.c.). A resinous matter thus produced sticked to the bottom of the vessel, which was extracted with ether, the ethereal extract was washed with dilute caustic potash and with saturated solution of sodium chloride, dried over calcium chloride, and the ether was removed leaving viscous matter (0.53 g.). It solidified on long standing at −15°C. It was recrystallised from dilute alcohol giving a small quantity of the required ketone melting at 40–41°C.

The semicarbazone was not obtained even after 140 days' standing of the solution of the ketone (0.2 g.), semicarbazide hydrochloride (0.2 g.) and potassium acetate (0.2 g.) in dilute alcohol, only a small quantity of white powder being thereby produced which decomposed at about 250°C.

The oxime was obtained in the usual way; the ketone (0.08 g.) and hydroxylamine hydrochloride (0.14 g.) were dissolved in hot dilute alcohol (2 c.c.), the solution was left to stand overnight and neutralized with dilute sulphuric acid. An oil (0.06 g.) was thrown down which on cooling solidified. It crystallised from dilute alcohol in colourless needles, m.p. 88.5°C. It was subjected to the Beckmann rearrangement; phosphorus pentachloride (0.05 g.) was added to the ether solution of the oxime (0.05 g. in 2 c.c. ether), which was shaken for 15 minutes and poured into ice water. White granules separated and was recrystallised from dilute

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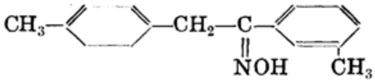
(65) *Monatsh.*, **37** (1916), 9.

(66) *Chem. Zentr.*, **1908**, **I**, 951.

(67) *Ber.*, **47** (1914), 767; *Monatsh.*, **37** (1916), 9.

alcohol in colourless plates or from ligroin in needles, m.p. 123–124°C., which was not depressed by the mixing of [*p*-tolyl-acetyl]-*m*-toluidide synthesised from *p*-tolyl acetic acid and *m*-toluidine, showing that the original oxime was of the following anti-*p*-methylbenzyl configuration:—



(Found: N, 5.9. $C_{16}H_{17}ON$ requires N, 5.9%). *m*-Toluyl *p*-methylbenzylamine, the compound isomeric to [*p*-tolyl-acetyl]-*m*-toluidide, was obtained by the condensation of m-toluic acid and *p*-methylbenzylamine, colourless leaflets from dilute alcohol, m.p. 116°C. (Found: N, 6.3, $C_{16}H_{17}ON$ requires N, 5.9%). *m*-Tolyl *p*-methylbenzyl ketone was oxidized slowly by atmospheric oxygen giving *p*- and *m*-toluic acids; on long standing white granules deposited on the wall of the vessel containing the ketone, which were separated into the above mentioned two isomeric acids by the fractional crystallisation from hot water, melting at 179°C. and 110°C. respectively alone or mixed with the authentic specimens.

Isomerization of m-tolyl p-tolyl acetaldehyde. The aldehyde (13.5 g.) was passed on the Japanese acid earth (25 g.) heated at 300°C. at a rate of 3.8 g. per hour, being accompanied by the slow current of carbon dioxide. A heavy yellowish brown oil covered by the thin layer of toluene (7.5 g. in total) was collected in the receiver during the passing of the aldehyde and the lapse of 1 hour after it. The temperature of the tube was then raised to 350°C. under the reduced pressure of 30 mm. and a thick brownish red oil (0.7 g.) was obtained. Both the products showed no colour reaction characteristic to aldehydes. They were combined, washed with dilute aqueous potassium hydroxide, with the saturated solution of sodium chloride and dried over calcium chloride. The calcium chloride was washed with ether to remove the absorbed reaction products, the ether was evaporated up and the residue was combined with the main part, which was distilled under the reduced pressure of 5 mm. giving the following fractions:—

Table 1.

Fraction	B.p. (°C)	Yields (g.)	Remarks
(1)	140–167	1.1	Light yellow oil with aromatic odour.
(2)	167–175	1.3	Light yellow oil, almost odourless.
(3)	175–180	4.0	Almost all amount came over constantly at 177°C. Odourless, yellow viscous oil.
(4)	Above 180	0.7	Very viscous, reddish brown oil.
		Total 7.1	

The alkaline washing liquid of the reaction product before subjected to the distillation was concentrated on the water bath and neutralised by dilute sulphuric acid. Oil drops were thrown down which crystallised on cooling (0.01 g.). They were recrystallised from hot water and found to be a mixture of *p*- and *m*-toluic acids.

The third fraction in Table I (b.p. 175–180°C./5 mm.) made the main part of the reaction products. It did not tend to solidify when cooled. 0.5 g. of it gave the solid oxime (0.4 g.), colourless needles, m.p. 86.5–87.5°C., which was confirmed to consist of *m*-tolyl *p*-methylbenzyl ketoxime exclusively. The oxime was identified by the mixed melting point with the authentic specimen as well as by the formation of [*p*-tolyl-acetyl]-*m*-toluidide by the Beckmann rearrangement. *p*-Tolyl *m*-methylbenzyl ketoxime was not found to exist in it, the fact which was also confirmed in the cases of the other fractions in Table 1. It may, therefore, safely be mentioned that in the molecule of *m*-tolyl *p*-tolyl acetaldehyde the migration of *m*-tolyl radical exclusively took place under the experimental condition given above.

In one run of the experiment carried out under the same condition, the reaction product was left to stand for just three months. A considerable quantity of white deposit was formed in the vessel containing the oily product, which revealed itself as a mixture of *m*- and *p*-toluic acids melting at 110 and 179°C. respectively when separated by the fractional crystallisation from hot water. The acids were most probably formed by the oxidation of *m*-tolyl *p*-methylbenzyl ketone with atmospheric oxygen.

(To be continued.)

The Tokyo Imperial Industrial Research
Laboratory, Hatagaya, Tokyo.