To one gram of the imine in 2 ml. of water was added one drop of 10% hydrochloric acid followed by an acidified solution of 2,4-dinitrophenylhydrazine in methanol. The precipitate of isobutyraldehyde 2,4-dinitrophenylhydrazone was purified by recrystallization from chloroform and gave m.p. 179°. The recorded[7] m.p. for this derivative is 182°.

Isobutyleneimine (43.5 g., 0.61 mole) containing 4.4 g. of nickel catalyst (U.O.P.) was hydrogenated in a glass insert tube in a rocker type bomb at 130° and 800 p.s.i. showing a total consumption of 0.65 mole of hydrogen. After cooling, the material was filtered and fractionated in a packed column to give 38 g. (85%) of isobutylamine, b.p. 70°, $n^{20}\text{D}$ 1.3970 and d^{24}_{4} 0.7343. The accepted[8] constants for isobutylamine are b.p. 69°, $n^{17}\text{D}$ 1.3988 and d^{25}_{4} 0.724.

One gram of the isobutylamine was treated with benzenesulfonyl chloride and the resultant sulfonamide gave a melting point of 54°. The recorded[9] m.p. for N-isobutylbenzenesulfonamide is 53°.

Identification of Fraction 2.—In several experiments, in which a low yield of diisobutylamine was realized, a fraction boiling at 129° was obtained. Since it showed evidence of unsaturation and gave analyses corresponding to $C_8H_{17}N$ it was tentatively assumed to be isobutylideneisobutylamine (VI). This was further confirmed from the boiling point (129°) and refractive index ($n^{20}\text{D}$ 1.4134), which correspond favorably with the literature values of b.p. 130–131°[10] and $n^{21.5}\text{D}$ 1.4135[11] for VI.

Anal. Calcd. for $C_8H_{17}N$: C, 75.60; H, 13.47; N, 11.01. Found: C, 75.46; H, 13.68; N, 11.20.

Identification of Fraction 3.—The yellow oil boiling at 142°, which did not show evidence of unsaturation was identified as diisobutylamine from its derivatives, namely, the benzenesulfonamide, m.p. 55°, phenylthiourea, m.p. 114° and the oxalate, m.p. 244°. The literature[12] values for the melting points of these three derivatives are 55°,[9] 113°[9] and 245–248°,[12] respectively. The boiling point of diisobutylamine is listed as 139°.[9]

Isolation of 2,2,5,5-Tetramethyl-3,6-dihydroxypiperazine (IX).—From the higher boiling fractions, 150–180°, 11 g. of a white crystalline substance separated upon standing and was purified by washing with benzene. It gave a melting point of 86°, was miscible with alkalies, sparingly soluble in water and evolved a gas, presumably carbon monoxide, with dilute acids. The substance did not react with benzenesulfonyl chloride nor show evidence of unsaturation with bromine. Since it gave molecular weight values (Rast) between 180–200 and analyses corresponding to $C_8H_{18}O_2N_2$, the substance appears to be the dimer of the amino aldehyde, 2-amino-2-methyl-1-propanal, 2,2,5,5-tetramethyl-3,6-dihydroxypiperazine (IX).

Anal. Calcd. for $C_8H_{18}O_2N_2$: C, 55.14; H, 10.41. Found: C, 55.10; H, 10.46.

Identification of Ammonia.—The hydrochloric acid solution in the first trap was treated with an excess of sodium hydroxide, a benzenesulfonamide, m.p. 154–155°, and a phenylthiourea, m.p. 149°, were prepared from the ammoniacal smelling gas. The literature melting point values for benzenesulfonamide, 153°,[13] and phenyl thiourea, 154°,[14] indicated that ammonia was the sole gaseous product of the reaction. No gaseous products were detected in the alkali trap.

SPOKANE, WASHINGTON
LISLE, ILLINOIS

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(7) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," Ed. 3, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 229.

(8) I. M. Heilbron and B. M. Bunbury, "Dictionary of Organic Compounds," Vol. 2, Oxford University Press, New York, N. Y., 1936, p. 412.

(9) Reference 7, p. 234.

(10) M. A. Berg, *Bull. soc. chim. (Paris)*, [3] **7**, 545 (1892).

(11) M. Delépine, *Ann. chim. phys.*, [8] **25**, 559 (1912).

(12) Reference 8, Vol. 1, p. 553.

(13) Reference 7, p. 232.

(14) Reference 8, Vol. 3, p. 461.

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Restricted Rotation About the Aliphatic Carbon–Carbon Bond

BY ROGER ADAMS, ROBERT S. VORIS[1] AND L. N. WHITEHILL

RECEIVED JUNE 26, 1952

Ethyl triphenylcarbinyl ketone, ethyl and methyl diphenyl-*o*-tolylcarbinyl ketone and ethyl and methyl phenyl-di-*o*-tolylcarbinyl ketone were prepared. All except the methyl diphenyl-*o*-tolylcarbinyl ketone were synthesized through intermediate triarylcarbinols, triarylchloromethanes, triarylacetic acids and triarylacetyl chlorides. By the action of ethylmagnesium bromide and carbon dioxide, the ethyl and methyl diphenyl-di-*o*-tolylcarbinyl ketones were converted to α-methyl-β-keto-γ-phenyl-γ,γ-di-*o*-tolylbutyric acid and β-keto-γ-phenyl-γ,γ-di-*o*-tolylbutyric acid, respectively. The former by the action of phosphorus pentachloride did not yield the corresponding β-chlorocrotonic acid, but instead the β-keto acid chloride. Diazomethane and this acid resulted merely in esterification to the β-keto acid ester.

The concept of restricted rotation has been effectively demonstrated by chemical resolution of properly substituted biphenyls,[2] aryl olefins[3] and aryl amines.[4] To date, however, the only evidence for restricted rotation about the aliphatic carbon–carbon bond has been furnished by thermodynamic data[5] and by physical data on dipole moments,[6] X-ray spectra,[7] Raman spectra,[8] and electron diffraction.[9]

As a logical extension from the biphenyls I, in which the hindrance centers about an aromatic–aromatic bond, and the aryl olefins II, in which the hindrance centers about an aromatic-aliphatic bond, it did not appear impossible that certain triarylcarbinyl III-a and trialkylcarbinyl III-b olefins might be resolvable because of the restriction of rotation about the aliphatic–aliphatic single bond attached to bulky tertiary groups.

Although the structure IIIa contains aromatic groups, the β,γ-pivotal bond is not attached to an

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(1) Allied Chemical and Dye Corporation Fellow, 1941–1943. Part of the experimental work on the diphenyl-*o*-tolyl derivatives and all of the work on the di-*o*-tolylphenyl derivatives was performed by R. S. Voris in partial fulfillment of requirements for the Degree of Doctor of Philosophy, 1943.

(2) R. Adams and H. C. Yuan, *Chem. Revs.*, **12**, 261 (1933).

(3) (a) H. Gilman, "Organic Chemistry," Vol. I, John Wiley and Sons, Inc., New York, N. Y., Second Edition, 1943, p. 377; (b) R. Adams and J. W. Mecorney, THIS JOURNAL, **67**, 798 (1945).

(4) R. Adams and M. Rothstein, *ibid.*, **71**, 1620 (1949); see also previous papers.

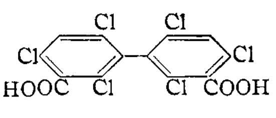
(5) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940, p. 90; K. S. Pitzer, THIS JOURNAL, **70**, 2140 (1948); E. L. Pace and J. G. Aston, *ibid.*, **70**, 566 (1948); E. N. Lassettre and L. B. Dean, *J. Chem. Phys.*, **17**, 317 (1949); J. O. Halford, *ibid.*, **17**, 111 (1949).

(6) S. Winstein and R. E. Wood, THIS JOURNAL, **62**, 548 (1940).

(7) J. D. McCullough, *ibid.*, **62**, 480 (1940).

(8) G. Glockler, *Rev. Modern Phys.*, **15**, 111 (1943); H. J. Taufen, M. J. Murray and F. F. Cleveland, THIS JOURNAL, **65**, 1130 (1943).

(9) Y. Morino and M. Iwasaki, *J. Chem. Phys.*, **17**, 216 (1949).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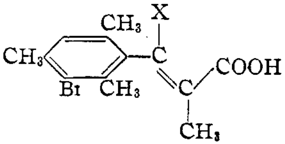
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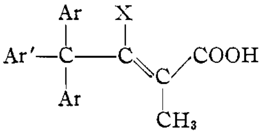
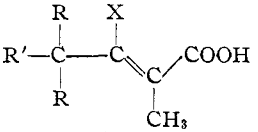
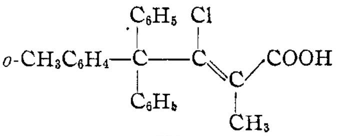
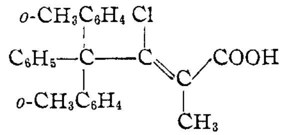

IIIa


IIIb

aromatic nucleus. Structure IIIb is a completely aliphatic molecule. Examination of Stuart and Fisher–Hirschfelder molecular models indicates that properly chosen triarylcarbinyl and trialkylcarbinyl olefins should be capable of existence as optical antipodes. While molecular models are reliable in many cases, they are by no means infallible in predicting the degree of restriction in proposed structures. Scalar planar representations, which proved helpful in the biphenyl and aryl olefin series, are of little value for compounds of the type of IIIa and IIIb, since the obstructing groups are not only non-coplanar but are also capable of motion with respect to each other. Thus they can assume a variety of positions so as to exhibit a minimum of interference. Hindrance to rotation of this kind has been used to explain the crystal polymorphism of tri-α-naphthylboron[10] and the light absorption behavior of crystal violet.[11]

The representative compounds for which suitable synthetic procedures have been sought in this investigation are α-methyl-β-chloro-γ,γ-diphenyl-γ-*o*-tolylcrotonic acid (IV) and α-methyl-β-chloro-γ-phenyl-γ,γ-di-*o*-tolylcrotonic acid (V).


IV


V

These particular molecules were chosen because molecular asymmetry, if shown by chemical resolution, could be attributed only to the restriction of rotation about the bond between the β- and γ-carbon atoms. Two of the groups on the γ-carbon atom must be identical since three different groups would confer optical activity to the molecule by virtue of the resulting asymmetry of this atom. On the other hand, three identical groups would permit complete symmetry even though restriction of rotation about the single bond in question did occur and resolution would consequently be impossible.

The choice of the other ethylenic substituents is based on the role of the various groups in the aryl olefins, in which a substituent alpha to the carboxyl (present for alkaloidal salt formation) definitely increases the degree of interference. Since the geometric configurations favored by the synthetic methods generally used previously are not known with certainty, an α-methyl group was selected to insure sufficient hindrance whether a *cis* or a *trans* isomer resulted. The size of the substituent beta to a carboxyl is of prime consideration, since no aryl olefins bearing hydrogen or methoxyl in that position have been resolved, while those holding chlorine, bromine and methyl all had appreciable half-life values.[3b,12]

The approach to the synthesis of compounds IV and V was through the alkyl triarylcarbinyl ketones[13] which like previously known hindered ketones should be readily converted to β-ketonic acids by action of the Grignard reagent and carbonation; $\mathrm{ArAr'Ar'CCOC_2H_5} \rightarrow \mathrm{ArAr'Ar'CCOCH(CH_3)CO_2H}$.[14]

Although methyl diphenyl-*o*-tolylcarbinyl ketone (VIII) was readily prepared by the forced addition of methylmagnesium iodide to diphenyl-*o*-tolylacetaldehyde (VI) and subsequent oxidation of the secondary carbinol VII, the corresponding ethyl ketone could not be obtained in this way because ethylmagnesium bromide failed to react with the aldehyde. As a consequence, the procedure of Schmidlin[13] was adopted for the synthesis

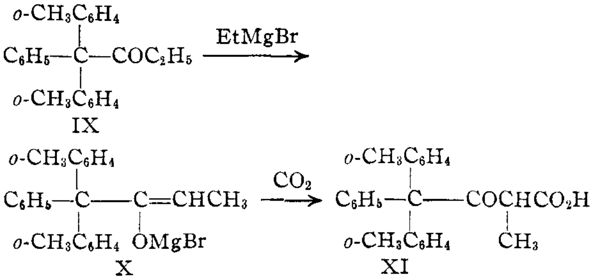
$$\mathrm{RCOCHOHR} \xrightarrow{\mathrm{R'MgBr}} \mathrm{R'RC(OH)CHOHR} \longrightarrow \underset{\mathrm{VI}}{\mathrm{RRR'CCHO}} \xrightarrow{\mathrm{CH_3MgI}}$$

$$\underset{\mathrm{VII}}{\mathrm{RRR'CCHOHCH_3}} \longrightarrow \underset{\mathrm{VIII}}{\mathrm{RRR'CCOCH_3}}$$

R = phenyl; R′ = *o*-tolyl

of the desired ketones, ethyl diphenyl-*o*-tolylcarbinyl ketone, ethyl phenyl-di-*o*-tolylcarbinyl ketone, required for IV and V and also for the synthesis of methyl phenyl-di-*o*-tolylcarbinyl ketone. The appropriate triarylchloromethane was converted

$$\mathrm{RR'R'CCl} \xrightarrow[\mathrm{CO_2}]{\mathrm{Mg}} \mathrm{RR'RCCO_2H} \longrightarrow \mathrm{RR'R'CCOCl} \xrightarrow{\mathrm{EtMgBr}}$$


IX X XI

$$\mathrm{C_6H_5C}(o\text{-}\mathrm{CH_3C_6H_4})_2\mathrm{COC_2H_5} \xrightarrow{\mathrm{EtMgBr}} \mathrm{C_6H_5C}(o\text{-}\mathrm{CH_3C_6H_4})_2\mathrm{C(OMgBr){=}CHCH_3} \xrightarrow{\mathrm{CO_2}} \mathrm{C_6H_5C}(o\text{-}\mathrm{CH_3C_6H_4})_2\mathrm{COCH(CH_3)CO_2H}$$

R = phenyl; R′ = *o*-tolyl

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[10] H. C. Brown and S. Sujishi, THIS JOURNAL, **70**, 2793 (1948).

[11] G. N. Lewis, T. T. Magel and D. Lipkin, *ibid.*, **64**, 1774 (1942).

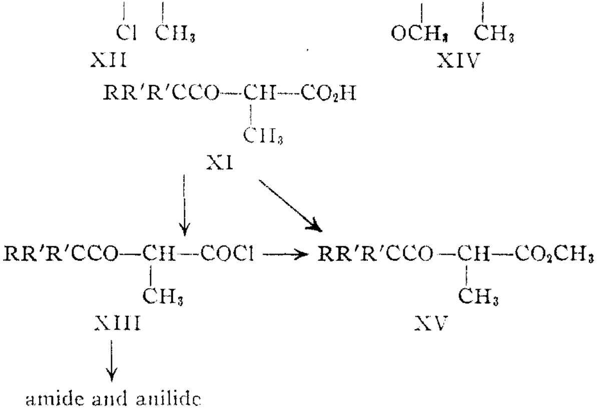
[12] R. Adams and C. W. Theobald, *ibid.*, **65**, 2383 (1943); R. Adams and R. S. Ludington, *ibid.*, **67**, 794 (1945).

[13] J. Schmidlin and H. H. Hodgson, *Ber.*, **41**, 438 (1908); J. Schmidlin, *ibid.*, **43**, 1137 (1910).

[14] R. C. Fuson, W. O. Fugate and C. H. Fisher, THIS JOURNAL, **61**, 2362 (1939); R. C. Fuson, *et al.*, *J. Org. Chem.*, **4**, 11 (1939); F. C. Whitmore and R. S. George, THIS JOURNAL, **64**, 1239 (1942); F. C. Whitmore and C. T. Lester, *ibid.*, **64**, 1251 (1942).

to the triarylacetic acid, then to the acid chloride. From the acid chloride with excess ethylmagnesium bromide, the ketone IX was formed which by subsequent treatment with ethylmagnesium bromide and carbon dioxide yielded the corresponding ketonic acid XI. The ketonic acids are much more stable to decomposition than most β-keto acids.[15]

The conversion of the β-keto acid XI to the desired α-methyl-β-chloro-γ-phenyl-γ,γ-di-*o*-tolylcrotonic acid (XII) was attempted in the same way that proved so satisfactory for the conversion of α-methyl-β-keto-β-bromomesitylpropionic acid to α-methyl-β-chloro-β-bromomesitylacrylic acid.[16] The desired product was never realized. The benzene solvate of XI reacted with phosphorus pentachloride in phosphorus oxychloride at room temperature to give not the β-chloroacrylic acid derivative XII but instead the keto acid chloride XIII, identical with the product formed by the action of thionyl chloride and pyridine on the acid XI. Boiling the acid XI with phosphorus oxychloride alone caused decarboxylation to ethyl phenyl-di-*o*-tolylcarbinyl ketone.



R = phenyl; R′ = *o*-tolyl

The action of excess of diazomethane on the acid XI which might have been expected to give the methyl ester of α-methyl-β-methoxy-γ-phenyl-γ,γ-di-*o*-tolylcrotonic acid (XIV) yielded merely the methyl ester (XV) of the β-keto acid which could also be formed from the acid chloride (XIII) and methanol.

Experimental

All melting points are corrected.

1,1-Diphenyl-1-*o*-tolyl-2-propanol.—To a solution of 15.1 g. (0.1 mole) of methylmagnesium iodide in 50 ml. of benzene, 2.86 g. (0.1 mole) of diphenyl-*o*-tolylacetaldehyde[17] in 40 ml. of benzene was added over a period of 30 minutes. The mixture was refluxed 27 hours, then decomposed in the usual way. The residual oil solidified when triturated with 10 ml. of petroleum ether (b.p. 30–60°). The resultant 2.63 g. (88%) of product was recrystallized from petroleum ether and from methanol, m.p. 93–94°.

Anal. Calcd. for $C_{22}H_{22}O$: C, 87.36; H, 7.35. Found: C, 86.51; H, 7.38.

In ether solution the reaction did not occur.

Ethylmagnesium bromide in place of methylmagnesium iodide failed to react under similar conditions.

Phenyl-di-*o*-tolylcarbinol.—The Grignard reagent from 5 moles of magnesium and 5 moles of *o*-bromotoluene in 2 l. of dry ether was prepared during a period of 8 hours. The ether was then distilled off and replaced by one liter of dry benzene. A solution of 2.4 moles of ethyl benzoate in 500 ml. of dry benzene was added over 4 hours; the orange-brown solution was then heated under reflux for 8 hours. After decomposition with ice and 150 ml. of sulfuric acid, the organic layer was washed, neutralized, dried, concentrated under diminished pressure, diluted with 800 ml. of petroleum ether (b.p. 30–60°) and cooled overnight. First, second and third crops of 207 g., 104 g. and 80 g., respectively, yielded 323 g. (44%). It was purified by crystallization from petroleum ether (b.p. 90–110°), m.p. 82–83°. Although this substance was previously mentioned as an intermediate in the formation of phenyl-di-*o*-tolylchloromethane, its constants were not reported.[18]

Anal. Calcd. for $C_{21}H_{20}O$: C, 87.46; H, 6.99. Found: C, 87.24; H, 7.04.

The carbinol crystallized from dioxane as fine white crystals, m.p. 104–105°, holding dioxane as solvate that was not removed by crystallization from petroleum ether. Heating *in vacuo* at 90° caused loss in weight of 0.36–0.39 mole of dioxane per mole of carbinol and left a residue, m.p. 82°, which was identical with phenyl-di-*o*-tolylcarbinol crystallized originally from petroleum ether. The analysis of the complex agreed satisfactorily with the composition calculated for 0.40 mole of dioxane per mole of carbinol.

Anal. Calcd. for $C_{21}H_{22}O{\cdot}(0.40\ C_4H_8O_2)$: C, 83.86; H, 7.23. Found: C, 83.90; H, 7.99.

Diphenyl-*o*-tolylcarbinol.—From *o*-bromotoluene and benzophenone by a similar procedure, an 80% yield of product resulted. It was purified by crystallization from petroleum ether; m.p. 97–99° (lit. m.p. 98°).[19]

Phenyl-di-*o*-tolylchloromethane.—A mixture of 243 g. of phenyl-di-*o*-tolylcarbinol, 700 ml. of dry benzene and 78.5 g. of distilled acetyl chloride was allowed to react for 2 hours and then heated under reflux for another hour. The solvent was removed under reduced pressure and the residual oil diluted with 400 ml. of petroleum ether (b.p. 90–110°) and allowed to crystallize overnight. A few drops of pyridine helped to remove dark colors from this solution. The total yield of product was 199 g. (89%). Recrystallization from petroleum ether containing 10% benzene and a few drops of acetyl chloride gave white crystals, m.p. 93–94°, which were extremely hygroscopic (lit. m.p. 92–94°).[18]

Diphenyl-*o*-tolylchloromethane.—From diphenyl-*o*-tolylcarbinol and acetyl chloride by the same procedure used for the phenyl-di-*o*-tolylchloromethane, white crystals in 84% yield were obtained. They were purified by recrystallization from petroleum ether–benzene, m.p. 135° (lit. 136–137°).[19b]

Diphenyl-*o*-tolylacetic Acid.—Using the procedure described for synthesis of triphenylacetic acid,[20] diphenyl-*o*-tolylchloromethane was converted to diphenyl-*o*-tolylacetic acid. A yield of 68% resulted. After purification by crystallization from glacial acetic acid glistening prisms were formed, m.p. 228–229°. This acid has been prepared previously by the carbonation of diphenyl-*o*-tolylmethyl sodium, m.p. 228°.[19b,21]

Anal. Calcd. for $C_{21}H_{18}O_2$: C, 83.42; H, 5.99. Found: C, 83.41; H, 6.34.

Methyl Diphenyl-*o*-tolylacetate.—The methyl ester was prepared by the action of diazomethane on the acid; white crystals from methanol–ethyl acetate, m.p. 145°.

Anal. Calcd. for $C_{22}H_{20}O_2$: C, 83.51; H, 6.37. Found: C, 83.36; H, 6.71.

Phenyl-di-*o*-tolylacetic Acid.—From phenyl-di-*o*-tolylchloromethane by a similar procedure, an orange gum remained after distillation of the ether. This was boiled with 10% aqueous sodium carbonate and filtered. The filtrate was diluted with boiling water, cooled and filtered. There

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[15] O. Widman and E. Wahlberg, *Ber.*, **44**, 2065 (1911); E. Wahlberg, *ibid.*, **44**, 2071 (1911).

[16] R. Adams and M. W. Miller, *ibid.*, **62**, 53 (1940).

[17] R. Roger and W. B. McKay, *J. Chem. Soc.*, 2234 (1931); 336 (1933).

[18] C. S. Marvel, J. F. Kaplan and C. M. Himel, This Journal, **63**, 1892 (1941).

[19] (a) S. F. Acree, *Ber.*, **37**, 990 (1904); (b) W. Schlenk and E. Bergmann, *Ann.*, **463**, 264 (1928).

[20] W. M. Cumming, I. V. Hopper and T. S. Wheeler, "Systematic Organic Chemistry," D. Van Nostrand, Inc., New York, N. Y., Third Edition, 1937, p. 120; G. Schmidlin, *Ber.*, **39**, 628 (1906).

[21] P. D. Bartlett and J. E. Jones, *ibid.*, **64**, 1840 (1942).

separated 11% of yellow solid, phenyl-di-*o*-tolylmethane. It was purified from petroleum ether, then glacial acetic acid; white plates, m.p. 101° (lit. m.p. 102–104°).[21]

The alkaline filtrate was extracted with ether, boiled with Darco, filtered, cooled by the addition of ice and acidified carefully with 6 *N* hydrochloric acid. From the white powder thus resulting, a 68% yield of product was obtained; after recrystallization from glacial acetic acid, glistening white crystals, m.p. 183–184° (lit. m.p. 184–185°).[21]

Anal. Calcd. for $C_{22}H_{20}O_2$: C, 83.50; H, 6.39. Found: C, 83.73; H, 6.45.

Methyl Phenyl-di-*o*-tolylacetate.—Diazomethane converted phenyl-di-*o*-tolylacetic acid to its methyl ester, which, after purification from methanol, melted at 155°.

Anal. Calcd. for $C_{23}H_{22}O_2$: C, 83.60; H, 6.71. Found: C, 83.76; H, 6.89.

Triphenylacetyl Chloride.—The reaction of 75 g. of triphenylacetic acid[20] in 300 ml. of dry benzene with 62 g. of purified thionyl chloride and 1 ml. of pyridine gave, after crystallizations from petroleum ether and benzene, an 80% yield of white prisms, m.p. 127–128°. This is a much superior method[22] to that using phosphorus pentachloride and acetyl chloride.[13,19]

Diphenyl-*o*-tolylacetyl Chloride.—A procedure similar to that for triphenylacetyl chloride was used except that the reaction mixture was heated on a water-bath for 3 hours. The yellow solution was filtered and evaporated to an orange oil which was treated with Norit in 20 ml. of boiling petroleum ether (b.p. 90–110°). The combined yield of first and second crops amounted to 82%; clumps of colorless needles, m.p. 86–87° (lit. 86.5–87°).[19b]

Phenyl-di-*o*-tolylacetyl Chloride.—An 85% yield of product was obtained. It was purified from benzene–petroleum ether (b.p. 30–60°); hard white crystals, m.p. 104°.

Anal. Calcd. for $C_{22}H_{19}ClO$: C, 78.91; H, 5.72. Found: C, 78.96; H, 5.96.

Ethyl Triphenylcarbinyl Ketone.—From 3.5 g. of powdered triphenylacetyl chloride and 0.1 mole of ethylmagnesium iodide, 1.2 g. of ketone, m.p. 103–104°, was obtained by the procedure of Schmidlin.[13] Since the material obtained by decomposition of the ether filtrate from the enolate melted over a wide range, it appears that the solid enolate is more satisfactory for the isolation of the ketone.

Ethyl Diphenyl-*o*-tolylcarbinyl Ketone.—From pulverized diphenyl-*o*-tolylacetyl chloride and ethylmagnesium iodide by a similar procedure, an oil was obtained which solidified under cold petroleum ether. After two recrystallizations from petroleum ether (b.p. 90–110°), 1.9 g. (24%) of colorless crystals resulted, m.p. 108–109°.

Anal. Calcd. for $C_{23}H_{22}O$: C, 87.90; H, 7.06. Found: C, 87.96; H, 7.19.

Ethyl Phenyl-di-*o*-tolylcarbinyl Ketone.—From phenyl-di-*o*-tolylacetyl chloride and ethylmagnesium bromide by the procedure just described, a thick sirup was obtained. When treated with 100 ml. of petroleum ether (b.p. 30–60°) white crystals deposited. After crystallization from ethanol 33 g. (67%) resulted, m.p. 103–104°.

Anal. Calcd. for $C_{24}H_{24}O$: C, 87.75; H, 7.38. Found: C, 87.90; H, 7.21.

Methyl Phenyl-di-*o*-tolylcarbinyl Ketone.—By a similar procedure from phenyl-di-*o*-tolylacetyl chloride and methylmagnesium bromide, a semi-solid was obtained. This was treated with petroleum ether to yield 72% of ketone. It was purified by recrystallization from ethanol, m.p. 123–124°.

Anal. Calcd. for $C_{23}H_{22}O$: C, 87.86; H, 7.05. Found: C, 87.92; H, 7.25.

An attempt to prepare this ketone by means of methylmagnesium iodide in place of methylmagnesium bromide resulted in an orange oil which resisted crystallization.

Methyl Diphenyl-*o*-tolylcarbinyl Ketone.—A solution of 13.9 g. of 1,1-diphenyl-1-*o*-tolyl-2-propanol in 150 ml. of glacial acetic acid was heated to 50°. A solution of 3.09 g. of chromic acid in 50 ml. of acetic acid and 50 ml. of water was added dropwise over 30 minutes; heating on a steam-bath was continued for another 30 minutes until the solution had turned green. The reaction mixture was poured onto ice; the white precipitate was collected on a filter and then dissolved in petroleum ether (b.p. 30–60°). This solution was concentrated to 100 ml. and cooled overnight to deposit 8.3 g. (60%) of hard white crystals. After two crystallizations from petroleum ether (b.p. 30–60°) 7.0 g. of crystals, m.p. 94–95°, was obtained.

Anal. Calcd. for $C_{22}H_{20}O$: C, 88.03; H, 6.72. Found: C, 88.00; H, 6.80.

α-Methyl-β-keto-γ-phenyl-γ,γ-di-*o*-tolylbutyric Acid.—To a twofold excess of ethylmagnesium bromide in 50 ml. of ether was added a solution of 16.4 g. of ethyl phenyl di-*o*-tolylcarbinyl ketone in 150 ml. of ether. The addition of the ketone during 30 minutes maintained gentle refluxing and gas was evolved. No precipitated enolate was evident, even after 3 hours of additional heating. The clear brown solution was transferred to a 400-ml. hydrogenation bottle, cooled in ice and attached to a hydrogenation apparatus which had been modified for carbonation. A heavy gum separated as carbon dioxide at 3 atm. was admitted; the system was then shaken at room temperature for 10 hours. The reaction mixture was decomposed by iced hydrochloric acid, washed with water and extracted with four 50-ml. portions of iced 3% aqueous sodium hydroxide. The alkaline extract, after dilution to 800 ml. and addition of ice, was acidified with cold 6 *N* hydrochloric acid. The granular acid was filtered immediately to prevent coagulation and washed with water.

The moist crude acid was dissolved in 100 ml. of benzene, filtered at once and decanted from the water layer. Soon thereafter, a white mass of crystals formed, they weighed 18 g. after drying. The filtrate yielded 3 g. more of product. This acid, solvated with 1.5 molecules of benzene, represents a yield of 86%. By evaporating benzene–ether solutions in a stream of air, a pure product was obtained, m.p. 95°.

Anal. Calcd. for $C_{25}H_{24}O_3 \cdot 1\frac{1}{2}C_6H_6$: C, 83.40; H, 6.79; neut. equiv., 489. Found: C, 83.32; H, 6.87; neut. equiv., 483, 491.

When heated, samples lost 34.8 and 32.3% in weight compared to 33% calculated for the loss of carbon dioxide plus 1.5 moles of benzene. The benzene was condensed and identified by melting point and index of refraction. Ethyl phenyl-di-*o*-tolylcarbinyl ketone was recovered.

The pure acid was isolated by dissolving the crude wet precipitated acid in ether, decanting from the water layer, evaporating at room temperature in an air stream and adding 50 ml. of petroleum ether (b.p. 30–60°). The crude product was recrystallized from petroleum ether (b.p. 90–110°) to form fine white crystals, m.p. 148–149° (dec.). The β-keto acid is quite stable when dry and free from acid. When heated above its melting point, the β-keto acid lost carbon dioxide and ethyl phenyl-di-*o*-tolylcarbinyl ketone remained.

Anal. Calcd. for $C_{25}H_{24}O_3$: C, 80.61; H, 6.50; neut. equiv., 372. Found: C, 80.73; H, 6.58; neut. equiv., 373, 373; active hydrogens, 1.79, 1.71.

Titration of the β-keto acid with methylmagnesium iodide according to the Zerewitinoff procedure indicated 1.75 active hydrogen atoms per molecule. The enolization of 75% may be either from the keto or carboxyl carbonyl group. The latter is the more probable because of the reactions found for this keto acid.

Attempted Conversion to α-Methyl-β-chloro-γ-phenyl-γ,γ-di-*o*-tolylcrotonic Acid.—No identifiable product resulted when pure α-methyl-β-keto-γ-phenyl-γ,γ-di-*o*-tolylbutyric acid was treated with a cold or warm (up to 85°) mixture of phosphorus oxychloride and phosphorus pentachloride.

A similar experiment with the methyl ester (described below) resulted primarily in the recovering of unchanged ester.

α-Methyl-β-keto-γ-phenyl-γ,γ-di-*o*-tolylbutyryl Chloride.—The benzene solvated α-methyl-β-keto-γ-phenyl-γ,γ-di-*o*-tolylbutyric acid was converted to the corresponding acid chloride by the procedure described for other acid chlorides in this Communication. The crude product was a thick oil. Crystallization from petroleum ether (b.p. 30–60°) gave 81% yield of white crystals, m.p. 123–124°.

Anal. Calcd. for $C_{25}H_{23}ClO_2$: C, 76.81; H, 5.93. Found: C, 76.85; H, 6.18.

α-Methyl-β-keto-γ-phenyl-γ,γ-di-*o*-tolylbutyranilide.—Upon addition of 1 ml. of aniline to a solution of 0.30 g. of

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(22) J. F. Norris and A. E. Bearse, THIS JOURNAL, **62**, 953 (1940).

the acid chloride in 10 ml. of benzene, a white precipitate formed immediately. After 20 minutes of refluxing, the solution was washed with dilute hydrochloric acid, dried and evaporated. The residual oil separated as a gum from petroleum ether. It was purified by crystallization from ethanol; white crystals, m.p. 175°.

Anal. Calcd. for $C_{31}H_{29}NO_2$: C, 83.19; H, 6.53. Found: C, 83.39; H, 6.83.

α-Methyl-β-keto-γ-phenyl-γ,γ-di-*o*-tolylbutyramide.—A stream of gaseous ammonia was bubbled through a solution of 0.40 g. of the β-keto acid chloride in 15 ml. of benzene for 40 minutes. The precipitated ammonium chloride was filtered; the oil left by evaporation of the solvent solidified when triturated with petroleum ether (b.p. 30–60°) but separated as a gelatinous mass from warm petroleum ether; 0.32 g. (84%). The amide was crystallized from ethanol-petroleum ether (b.p. 90–110°); m.p. 161°.

Anal. Calcd. for $C_{25}H_{25}NO_2$: C, 80.83; H, 6.78. Found: C, 80.70; H, 6.92.

Methyl α-Methyl-β-keto-γ-phenyl-γ,γ-di-*o*-tolylbutyrate.—Treatment of 2 g. of pure α-methyl-β-keto-γ-phenyl-γ,γ-di-*o*-tolylbutyric acid or the benzene solvate in 25 ml. of ether with approximately 1 g. of diazomethane in 70 ml. of ether resulted in partial decolorization during the first fifth of the addition and complete decolorization after 2 days. After filtration and evaporation of the solvent, the residual oil was stirred with 25 ml. of petroleum ether (b.p. 90–110°). The crystals were purified from methanol-methyl acetate to give 1.67 g. (80%), m.p. 113–114°. A melting point of a mixture of the compound and the ester prepared by the reaction of the β-keto acid chloride with methanol showed no depression.

Refluxing of 0.40 g. of α-methyl-β-keto-γ-phenyl-γ,γ-di-*o*-tolylbutyric acid chloride in 15 ml. of methanol for 3 hours and subsequent evaporation of the solvent gave an oil which crystallized; 0.30 g. (69%). Recrystallization from methanol was used for purification, m.p. 113–114°.

Anal. Calcd. for $C_{26}H_{26}O_3$: C, 80.80; H, 6.78. Found: C, 80.38; H, 7.09.

β-Keto-γ-phenyl-γ,γ-di-*o*-tolylbutyric Acid.—The carbonation of the methyl phenyl-di-*o*-tolylcarbinyl ketone was carried out as described for the corresponding ethyl ketone. The acid was obtained in 31% yield. It was purified from petroleum ether (b.p. 30–60°), m.p. 158–159° (dec.). When heated above the melting point, decarboxylation to the original ketone occurred. This β-keto acid did not form a solvate with benzene.

Anal. Calcd. for $C_{24}H_{22}O_3$: C, 80.24; H, 6.19. Found: C, 80.35; H, 6.87.

The formation of α-methyl-β-keto-γ,γ,γ-triphenylbutyric acid from ethyl triphenylcarbinyl ketone and the formation of β-keto-γ,γ-diphenyl-γ-*o*-tolylbutyric acid from methyl diphenyl-*o*-tolylcarbinyl ketone by this procedure of carbonylation were unsuccessful.

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[CONTRIBUTION FROM RESEARCH AND DEVELOPMENT DEPARTMENT, PHILLIPS PETROLEUM CO.]

Condensation of 1-Alkanols to Dialkylcarbinols

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1-Alkanols were converted, by passage over soda lime at 400° and 40 atmospheres, into dialkylcarbinols, apparently in accordance with equation (1). Mixtures of 1-alkanols gave corresponding intercondensation products. Minor amounts of a by-product were formed in accordance with the Guerbet reaction, equation (2). The yield of product alcohols was in many cases about 40–60% by weight of the 1-alkanol consumed, or about 55–67% of theoretical. When calcium oxide was used, products resulting from both reactions, $RCH_2CH_2CHRCH(OH)CH_2R$, were observed. Of several solids tested, soda lime appeared the most effective.

Introduction

In a study of base-induced reactions of alcohols, an apparently novel synthesis of dialkylcarbinols was effected by the action of soda lime on 1-alkanols. The reaction requires both elevated temperature and pressure, and takes place apparently in accordance with the equation

$$2RCH_2CH_2OH + Ca(OH)_2 \longrightarrow RCH_2CH(OH)CH_2R + CaCO_3 + 3H_2 \quad (1)$$

In a preliminary study of some aspects of this reaction, a variety of 1-alkanols and mixtures of 1-alkanols were subjected to the action of soda lime at 400° and 40 atmospheres and several solids other than soda lime were tested as condensing agents with 1-propanol.

Results

When 1-propanol was distilled over soda lime at atmospheric pressure, little change occurred until the temperature was increased to about 400°, whereupon copious evolution of gas set in with the formation of a complex liquid mixture of aldehydes, ketones, alcohols, water, propyl ether and possibly other compounds; 3-pentanone and 3-pentanol were identified, and together made up 40% of the weight of 1-propanol converted. Ethanol gave a large amount of acetaldehyde and an amount of 2-propanol corresponding to 21% of the weight of ethanol converted.

When the product from such an experiment with 1-propanol was hydrogenated over Raney nickel at 150° before distillation, the number of components was advantageously reduced, and the 3-pentanol amounted to 44% of the 1-propanol converted (60% of theory).

Data for several experiments at 40 atmospheres are presented in Table I. Under these conditions, the liquid product was relatively saturated, and 3-pentanol was the major product from 1-propanol. Some 2-methyl-1-pentanol was also formed, evidently by Guerbet's condensation[1]

$$2RCH_2CH_2OH \longrightarrow RCH_2CH_2CHRCH_2OH + H_2O \quad (2)$$

Straight-chain 1-alkanols, especially 1-propanol, 1-octanol and a mixture of these, gave good yields of dialkylcarbinols (Expts. 1–5). Branched-chain 1-alkanols did not give good yields. This is shown not only by Expt. 6 with 2-methyl-1-propanol, but also by experiments with 3-methyl-1-butanol and benzyl alcohol described in the Experimental part. In admixture with 1-propanol, 2-methyl-1-

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[1] M. Guerbet, *Compt. rend.*, **133**, 1220 (1901); **134**, 467 (1902); **146**, 298, 1407 (1908); **149**, 129 (1909); **150**, 183 (1910); **155**, 1156 (1913); C. Weizmann and S. F. Garrard, *J. Chem. Soc.*, **117**, 324 (1920).