[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

Tri-*o*-tolylmethane

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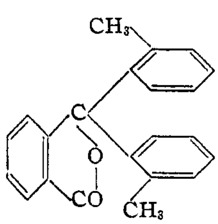
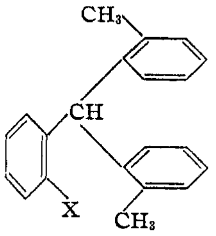
The results of Marvel and his co-workers[2] suggest that the unknown hexa-*o*-tolylethane would, if prepared, be largely if not completely dissociated into free radicals. Because the ortho-substituted triarylmethyls are incapable of assuming the coplanar arrangement demanded by the usual resonance structures,[3] their further study seems to offer an approach to the puzzling question of the role of resonance in promoting free radical dissociation. In connection with another research we had some 2,2′-dimethyl-2″-carboxytriphenylmethane (II); from this we have prepared the hydrocarbon tri-*o*-tolylmethane and studied its exchange reaction with phenylisopropylpotassium. This was done in the hope that from the potassium derivative so formed the free radical might be made by means of tetramethylethylene dibromide.

Our starting material was produced from di-*o*-tolylphthalide (I)[4] by high-pressure hydrogenation over copper chromite.



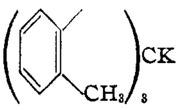
I



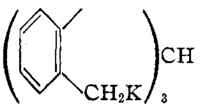
II X = COOH
III X = $CONHC_6H_5$
IV X = $CH{=}NC_6H_5$
V X = CHO
VI X = CH_3

This was reduced by way of the anilide (III) to the anil (IV) of the related aldehyde (V), which was characterized through its oxime. Wolff–Kishner reduction converted this aldehyde into tri-*o*-tolylmethane (VI), m. p. 130.5–131.5°. This hydrocarbon showed a behavior on melting like that of camphor, in that it sintered 4–5° below its melting point and showed large depressions of the melting point when impure.

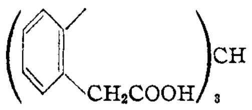
When tri-*o*-tolylmethane was treated in ethereal solution with phenylisopropylpotassium a smooth exchange reaction took place with the precipitation of an orange–red potassium derivative. However, this was not the hoped-for potassium tri-*o*-tolylmethide (VII), but instead the tripotassium derivative VIII. Its structure was shown by carbonation yielding a tribasic acid which could be recovered unchanged after solution in concentrated sulfuric acid at 100°, and which was accordingly neither a triarylacetic acid nor a malonic acid. Since only the aliphatic hydrogen atoms would be expected to be acidic enough to yield potassium exchange, this constitutes evidence that the triacid has the structure IX. The triester could be formed by Fischer's method, showing that the carboxyl groups were not highly hindered.



VII



VIII



IX

In view of the fact[5] that triphenylmethane is much more strongly acidic than less arylated methanes, the metalation of tri-*o*-tolylmethane in the methyl groups, rather than on the central carbon atom, indicates an abnormally low activity of the hydrogen in the latter position. In seeking to explain this we investigated the potassium exchange by *o*-tolyldiphenylmethane, phenyldi-*o*-tolylmethane and tri-*p*-tolylmethane for comparison. All these hydrocarbons yielded monopotassium derivatives, which were carbonated to carboxylic acids that readily lost carbon monoxide on gentle warming in concentrated sulfuric acid. Even 3,3′,3″,5,5′,5″-hexamethyltriphenylmethane does likewise.[6] Tri-*o*-tolylmethane is, therefore, unique in its series in yielding only a side-chain rather than a central metalation product.

Phenyldi-*o*-tolylmethane represents a curious intermediate case. In 0.059 *N* solution of phenylisopropylpotassium it yields an exchange product which is carbonated to a mixture containing at

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(1) Du Pont Post-Doctorate Fellow in Chemistry, 1941–1942.

(2) Marvel, Kaplan and Himel, THIS JOURNAL, **63**, 1892 (1941); Marvel, paper presented at the Ninth National Organic Symposium, Ann Arbor, Michigan, December 30, 1941.

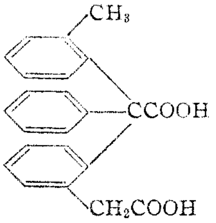
(3) Pauling and Wheland, *J. Chem. Phys.*, **1**, 362 (1933).

(4) Weiss and Korczyn, *Monatsh.*, **45**, 207 (1924).

(5) Conant and Wheland, THIS JOURNAL, **54**, 1212 (1932).

(6) Kleene and Wheland, *ibid.*, **63**, 3321 (1941).

least 86% phenyldi-*o*-tolylacetic acid and at least 8.6% of a dibasic acid. The latter, in contrast to the tribasic acid IX, is sensitive to concentrated sulfuric acid, no crystalline material being recoverable from the solution, although carbon monoxide is not evolved. In the absence of a satisfactory proof of structure it seems most likely that this is the acid X, with one carboxyl group on the central carbon atom and one on a methyl group. Increasing the concentration of the reactants to saturation (0.083 *N*) for phenylisopropylpotassium and 0.107 *N* for the hydrocarbon increases the fraction of the dibasic acid to 39%.


X

There are at least two admissible explanations of the behavior of tri-*o*-tolylmethane on metalation. In the first place, the acidity of the central hydrogen atom must bear some relation to the resonance energy of the carbanion which remains when the proton is transferred to another base. The resonance of the tri-*o*-tolyl carbanion involves the same type of secondary structures (with double bond character between the central carbon and the benzene rings) as is required for the resonance of the free radical, and this resonance must be damped in a carbanion which cannot occupy the coplanar position which this double-bond character demands. This explanation leaves something to be desired since, according to it, the central hydrogen atom should still be as acidic as the hydrogens in the *o*-methyl groups themselves, which are easily replaced by potassium. The second possible explanation is that the transfer of the central proton to the base, phenyldimethylcarbanion, naturally requires these two molecules to come into direct juxtaposition in the act of effecting the transfer. The hindrance in tri-*o*-tolylmethane is probably sufficient to make an effective collision of this kind very improbable. If this is the correct explanation, it is a rare example of prohibitive steric hindrance to a reaction which is essentially an acid–base interchange.

Another explanation has been considered, based upon the fact that only the acid and not the potassium derivative has been isolated and analyzed. The precipitated potassium derivative might in fact be a tetra-potassium compound, but the *carbonation* of the central potassium might be prohibitively hindered, in which case this link would merely be hydrolyzed eventually with the formation of the tribasic acid. Against this is the high yield of triacid on the basis of phenylisopropylpotassium used: 0.024 mole of the latter metalated 0.0073 mole of tri-*o*-tolylmethane with the final isolation of 0.0071 mole of pure triacid. The hypothesis of hindered carbonation would demand the waste of one potassium atom in four, which did not occur.

The fact that the *o*-methyl groups are metalated in the tri-*o*-tolylmethane, less in the di-*o*-tolylphenylmethane and not at all in *o*-tolyldiphenylmethane is probably not a sign of any enhanced activity of the side-chain hydrogens in the first compound, but merely a case of a reaction proceeding in the direction of the first insoluble product. We have observed a similar example in the interaction of excess phenylisopropylpotassium with toluene in dry ether solution to yield benzylpotassium. The difference in acidity of the α-hydrogen in the two benzene derivatives is probably small, but the equilibrium is shifted toward benzylpotassium by reason of its insolubility.

In contrast to the observations of Conant and Wheland[5] in the case of the exchange between triphenylmethane and phenylisopropylpotassium, in which the reaction was judged to go to completion almost instantaneously, the corresponding exchanges involving the various tolylmethanes appeared to proceed slowly, over a period of hours, to an equilibrium between the hydrocarbons and potassium derivatives involved. This may be regarded as somewhat favoring the idea that there is hindrance to the actual metal-exchange reaction and not merely to the carbonation, in the case of the tri-*o*-tolylmethane.

Experimental

Preparation of the Hydrocarbons

Di-*o*-tolylphthalide (I).[4]—To 75 g. of magnesium in a three-necked flask equipped with a mercury-sealed stirrer was added 370 cc. of *o*-bromotoluene in 1 liter of absolute ether over the course of seven hours. It was often necessary to add a crystal of iodine in order to start the reaction. After all the bromo compound had been added and the ether solution had ceased boiling, a hot suspension of 215 g. of phthalic anhydride in 2250 cc. of anhydrous benzene was added at a rate such that the solution boiled gently (two hours), after which the solution was allowed to stand overnight at room temperature. Decomposition by dilute hydrochloric acid and steam distillation of the solvents produced a yellow solid from which the last traces of solvent were removed with difficulty. The residue was boiled with five 2-liter portions of 8% aqueous sodium hydroxide, filtered, washed thoroughly with water and sucked dry. Crystallization from glacial acetic acid produced 280 g. (61.5%) of the phthalide in two crops, m. p. 173–176°, suitable for use in the next step.

Di-*o*-tolylphenylmethane-*o*-carboxylic Acid (II).—A mixture of 31.4 g. of the phthalide and 3.0 g. of copper chromite 37KAF was shaken under hydrogen at 2325 lb. initial pressure and at 235°. In ten minutes the temperature had risen to 250° and the theoretical amount of hydrogen had been absorbed. The product was dissolved in 500 cc. of hot 1% aqueous sodium hydroxide and filtered to remove the catalyst. Acidification of the filtrate produced a white solid which was separated and crystallized from glacial acetic acid. There was obtained 26.2 g. (83%) of colorless needles in two crops, m. p. 241–242°. The acid was suitable for use in the next steps without further purification. Larger runs on one mole of slightly less pure phthalide afforded yields of 70–75%.

In one preliminary run a mixture of 6.28 g. of the phthalide, 0.6 g. of copper chromite, and 10 cc. of dioxane was shaken with hydrogen at 2000 lb. and 250°. In eight hours the theoretical amount of hydrogen had been absorbed. The contents of the bomb were added to 25 cc. of a hot 10% sodium hydroxide solution and the catalyst filtered. A small amount of an oily substance insoluble in alkali was noted at this point. Acidification produced a white precipitate which was crystallized from ethanol after being decolorized by Norit. Five fractional crystallizations afforded 3.24 g. (51%) of the monoacid and 0.18 g. (2.8%) of neutral colorless rhombic plates, m. p. 145.5–146.0°.[7] Mixed melting points with phthalide and with the monoacid were lower.

Anal.[8] Calcd. for $C_{22}H_{20}O_2$: C, 83.50; H, 6.38. Found: C, 83.78, 84.37, 84.31; H, 6.00, 6.13, 5.95.

Because of the small amount of material obtained and the fact that in no other reductions was it isolated, it was not investigated further. The analysis did not correspond to that calculated for any logical reduction product.

Di-*o*-tolylphenylmethane-*o*-carboxylic Acid Anilide (III).—To a suspension of 95.0 g. of the monoacid in 200 cc. of anhydrous benzene was added 65 g. of phosphorus pentachloride. After the initial vigorous reaction at room temperature had subsided, the solution was refluxed with gentle heating for one hour. The solvent and phosphorus oxychloride were removed by vacuum distillation at 120° (10 mm.), and 100 cc. of aniline was added. The solution became very hot and slowly solidified on cooling. The solid was dissolved in benzene–ether, and the solution was extracted with dilute hydrochloric acid, washed with a solution of 10% sodium carbonate, and finally with water. After drying over sodium sulfate, the solution was boiled down to a volume of about 100 cc. and 300 cc. of ligroin (70–90°) was added. Cooling to 0° produced a dark crystalline solid which was filtered and sucked dry. Crystallization from ethanol at 0° after clarification by Norit afforded 83.4 g. (71%) of the anilide in three crops, m. p. 163–165°. The third crop (5.2 g.) was somewhat dark in color, but it could be used in the next step without further purification.

Repeated crystallization from ethanol did not produce a product having a sharp melting point and seemed to cause some decomposition. The anilide crystallized from benzene–hexane in clusters of colorless prisms, m. p. 164.0–164.7°.

Anal. Calcd. for $C_{28}H_{25}ON$: C, 85.90; H, 6.44; N, 3.58. Found: C, 85.62, 86.33; H, 6.61, 6.69; N, 3.63.

Di-*o*-tolylphenylmethane-*o*-aldehyde (V).—To a solution of 66.0 g. of the anilide in 80 cc. of dry toluene was added 50.0 g. of phosphorus pentachloride. After the initial reaction at room temperature had subsided, the solution was heated on the steam-bath for one and one-half hours. The viscous oily residue remaining after removal of the toluene and phosphorus oxychloride by vacuum distillation at 100° was poured into a solution of 125 g. of anhydrous stannous chloride in 500 cc. of absolute ether saturated with dry hydrogen chloride at 0°. The mixture slowly turned deep red, two phases formed, and an orange-red solid crystallized from the solution. After two days the complex was filtered and boiled for four hours with 300 cc. of 3 *N* hydrochloric acid. The yellow solid was filtered, washed with water and sucked dry. There was obtained 22.4 g. (44%) of the aldehyde melting at 124–132° with previous sintering at 120°. This product was suitable for the next step without purification.

The aldehyde was purified best by sublimation at 140–150° (3 mm.). It formed colorless prisms, m. p. 134.5–135.5°, with previous sintering at 131°. The later sublimates were yellow but had essentially the same melting point.

Anal. Calcd. for $C_{22}H_{20}O$: C, 87.96; H, 6.71. Found: C, 88.18; H, 6.83.

The **oxime** crystallized from ligroin (70–90)–(90–120) in pale yellow micro-crystalline prisms, m. p. 174.8–175.2°.

Anal. Calcd. for $C_{22}H_{21}ON$: C, 83.78; H, 6.71; N, 4.44. Found: C, 83.64; H, 6.70; N, 4.92, 4.62.

In an attempt to make the semicarbazone colorless blades were obtained which melted at 208.5–209.5°, after crystallization three times from ethanol–water. Recrystallization and drying at 150° *in vacuo* did not alter the analysis.

Anal. Calcd. for $C_{23}H_{22}ON_3$: C, 77.50; H, 6.22; N, 11.08. Calcd. for: $C_{23}H_{24}O_2N_3$: C, 73.78; H, 6.46; N, 11.22. Found: C, 75.29, 75.33, 75.51; H, 6.49, 6.40, 6.51; N, 10.46.

All attempts to make a pure hydrazone failed. It is very likely that the aldehyde group is too hindered to allow the formation of a stable hydrazone.

Tri-*o*-tolylmethane (VI).—A mixture of 29.0 g. of the aldehyde, 4.0 g. of sodium dissolved in 50 cc. of absolute ethanol, and 30 cc. of 85% aqueous hydrazine hydrate was heated in the autoclave at 200–210° for twenty-four hours. The contents of the bomb were neutralized with dilute acetic acid and the hydrocarbon was extracted with benzene–ether. The residue obtained after boiling the extract to dryness was dissolved in ethanol and 10 g. of semicarbazide hydrochloride and 20 g. of sodium acetate were added

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[7] All melting points below 230° are corrected. Those above 230° were made on a copper block and are correct to ±2°.

[8] All microanalyses are by Miss E. Werble.

to the boiling solution. Water was added until the solution became milky, and the hydrocarbon crystallized on cooling. Recrystallization from ethanol after decolorizing with Norit produced 15.8 g. (83%) of colorless blades, m. p. 130.5–131.5°, in three crops. The melting point of the product was similar to that of camphor in that noticeable sintering was observed about 4–5° below the true melting point. Slight amounts of impurities caused large depressions in the melting point.

Anal. Calcd. for $C_{22}H_{22}$: C, 92.26; H, 7.74. Found: C, 91.07, 92.03; H, 7.90, 7.75.

Diphenyl-*o*-tolylmethane.[9]—To 7.0 g. of magnesium was added a small amount of a solution of 50 g. of *o*-bromotoluene in 100 cc. of absolute ether. After the reaction had been started by the addition of a few drops of an ethylmagnesium bromide solution, the rest of the *o*-bromotoluene solution was added with stirring over the course of three and one-half hours, and the reaction mixture was refluxed for one and one-half hours longer. A solution of 18.0 g. of benzophenone in 100 cc. of dry benzene was added and the resulting solution was refluxed overnight. On decomposing the reaction mixture with dilute sulfuric acid and distilling volatile by-products with steam, there was obtained a viscous reddish-orange oil, which was taken up in ether. After removal of the ether, the residual oil was refluxed with 100 cc. of 85% formic acid[10] until the evolution of carbon dioxide ceased. The mixture was poured into water and extracted with ether. The ether extract was washed with 10% sodium hydroxide solution and by water and was dried over potassium carbonate. Vacuum distillation produced a colorless oil, b. p. 180–210° (9 mm.), which solidified on standing. Crystallization from methanol after cooling in ice afforded 13.5 g. (53%) of colorless prisms, m. p. 81–83°, in two crops. Recrystallization for use in the exchange experiments did not alter the melting point of the hydrocarbon.

Phenyldi-*o*-tolylmethane.[12]—The phenyldi-*o*-tolylcarbinol was prepared by the above procedure using 9.7 g. of magnesium, 62.8 g. of *o*-bromotoluene and 23.0 g. of ethyl benzoate. Treatment of the crude carbinol with 85% formic acid and vacuum distillation of the ethereal extract produced a colorless oil, b. p. 190–220° (11 mm.), which solidified on scratching. Crystallization from methanol afforded 18.7 g. (45%) of colorless prisms of the hydrocarbon, m. p. 100–104°. Recrystallization for use in the exchange reaction raised the melting point to 102–104°.

Tri-*p*-tolylmethane.—Tri-*p*-tolylchloromethane (14.0 g.), m. p. 163–168°, prepared by the method of Tousley and Gomberg,[11] was boiled under reflux with 100 cc. of 85% formic acid. Isolation by the usual procedure produced 10 g. (80%) of a colorless oil, b. p. 232° (11 mm.). Since a crystalline product could not be obtained, the oil was used in the exchange reaction.

Exchange Reactions with Phenylisopropyl Potassium

Tri-*o*-tolylmethane.—To 5.0 g. of tri-*o*-tolylmethane under an atmosphere of nitrogen was added 400 cc. of a 0.059 *N* ethereal solution of phenylisopropylpotassium. The resulting solution was allowed to stand at room temperature in the dark for twenty-four hours, during which time the deep red color slowly faded and an orange-red solid crystallized. Dry carbon dioxide was passed through the mixture slowly until all of the solid had been decolorized. By extraction of the ether suspension of the potassium salt with water and acidification of the extract with hydrochloric acid, there was obtained a white flocculent precipitate. Filtration and crystallization of the residue from glacial acetic acid afforded 2.95 g. (98.3% on the basis of the hydrocarbon used in the reaction) of microcrystalline prisms of the triacid (IX) in two crops. When heated on the copper block, the compound decomposed over the range 265–295°, but when it was dusted on the block at 310° and above, the product melted with subsequent decomposition. The triacid dissolves in concentrated sulfuric acid and can be recovered unchanged by dilution of the solution with water. Heating the sulfuric acid solution to 100° does not change the acid.

Anal. Calcd. for $C_{25}H_{22}O_6$: C, 71.76; H, 5.30; neut. equiv., 139.5. Found: C, 71.94; H, 5.50; neut. equiv., 139, 141.

After removal of the ether from the ether layer in the above extraction, there was obtained an oil from which 2.4 g. (86%) of isopropylbenzene, b. p. 150–160°, was distilled. The residue consisted of slightly impure tri-*o*-tolylmethane (2.9 g.) from which there was obtained 2.6 g. of pure hydrocarbon on crystallization from ethanol after decolorizing with Norit.

The **triethyl ester** was prepared by saturating a suspension of the acid in absolute ethanol with dry hydrogen chloride and refluxing it for twenty-four hours. At the end of this time the mixture was cooled and filtered. Recrystallization of the residue from ethanol afforded colorless blades, m. p. 196.5–197.5°.

Anal. Calcd. for $C_{31}H_{34}O_6$: C, 74.08; H, 6.82. Found: C, 74.08; H, 6.91.

Diphenyl-*o*-tolylmethane.—The solution from the addition of 200 cc. of a 0.059 *N* ethereal solution of phenylisopropylpotassium to 3.0 g. of diphenyl-*o*-tolylmethane was allowed to stand in the dark at room temperature for twenty-four hours. During this time the color of the solution did not change appreciably, and a small amount of a reddish-orange solid precipitated. Dry carbon dioxide was bubbled through the solution until it had been decolorized completely, and the white suspension was extracted with water. Acidification of the aqueous extract and crystallization of the residue from glacial acetic acid afforded 1.73 g. (98.7% based on the hydrocarbon used) of **diphenyl-*o*-tolylacetic acid** as colorless prisms, m. p. 228–229°. On a copper block the acid melts with decomposition at 190–200°.

A solution of 0.8 g. of the acid in 20 cc. concentrated sulfuric acid started evolving carbon monoxide at an appreciable rate at 50° and slowly changed in color from yellow to bright reddish-orange. On pouring the solution into water there was obtained a white suspension which was extracted with ether. A red color and all fluorescence from the ether solution were removed by washing it with 10% sodium hydroxide solution. Drying over potassium carbonate and removal of the ether produced 0.6 g. (82.5%) of diphenyl-*o*-tolylcarbinol, m. p. 95–98°. Recrystallization

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[9] Acree, *Ber.*, **37**, 993 (1904).

[10] Kaufmann and Pannwitz, *ibid.*, **45**, 766 (1912); Kovache, *Ann. chim.*, [9] **10**, 184 (1918).

[11] Tousley and Gomberg, This Journal, **26**, 1516 (1904).

from ligroin (70–90°) raised the melting point to 98–99° (lit., 98°).[9]

Anal. Calcd. for $C_{21}H_{18}O_2$: C, 83.35; H, 6.00; CO, 9.26; neut. equiv., 302.4. Found: C, 82.66, 83.72; H, 5.92, 6.00; CO, 8.94; neut. equiv., 298.

From the ether solution after removal of the acid was isolated 1.0 g. of isopropylbenzene and 1.5 g. of impure diphenyl-*o*-tolylmethane.

In another run in which 4.0 g. of the hydrocarbon was used and the reaction time was extended to forty-eight hours, there was obtained 2.25 g. of the acid.

Phenyldi-*o*-tolylmethane.—Upon standing for forty-eight hours in the dark at room temperature, a solution of 8.8 g. of phenyldi-*o*-tolylmethane in 400 cc. of a 0.059 *N* ethereal solution of phenylisopropylpotassium deposited a red–black film on the sides and bottom of the flask. Carbon dioxide was bubbled through the deep red solution until it and the sediment had been decolorized. The pale orange suspension was extracted with water, and the cold extract was acidified. Extraction with ether and evaporation of the ethereal solution produced a yellow oil which was taken up in dilute sodium hydroxide, filtered, and reprecipitated with acid. There was obtained 3.5 g. of a colorless product (neut. equiv., 318), m. p. 100–140°, which was a mixture of **phenyldi-*o*-tolylacetic acid** and a dibasic acid.

The high neutral equivalent shows that some inert material, possibly hydrocarbon retained in the aqueous layer in the extraction process, must be present in the crude mixture. From the ether solution after removal of the salts were obtained 2.0 g. of isopropylbenzene and 5.6 g. of the methane.

The crude product was boiled with two 300-cc. portions of ligroin (70–90°), and the filtered solution was allowed to crystallize at 0°. Three further crystallizations afforded 3.0 g. (80.7% based on the hydrocarbon used) of clusters of colorless prisms, m. p. 184.0–185°.

As the powdered acid dissolved at room temperature in concentrated sulfuric acid it started evolving carbon monoxide immediately at a high rate, and the color of the solution changed rapidly from orange to deep red. After the initial reaction had subsided, the removal of the carbon monoxide was completed by heating the solution to 100°.

Anal. Calcd. for $C_{22}H_{20}O_2$: C, 83.51; H, 6.37; CO, 8.83; neut. equiv., 316.4. Found: C, 83.65; H, 6.80; CO, 8.94; neut. equiv., 315.

Working up the product from the above carbon monoxide fission by the procedure outlined previously produced only a viscous red oil. By repeating the reaction but allowing the solution to stand at room temperature without heating until the reaction was complete, a colorless substance, m. p. 68–73°, could be isolated from the reaction mixture. Crystallization from ligroin (70–90°) gave colorless prisms with the same melting point. The product dissolved in concentrated sulfuric acid with an orange color.

Anal. Calcd. for $C_{21}H_{20}O$: C, 87.46; H, 6.99. Found: C, 87.34; H, 6.62.

Since presence of ketonic cleavage products was suspected, the substance was dissolved in ethanol with hydroxylamine hydrochloride and a few cc. of 10% sodium hydroxide solution was added. On evaporation the solution became cloudy, and cooling caused the separation of a colorless oil. Crystallization of the oil from ligroin (70–90°) produced a small amount of colorless prisms, m. p. 82–95°, possibly impure phenyldi-*o*-tolylcarbinol (m. p. 107–108°).[12] There was too little material for further crystallization.

Anal. Calcd. for $C_{21}H_{20}O$: C, 87.46; H, 6.99. Found: C, 86.98; H, 6.93.

From the ethanol solution there crystallized after further evaporation a small amount of colorless prisms, m. p. 75–81°, possibly impure di-*o*-tolylketoxime (m. p. 105°).[13]

Anal. Calcd. for $C_{15}H_{15}ON$: C, 79.97; H, 6.71. Found: C, 80.43; H, 7.03.

The residue from the ligroin extraction of crude phenyldi-*o*-tolylacetic acid was crystallized from glacial acetic acid, and there was obtained 0.30 g. (7.1%) of a dibasic acid in microscopic prisms, m. p. 265–267°, dec. A mixed melting point with the acetic acid was forty degrees lower. Its bright orange solution in concentrated sulfuric acid did not evolve carbon monoxide even at 125°, but all attempts to isolate any cleavage products or the unchanged acid were unsuccessful.

Anal. Calcd. for $C_{23}H_{20}O_4$: C, 76.65; H, 5.59; neut. equiv., 180.2. Found: C, 76.85; H, 5.89; neut. equiv., 182.

The **dimethyl ester**, prepared by refluxing a methanol solution of the acid saturated with dry hydrogen chloride for two hours, crystallized from methanol in colorless needles, m. p. 105.0–106°.

Anal. Calcd. for $C_{25}H_{24}O_4$: C, 77.31; H, 6.23. Found: C, 77.56; H, 6.24.

In a reaction in which a solution of 11.7 g. of the hydrocarbon and 10 g. of the methyl ether of phenyldimethylcarbinol in 400 cc. of absolute ether was shaken with sodium–potassium alloy (80% potassium) for three days, there was obtained 3.2 g. of the dibasic acid from 7.6 g. of hydrocarbon used up in the reaction. This doubling of concentration shifted the product composition in favor of the more insoluble product, a dipotassium derivative of the hydrocarbon.

Tri-*p*-tolylmethane.—A solution of 6.0 g. of tri-*p*-tolylmethane in 450 cc. of a 0.059 *N* ethereal solution of phenylisopropylpotassium was carbonated after standing for twenty-six hours. Acidification of the aqueous extract and crystallization from glacial acetic acid afforded 3.3 g. (73.5% based on the hydrocarbon used) of tri-*p*-tolylacetic acid as colorless prisms, m. p. 224–226° (lit.,[14] 226–228°).

Anal. Calcd. for $C_{23}H_{22}O_2$: CO, 7.84; neut. equiv., 320.4. Found: CO, 8.68; neut. equiv., 332.

The solution of the acid in sulfuric acid started evolving carbon monoxide slowly at 50–60° and the reaction was completed at 100°. Working up the product in the usual way afforded the tri-*p*-tolylcarbinol, m. p. 85–88°. Crystallization twice from ligroin (70–90°) raised the melting point to 92–94° (lit.,[11,15] 94°, 96.4°).

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[12] Bredereck, Lehmann, Schönfeld and Fritzsche, *Ber.*, **72**, 1414 (1939).

[13] Grignard, Bellet and Cortot, *Ann. chim.*, [9] **12**, 381 (1919).

[14] Schmidlin and Hodgson, *Ber.*, **41**, 438 (1908).

[15] Kovache, *Ann. chim.*, [9] **10**, 199 (1918); Motwurf, *Ber.*, **37**, 3153 (1904).

From the ether solution there were isolated 2.55 g. of isopropylbenzene and 2.0 g. of tri-*p*-tolylmethane, b. p. 230–240° (13 mm.). The recovered methane contained an impurity, probably an anthracene derivative, which exhibited an intense blue–violet fluorescence. Not all the unused hydrocarbon was recovered as some of it could not be distilled from the tar remaining in the distilling flask, and some was carried into the aqueous layer by the salt in the extraction process.

Summary

Tri-*o*-tolylmethane undergoes slow exchange with phenylisopropylpotassium to yield a tripotassium derivative which is converted by carbonation into the potassium salt of triphenylmethane-2,2′,2″-triacetic acid. The related compounds, phenyldi-*o*-tolylmethane, diphenyl-*o*-tolylmethane and tri-*p*-tolylmethane, under the same conditions, all form monopotassium derivatives which by carbonation yield triarylacetic acids. Explanations based upon damped resonance and steric hindrance are considered for the relative inertness of the central carbon atom of tri-*o*-tolylmethane.

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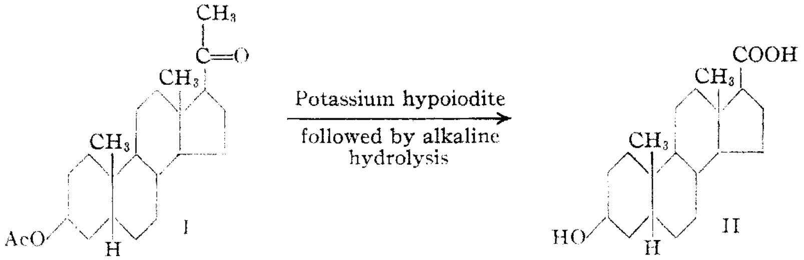
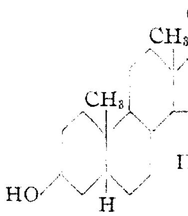
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

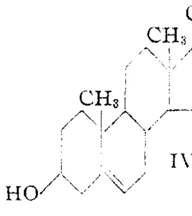
Sterols. CXLIX. The Hypoiodite Oxidation of Pregnanolones and Pregnenolones

BY RUSSELL E. MARKER AND R. B. WAGNER

St. Goldschmidt, Middelbeek and Boasson[1] have recently shown that the claims of various patents[2] to the oxidation of 5-pregnen-3(β)-ol-20-one acetate with hypoiodite to obtain 3(β)-hydroxy-etio-5-cholenic acid are erroneous. We have investigated this type of reaction, treating not only 5-pregnen-3(β)-acetoxy-20-one but also 16-pregnen-3(β)-acetoxy-20-one, pregnan-3(β)-acetoxy-20-one (I) and 5,16-pregnadien-3(β)-acetoxy-20-one with excess hypoiodite. The reactions used by us gave in every case the corresponding etio-cholanic (II) and etio-cholenic acids (III), (IV), (V).




III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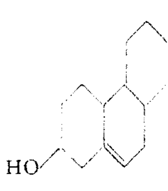
V

We wish to thank Parke, Davis and Company for their assistance.

Experimental

3(β)-Hydroxy-etio-cholanic Acid.—To a solution of 2 g. of pregnan-3(β)-ol-20-one acetate in 300 cc. of dioxane was added simultaneously in 5-cc. portions, 80 cc. of an aqueous solution of 20 g. of potassium iodide and 10 g. of iodine, and 80 cc. of an aqueous 10% potassium hydroxide solution. The mixture was stirred at room temperature for one hour and then warmed to 80°. The reaction mixture was cooled and acidified. After the excess iodine was destroyed with sodium bisulfite, the mixture was concentrated *in vacuo* and extracted with ether. The ethereal solution was washed with 10% potassium hydroxide and the combined alkaline washings were warmed for thirty minutes on a steam-bath. After acidification the solid was extracted with ether. The product crystallized from methanol as white needles; m. p. and mixed m. p. with 3(β)-hydroxy-etio-cholanic acid, 224–226°; yield 0.6 g.

Anal. Calcd. for $C_{20}H_{32}O_3$: C, 74.9; H, 10.1. Found: C, 74.6; H, 10.0.

The methyl ester was prepared by treating an ethereal solution of 50 mg. of the above acid with an ethereal solution of diazomethane. The solvent was evaporated and the residue crystallized from methanol to give white needles; m. p. 128°. This material gave no depression in the melting point of the methyl ester of an authentic sample of 3(β)-hydroxy-etio-cholanic acid methyl ester.

Anal. Calcd. for $C_{21}H_{34}O_3$: C, 75.4; H, 10.3. Found: C, 75.6; H, 10.2.

3(β)-Hydroxy-etio-16-cholenic Acid.—A solution of 2 g. of 16-pregnen-3(β)-ol-20-one acetate in 300 cc. of dioxane was treated as described above with hypoiodite. After hydrolysis the product crystallized from methanol; m. p.

[1] St. Goldschmidt, Middelbeek and Boasson, *Rec. trav. chim.*, **60**, 209 (1941).

[2] British Patent 493,055; French Patent 819,974; Swiss Patent 197,580; U. S. Patent 2,171,959.