NOTES.

The Action of Formic Acid on Triphenylmethyl Ethyl Ether and on Triphenylmethyl Chloride.

By Sydney T. Bowden and T. Frederick Watkins.

Triphenylcarbinol dissolves in anhydrous formic acid to form a yellow solution of triphenylmethyl formate: (1) $CPh_3{\cdot}OH + H{\cdot}CO_2H \rightleftharpoons H{\cdot}CO_2CPh_3 + H_2O$. The solution is stable at room temperature, but when heated to 49° the formate begins to decompose and the triphenylmethyl cation is reduced to the homopolar triphenylmethane. The reaction is actually an ionic one, but for simplicity may be represented as (2) $H{\cdot}CO_2CPh_3 \longrightarrow CHPh_3 + CO_2$. The rate of decomposition was measured by dropping a known weight of the dry, finely powdered carbinol into anhydrous formic acid (10 g.) held in a thermostat at $100° \pm 0{\cdot}02°$, and leading the carbon dioxide through a vertical condenser into a gas burette. At this temperature, salt formation is practically instantaneous, and the rate of evolution of carbon dioxide thus furnishes a measure of the rate of decomposition of triphenylmethyl formate in a formic acid solution containing water generated during the initial process of salt formation. The results of a typical experiment were as follows.

Weight of triphenylcarbinol, 0·8130 g.

Time, mins.	0·5	1	1·5	2	2·5	3	5	10
CO_2 evolved, c.c.	18·6	32·3	41·4	46·4	48·9	50·2	51·2	51·3
Reduction, %	26	46	59	66	69	71	73	74

The facility with which triphenylcarbinol is reduced by formic acid under these conditions led us to examine the behaviour of its ethyl ether. This was prepared by boiling a solution of triphenylmethyl chloride with absolute alcohol, removing the solvent under reduced pressure, and crystallising the residue from light petroleum; it melted at 81° (Herzig and Wengraf, *Monatsh.*, 1901, **22**, 601). The powdered material was freed from solvent vapours by means of silica gel before treatment with formic acid as described above. The results were as follows:

Weight of triphenylmethyl ethyl ether, 0·5398 g.

Time, mins.	2	3	4	5	10	30
CO_2 evolved, c.c.	20·5	32·7	35·7	36·9	37·0	37·9
Reduction, %	49	79	87	89	90	92

The ethyl ether is rapidly reduced under these conditions, and the initial reaction may be represented by (3) $CPh_3{\cdot}OEt + H{\cdot}CO_2H \rightleftharpoons H{\cdot}CO_2CPh_3 + EtOH$. The decomposition of the formate proceeds normally, and the extent of reduction, as shown by the above figures and by the amount of triphenylmethane (88%) isolated at the conclusion of the experiment, is greater than that found in the case of triphenylcarbinol. This is due to the fact that the reversibility of reaction (3) is lower than that of reaction (1). From the preparative standpoint, it is therefore preferable to reduce the ethyl ethers rather than the carbinols themselves.

The behaviour of triphenylmethyl chloride is also of interest in this connexion. The chloride, prepared by warming a solution of the carbinol (5 g.) in ether–light petroleum with acetyl chloride (5 c.c.) for 30 mins. with suitable precautions against the intrusion of moisture, was deposited on cooling, and was obtained colourless after two recrystallisations from the same solvent mixture; it was filtered off in a stream of dry air and melted at 112°. The reactions with formic acid are similar to the above, but in this case the formation of triphenylmethane is accompanied by simultaneous evolution of carbon dioxide and hydrogen chloride, the latter produced by the reaction $CPh_3Cl + H\cdot CO_2H \rightleftharpoons H\cdot CO_2CPh_3 + HCl$. The rate of evolution of the two gases was as follows.

Weight of triphenylmethyl chloride, 0·5212 g.

Time, mins.	2	4	6	8	10	12	15	20	30
CO_2 + HCl evolved, c.c.	13·2	24·1	31·4	37·5	44·0	47·6	53·2	58·6	65·3
Reduction, %	16	29	38	45	53	58	64	71	79

It is evident from these results that the reaction involving the formation of triphenylmethyl formate is slower than the corresponding reaction with the carbinol or the ethyl ether. The reaction, however, is not reversible under the present experimental conditions owing to the removal of hydrogen chloride from the system. This is further confirmed by the fact that a 90% yield of triphenylmethane is obtained after 2 hours.—Tatem Laboratories, University College, Cardiff. [*Received, June 29th,* 1940.]

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p-*Phenoxytriphenylmethane and the Corresponding Free Radical.* By D. Leslie Clarke and Sydney T. Bowden.

Since tertiary aromatic carbinols containing the *o*-phenoxyphenyl group undergo ring closure with the formation of colourless spirans (Clarkson and Gomberg, *J. Amer. Chem. Soc.*, 1930, **52**, 2881), the preparation of the corresponding free radical is not possible, but as such ring closure is not to be anticipated if the phenoxyl group is in the *p*-position, we have examined the behaviour of *p*-phenoxytriphenylmethane and its derivatives.

An ethereal solution of phenylmagnesium bromide (1·2 mols.) was treated with a suspension of *p*-phenoxybenzophenone (1 mol.), and the red solution refluxed for an hour. The mixture was decomposed with ice and sulphuric acid, and steam passed through it to remove volatile material. The residual carbinol could not be crystallised from ordinary organic solvents and slowly changed into a brown resinous mass on standing. The oil dissolved readily in liquid sulphur dioxide to form a reddish-brown solution, which deposited a pink, crystalline addition compound on slow evaporation. On standing in the air or in a desiccator, the compound lost sulphur dioxide and reverted to the original oily material. Attempts to distil the oil under reduced pressure led to decomposition. However, the substance gave the characteristic tests for triarylcarbinols, and its identity was further established by its reduction to the corresponding methane as described below.

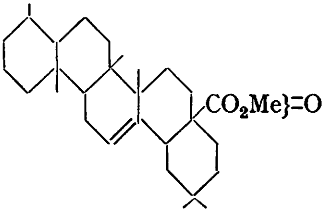
The chloride was also obtained as an oil by treatment of benzene or light petroleum solutions of the carbinol with hydrogen chloride and calcium chloride, or acetyl chloride, respectively. It dissolved in ether to form a very pale yellow solution, which on shaking with molecular silver out of contact with air became deep orange in colour. On shaking this solution with oxygen the colour was discharged. These reactions indicate the presence of the free radical *p*-phenoxytriphenylmethyl.

The reduction of the carbinol was easily effected by dissolving the material (2 g.) in glacial acetic acid (20 c.c.) and heating the solution with zinc dust (2 g.) on a steam-bath for 3 hours. The liquid was filtered hot, and the deposited p-*phenoxytriphenylmethane* recrystallised from the same solvent (yield, 80%). The pure material was white and melted at 142° (Found: C, 89·0; H, 6·1. $C_{25}H_{20}O$ requires C, 89·2; H, 6·0%).—Tatem Laboratories, University College, Cardiff. [*Received, June 29th,* 1940.]

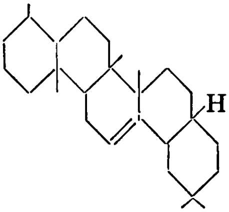
The Conversion of Quillaic Acid into a Hydrocarbon.

By George A. R. Kon and Henry R. Soper.

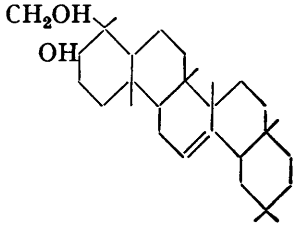
Methyl quillaate has been converted by oxidation and subsequent reduction of one carbonyl group into a monoketonic ester. We have now reduced the remaining carbonyl group of this ester with the simultaneous elimination of the carbomethoxy-group, the product being a *hydrocarbon*, $C_{28}H_{46}$.



(I.)



(II.)



(III.)

As the monoketonic ester has been formulated as (I) on the assumption that the carbon skeleton of quillaic acid is the same as that of the triterpene acids of the hederagenin group (Elliott, Kon, and Soper, this vol., p. 612), the hydrocarbon should have formula (II) and be termed norhederabetulene. We hope to obtain this hydrocarbon by the oxidation of hederabetulin (III) (Winterstein and Stein, *Z. physiol. Chem.*, 1931, **199**, 75) and subsequent reduction of the nor-ketone formed.

The method of reduction used by us is a variant of the Kishner–Wolff process and was suggested by the observations of Dutcher and Wintersteiner (*J. Amer. Chem. Soc.*, 1939, **61**, 1992). We find that it is not necessary to isolate the hydrazone or azine of the carbonyl compound to be reduced; the latter is simply heated with sodium ethoxide and hydrazine. The process is successful with Δ^4-cholestenone and especially with quillaic acid, which gives an almost quantitative yield of deoxyquillaic acid.

Reduction of the Ester (I).—0·2 G. of the ester was heated for 16 hours in a sealed tube at 200° with 0·4 g. of sodium in 8 c.c. of absolute alcohol and 0·8 c.c. of 95% hydrazine hydrate. The product was dissolved in ether, and the extract washed with water, dried, and evaporated. The yellow crystalline residue was dissolved in light petroleum (b. p. 60—80°) and percolated through a column of activated alumina. The colourless, crystalline residue obtained after removal of the solvent was recrystallised from acetic acid, in which it was only moderately soluble, forming large plates, m. p. 154°; the specimen for analysis was dried for 2 hours at 100° in a high vacuum. The *hydrocarbon* gave a yellow colour with tetranitromethane and had $[\alpha]_D + 33°$ ($c = 1·638$ in hexane) (Found: C, 87·5; H, 12·5. $C_{28}H_{46}$ requires C, 87·9; H, 12·1%).—Imperial College of Science and Technology, London, S.W.7. [*Received, July* 18*th*, 1940.]