Rotation. (*d*-Acid) 0.0292 g. made up to 5 cc. with absolute ethanol to 26° gave α_D +0.205°; *l*, 1; $[\alpha]^{26}_D$ +35.7°.

Racemization of *l*-β-Chloro-β-(2,3,4,6-tetramethylphenyl)-acrylic Acid.—0.2789 g. of *l*-acid made up to 15 cc. in *n*-butanol gave α_D −0.60; after one hour, α_D −0.454; two hours, α_D −0.355; three hours, α_D −0.273; four hours, α_D −0.214; five hours, α_D −0.167; twenty-four hours α_D 0. The average half-life calculated from these values was one hundred sixty-three minutes. In a repetition of this experiment a half-life of one hundred eighty-four minutes was obtained.

Attempted Resolution of β-Methoxyl-β-(3-bromo-2,4,6-trimethylphenyl)-acrylic Acid.—Solutions of 5.595 g. of β-methoxy-β-(3-bromo-2,4,6-trimethylphenyl)-acrylic acid in 50 cc. of ethyl acetate and 6.070 g. of quinine in 100 cc. of ethyl acetate were mixed and filtered and the total volume of solvent made up to 400 cc. The cooled solution deposited 6.038 g. of salt (fraction I). Fractions of 1.355 g., 2.512 g.and 1.850 g. were removed at 250 cc., 80 cc. and by evaporation to dryness, respectively. All the fractions were obtained with the same rotation. Fraction I was separated into three fractions from ethyl acetate and the largest of these three fractions was subdivided by fractional precipitation from benzene with petroleum ether. No differentiation, as indicated by the specific rotation, could be ascertained during this fractionation. The salt obtained did not mutarotate at room temperature or at 0° and no active acid was obtained by decomposition of the salt at −5° with 10% hydrochloric acid.

Anal. Calcd. for $C_{33}H_{39}N_2O_5Br$: C, 63.56; H, 6.30; N, 4.49. Found: C, 63.20; H, 6.46; N, 4.39.

Rotation. (*l*B·*dl*A) 0.0527 g. made up to 10 cc. with absolute ethanol at 27° gave α_D −0.460; *l*, 1; $[\alpha]^{27}_D$ −87.3°.

A solution of 0.500 g. of β-methoxy-β-(3-bromo-2,4,6-trimethylphenyl)-acrylic acid in 5 cc. of ethyl acetate was added to a solution of 0.659 g. of *l*-brucine in 10 cc. of ethyl acetate and filtered. When the volume of the solution had reached 10 cc. by spontaneous evaporation 0.960 g. of salt was removed (fraction A). A second crop of salt weighing 0.205 g. was removed at 3 cc. These two fractions and the crops obtained by recrystallization of fraction A were obtained with the same rotation. The salt gave no evidence of mutarotation and gave no active acid when decomposed.

Rotation. (*l*B·*dl*A) 0.0293 g. made up to 5 cc. with absolute ethanol at 30° gave α_D −0.22; *l*, 1; $[\alpha]^{30}_D$ −37.5°.

Summary

1. β-Bromo-β-(3-bromo-2,4,6-trimethylphenyl)-acrylic acid was synthesized by addition of hydrogen bromide to 3-bromo-2,4,6-trimethylphenylpropiolic acid. It was resolved and the half-life of the active form shown to be sixty-four hours in boiling *n*-butanol. This is to be compared with a half-life of two hundred minutes for the corresponding chloro compound, β-chloro-β-(3-bromo-2,4,6-trimethylphenyl)-acrylic acid, made by the action of phosphorus pentachloride on 3-bromo-2,4,6-trimethylbenzoylacetic acid.

2. β-Chloro-β-(2,3,4,6-tetramethylphenyl)-acrylic acid was resolved. The half-life was one hundred seventy-four minutes.

3. β-Methoxy-β-(3-bromo-2,4,6-trimethylphenyl)-acrylic acid was prepared from the appropriate aroylacetic acid and from the arylpropiolic acid but resolution failed.

4. The arrangement of the groups about the double bond in each of these compounds is discussed.

URBANA, ILLINOIS RECEIVED JULY 28, 1943

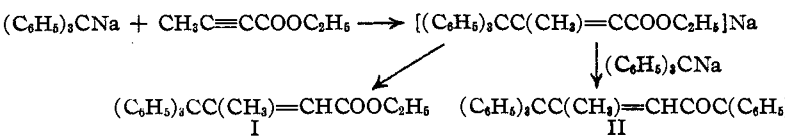
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

The Reaction of Triphenylmethylsodium with Esters of Acetylenic Acids

BY EDDIE G. LINDSTROM AND WARREN D. MCPHEE

In a previous communication from this Laboratory,[1] the 1,4-addition of triphenylmethylsodium to ethyl crotonate and methyl acrylate was reported. The study has now been extended to esters of acetylenic acids, ethyl tetrolate (ethyl 2-butynoate) and ethyl 2-pentynoate.

Ethyl tetrolate differs from ethyl crotonate only in having a triple instead of a double bond, but its reaction with triphenylmethylsodium is more complex. Less than one mole of ester is required to consume one mole of the reagent. Besides the expected ester, ethyl 3-methyl-4,4,4-triphenylcrotonate (I), there was isolated a considerable amount of the ketone, 4-methyl-1,1,1,-5,5,5-hexaphenyl-3-pentene-2-one (II).



The ketone crystallized out of the ether solution upon evaporation, and the ester remained in the filtrate. Hydrolysis of the ester afforded the crystalline 3-methyl-4,4,4-triphenylcrotonic acid.

Oxidation of 3-methyl-4,4,4-triphenylcrotonic acid with permanganate gave in low yield methyl triphenylmethyl ketone, which proved to be identical with the ketone prepared by rearrangement of the pinacol obtained from phenylbenzoin and methylmagnesium iodide. This reaction confirms the structure assigned to the acid.

Attempts to reduce 3-methyl-4,4,4-triphenylcrotonic acid to 3-methyl-4,4,4-triphenylbutyric acid[1] with Raney nickel or Adams platinum oxide catalysts at 60 pounds pressure and 75° were unsuccessful. Also, attempts to synthesize this unsaturated acid through the Reformatsky reaction of ethyl bromoacetate and methyl triphenylmethyl ketone with subsequent dehydration failed.

The formation of the ketone (II) was unexpected since the analogous reaction with ethyl crotonate gives a high yield of but one

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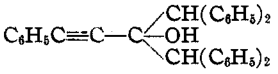
(1) McPhee and Lindstrom, THIS JOURNAL, 65, 2177 (1943).

product, the ester corresponding to (I). In a somewhat similar experiment employing diphenylmethylsodium and ethyl phenylpropiolate, Bergmann[2] isolated a product to which he assigned the carbinol structure (III) because it was "attacked by acetyl chloride." He concluded that 1,4-addition did not take place in this reaction, but instead two molecules of diphenylmethylsodium reacted with the ester function, as would be expected with an ester of a saturated acid.



$$C_6H_5C\equiv C-C\begin{array}{l}\diagup CH(C_6H_5)_2\\ -OH\\ \diagdown CH(C_6H_5)_2\end{array}$$

III

In order to establish the structure of the ketone (II), methyl 3-methyl-4,4,4-triphenylcrotonate was prepared by direct esterification of the pure acid. This ester was treated with triphenylmethylsodium in ether and the ketone obtained was identical with (II). No evidence was obtained for the formation of the isomeric carbinol corresponding to Bergmann's compound (III). Ketone (II) exhibits no carbonyl reactions and attempts to oxidize it with permanganate or chromic acid gave no tractable product; ozonization was likewise unsuccessful.

Ketone (II) was evidently formed from ethyl tetrolate by a combination of 1,4- and 1,2-addition. The 1,2-addition of triphenylmethylsodium to methyl 3-methyl-4,4,4-triphenylcrotonate is apparently due to the presence of the triphenylmethyl group. In contrast, the unsubstituted ester, ethyl crotonate, gives only the 1,4-addition product in high yield both when the ester was added to the triphenylmethylsodium reagent and when the triphenylmethylsodium was added to the ester.[1]

When the mode of addition is reversed, that is, the triphenylmethylsodium added to the ether solution of ethyl tetrolate, the yield of ketone (II) is decreased markedly although the amount of ester (I) obtained is not appreciably changed. In this case, a large amount of triphenylmethane was obtained, whereas very little had been noted when the ester was added to the triphenylmethylsodium reagent. It does not seem reasonable to attribute this triphenylmethane to enolization, since it was not found in the other experiments.

Ethyl 2-pentynoate undergoes similar reactions with triphenylmethylsodium, giving rise to a ketone, 4-ethyl-1,1,1,5,5,5-hexaphenyl-3-pentene-2-one, in 70% yield, and an acid, 3-ethyl-4,4,4-triphenylcrotonic acid, after hydrolysis, in 16% yield. The acid was converted to its methyl ester and treated with triphenylmethylsodium, resulting in the above ketone. The products obtained from ethyl 2-pentynoate are undoubtedly analogous to those from ethyl tetrolate and are assigned similar structures.

Experimental[3]

Ethyl Tetrolate.—Tetrolic acid was prepared by the method of Feist,[4] and the crude product was esterified with absolute ethanol and a small amount of sulfuric acid. From 315 g. of ethyl acetoacetate, 22 g. of ethyl tetrolate was obtained, b. p. 162–164°, n^{20}_{D} 1.4372.

Ethyl Tetrolate and Triphenylmethylsodium.—The equimolar amount of ethyl tetrolate (6.0 cc.) was added dropwise to 545 cc. of 0.109 *N* triphenylmethylsodium reagent, prepared according to the directions of Renfrow and Hauser.[5] Heat was evolved and the solution changed from red to dark amber. The reaction mixture was treated with water, and the ether layer was separated, washed with water and dried.

4-Methyl-1,1,1,5,5,5-hexaphenyl-3-pentene-2-one (II).—After partial evaporation of the ether, a yellow solid settled out. It was filtered and dried; m. p. 218–222°; yield, 8.75 g. (53%). Four recrystallizations from benzene–petroleum ether gave white micro crystals, m. p. 226–226.5°.

Anal. Calcd. for $C_{42}H_{34}O$: C, 90.94; H, 6.18. Found: C, 91.13; H, 6.29.

3-Methyl-4,4,4-triphenylcrotonic Acid.—The filtrate from the ketone (II) was subjected to hydrolysis in 100 cc. of 10% alcoholic potassium hydroxide solution for three hours. The alcohol was evaporated and the residue dissolved in water. The salt of the acid was thrown down by treatment of the hydrolysis mixture with saturated sodium chloride solution. It was washed with ether several times and then treated with dilute hydrochloric acid to liberate 5.3 g. of the impure acid, m. p. 220–235°. As the acid appeared to be contaminated with some of the ketone, it was dissolved in 150 cc. of benzene and extracted with several 15-cc. portions of Claisen alkali. Acidification of the extracts produced 4.6 g. (24% yield) of the acid, m. p. 244–255°. After five recrystallizations from dilute alcohol, fine white needles were obtained, m. p. 256–257°, with gas evolution on melting and sintering from 245°.

Anal. Calcd. for $C_{23}H_{20}O_2$: C, 84.10; H, 6.14. Found: C, 83.60, 83.92; H, 6.24, 6.39.

An attempt was made to increase the yield of the ester (I) by adding the triphenylmethylsodium reagent to the ethyl tetrolate. Four hundred and eighty cubic centimeters of 0.0935 *N* reagent (10 cc. excess) was added rapidly to 4.4 g. of ethyl tetrolate in 100 cc. of dry ether. The mixture was worked up as before, and 2.9 g. (23% yield) of the crude ketone (II) was isolated. After hydrolysis, 4.1 g. (28% yield) of the acid was obtained, m. p. 254–255° after recrystallization from dilute acetic acid.

A neutral fraction of light yellow crystals was obtained from the hydrolysis mixture. Two recrystallizations from dilute alcohol gave colorless crystals of triphenylmethane, m. p. 84–91°; weight 5 g. (45% yield). One more crystallization from alcohol raised the melting point to 87–90°; there was no depression in a mixed melting point with triphenylmethane.

Oxidation of 3-Methyl-4,4,4-triphenylcrotonic Acid.—A solution of 0.45 g. of the acid, 0.5 g. of potassium hydroxide and 60 cc. of water was treated with the calculated amount (0.58 g.) of potassium permanganate and refluxed. In fifteen minutes the permanganate was reduced, and 0.40 g. more was added. The solution was refluxed thirty minutes longer and filtered. The filter cake was extracted with hot benzene and the solvent evaporated. The residue was recrystallized from dilute acetic acid as long white needles, m. p. 136–138°, weighing 0.1 g. Two further recrystallizations raised the m. p. to 137.5–139° with slight sintering from 135°. The mixed m. p. with known methyl triphenylmethyl ketone, m. p. 139–139.5°, was 138.5–139.5° with sintering from 137°.

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(2) Bergmann, *J. Chem. Soc.*, 412 (1936).

(3) Analyses by Robert Bauman. Melting points are not corrected. Yields are based on triphenylmethylsodium.

(4) Feist, *Ann.*, **345**, 100 (1906).

(5) Renfrow and Hauser, "Organic Syntheses," **19**, 83 (1939).

In one oxidation experiment, a small amount of triphenylcarbinol was isolated instead of the expected ketone.

Methyl Triphenylmethyl Ketone.—Phenylbenzoin, m. p. 86–87°, was prepared by the method of Acree[6] from benzil and phenylmagnesium bromide. It was treated with methylmagnesium iodide according to Schlenk and Bergmann[7] and converted into the desired ketone. From 13.6 g. of phenylbenzoin, 7.8 g. of methyl triphenylmethyl ketone, b. p. 223–233° (15 mm.), was obtained. After repeated recrystallization from methanol, it melted at 139–139.5°.

Methyl 3-Methyl-4,4,4-triphenylcrotonate.—This ester was prepared in the usual manner in nearly quantitative yield by refluxing a solution of 0.8 g. of acid and 1 cc. of concentrated hydrochloric acid in 50 cc. of methanol for seven hours. The acid was not very soluble in the methanol and three hours of refluxing of the esterification mixture was necessary for complete solution. The ester formed white feathery needles, m. p. 162.5–163.5° after three recrystallizations from methanol.

Anal. Calcd. for $C_{24}H_{22}O_2$: C, 84.17; H, 6.48. Found: C, 84.73, 83.56; H, 6.59, 6.66.

Triphenylmethylsodium and Methyl 3-Methyl-4,4,4-triphenylcrotonate.—An ether solution of 0.25 g. of methyl 3-methyl-4,4,4-triphenylcrotonate was added to an excess of triphenylmethylsodium reagent. The reaction mixture was treated with water and the ether layer separated and dried with drierite. Evaporation of the solvent gave 0.45 g. of the desired ketone as fine white needles, m. p. 213–220°. After one recrystallization from benzene-petroleum ether and two from glacial acetic acid, the ketone melted at 225–230°. The mixed melting point with the ketone (II) prepared from ethyl tetrolate (m. p. 226–227° after recrystallization from benzene-petroleum ether) was 226–230°.

Slightly different melting points, possibly due to changes in crystal form, are obtained when different solvents are used for recrystallization. The ketone, prepared either from ethyl tetrolate or from methyl 3-methyl-4,4,4-triphenylcrotonate, may be obtained with m. p. 226–227° from benzene-petroleum ether or with m. p. 226–230.5° from glacial acetic acid. The melting point of a mixture of the two forms shows no depression, and the forms are interconvertible.

Ethyl 2-Pentynoate.—2-Pentynoic acid was synthesized in 45% yield by the method of Zoss and Hennion.[8] The ester was prepared with absolute ethanol and sulfuric acid in 84% yield; b. p. 78–80° (16–18 mm.), $n^{20}\text{D}$ 1.4404.

Triphenylmethylsodium and Ethyl 2-Pentynoate.—Four hundred cubic centimeters of 0.0959 *N* triphenylmethylsodium reagent was treated with 5.3 cc. (equimolar amount, 5.03 cc.) of ethyl 2-pentynoate. Heat was evolved and the color lightened to a red-orange. Water was added and the ether layer separated and dried.

4-Ethyl-1,1,1,5,5,5-hexaphenyl-3-pentene-2-one.—The ether was evaporated slowly and the solid that precipitated was collected. The yield of the ketone, m. p. 196–199°, was 7.6 g. (70%). It was recrystallized four times from benzene-petroleum ether to yield fine white needles, m. p. 201–202°.

Anal. Calcd. for $C_{43}H_{36}O$: C, 90.81; H, 6.38. Found: C, 90.86; H, 6.32.

3-Ethyl-4,4,4-triphenylcrotonic Acid.—After removal of the ketone the acid was isolated from the ether filtrate by the procedure used with 3-methyl-4,4,4-triphenylcrotonic acid, except that the extraction with Claisen alkali was omitted. Two and one-tenth grams of acid (16% yield) was obtained, m. p. 209–216°. Four recrystallizations from dilute alcohol and one from dilute acetic acid yielded glistening slender white needles, m. p. 215–217°, with sintering from 208°.

Anal. Calcd. for $C_{24}H_{22}O_2$: C, 84.17; H, 6.48. Found: C, 84.57; H, 6.34.

Methyl 3-Ethyl-4,4,4-triphenylcrotonate.—The ester was prepared in nearly quantitative yield by refluxing 0.8 g. of acid in 50 cc. of methanol and 1 cc. of concentrated hydrochloric acid for seven hours. Three recrystallizations from methanol gave stout white needles, m. p. 170–171°.

Anal. Calcd. for $C_{25}H_{24}O_2$: C, 84.26; H, 6.79. Found: C, 84.25; H, 6.86.

Triphenylmethylsodium and Methyl 3-Ethyl-4,4,4-triphenylcrotonate.—Fifty cubic centimeters of dry ether containing 0.35 g. of ester was added to an excess of triphenylmethylsodium reagent. The mixture was worked up in the usual manner. On partial evaporation of the ether, 0.37 g. of crystals was obtained. After six recrystallizations from glacial acetic acid the ketone melted at 200.5–201.5°, with sintering from 199°. The mixed melting point with the ketone from ethyl 2-pentynoate, m. p. 201–202°, was not depressed.

Summary

Triphenylmethylsodium reacts with ethyl tetrolate to form ethyl 3-methyl-4,4,4-triphenylcrotonate by 1,4-addition, and 4-methyl-1,1,1,5,5,5-hexaphenyl-3-pentene-2-one by combined 1,4- and 1,2-addition. Ethyl 2-pentynoate undergoes similar reactions.

Methyl 3-methyl-4,4,4-triphenylcrotonate and methyl 3-ethyl-4,4,4-triphenylcrotonate are converted by 1,2-addition of triphenylmethylsodium into the corresponding ketones, 4-methyl-1,1,1,5,5,5-hexaphenyl-3-pentene-2-one and 4-ethyl-1,1,1,5,5,5-hexaphenyl-3-pentene-2-one, respectively.

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[6] Acree, *Ber.*, **37**, 2759 (1904).

[7] Schlenk and Bergmann, *Ann.*, **479**, 51 (1930).

[8] Zoss and Hennion, THIS JOURNAL, **63**, 1151 (1941).