pionic acid described earlier showed no depression in melting point.

Lactone formation was effected by allowing a solution of 3.9 g. of the keto acid (IV) in acetyl chloride to stand in a vacuum desiccator. After three recrystallizations from methylcyclohexane the lactone formed white, silky needles (3.1 g.); m.p. 142°.

Anal. Calcd. for $C_{20}H_{20}O_2$: C, 82.16; H, 6.90. Found: C, 82.22; H, 7.12.

The lactone sublimed without change at 165–175° (0.01 mm.). The infrared spectrum contained bands at 1656 and 1801 cm.$^{-1}$, which correspond to the olefinic and lactone functions, respectively.

The lactone (1 g.) was dissolved in a mixture of 20 ml. of dioxane, 50 ml. of water and 2 g. of potassium hydroxide; acidification of this mixture produced β-duroyl-β-phenylpropionic acid (0.7 g.).

To a benzene solution of 1 g. of the lactone and 0.5 g. of *p*-chlorobenzaldehyde was added a few drops of diethylamine and the mixture was heated under reflux for 30 minutes, additional quantities of amine being added from time to time. The ***p*-chlorobenzal derivative** (0.3 g.) separated from methylcyclohexane in yellow crystals; m.p. 204–205°.

Anal. Calcd. for $C_{27}H_{23}O_2Cl$; C, 78.15; H, 5.59. Found: C, 78.29; H, 5.70.

Methyl β-Duroyl-β-phenylpropionate.—A solution of the acid (3 g.) in methanol, previously saturated with hydrogen chloride, was heated under reflux for 8 hours. The methyl ester was recrystallized three times from methanol; m.p. 88–89°.

Anal. Calcd. for $C_{21}H_{24}O_3$: C, 77.75; H, 7.46. Found: C, 77.51; H, 7.68.

Condensation of Phenylsuccinic Anhydride with Durene.—A mixture of 30 g. of phenylsuccinic anhydride, 22 g. of durene, 50 g. of anhydrous aluminum chloride and 300 ml. of carbon disulfide was heated for a few minutes in order to break up the lumps formed initially. After a reaction time of 3 hours the mixture was poured on ice. Hydrochloric acid was added and the carbon disulfide distilled. A solution of the mixture of acids in 95% ethanol was boiled with Darco and filtered. The yield of crystalline material from the fitrate was 21.4 g. (41%). A solution of the product in ethyl acetate was seeded alternately with the α- (III) and β-phenyl (IV) derivatives of β-duroylpropionic acid. Successful separation was achieved only when 0.5–1.0 g. was removed at a time. Very little of the α-phenyl acid could be recovered from ethyl acetate solution; however, nitromethane proved to be a good solvent for the isolation of this acid. By recrystallizing the acids twice from ethyl acetate it was possible to obtain 7.6 g. of the pure β-phenyl acid and 3.5 g. of the pure α-phenyl acid. Mixture melting points with authentic samples were taken as criteria of identity. At the end of this procedure 5.0 g. of crystalline residue remained; m.p. 161–165°. It was not identified.

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

The Conjugate Addition of Hydrogen Cyanide to β-Mesityl Ketones

BY REYNOLD C. FUSON AND ROBERT G. BANNISTER[1]

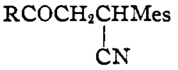
Hydrogen cyanide condenses in the conjugate manner with mesitalacetomesitylene, mesitalacetophenone and mesitalacetone, producing the corresponding keto nitriles in high yields.

It has been established that a mesityl radical in the β-position in an α,β-unsaturated carbonyl compound does not block entry by the hydrocarbon radical of a Grignard reagent at that position even when the reagent is mesitylmagnesium bromide. Attack at the β-position can occur whether the carbonyl group itself is hindered[2,3] or not.[4] It remains to be shown whether other reagents, less active toward the carbonyl function than Grignard reagents, are capable of conjugate addition to such systems. In the present work it has been found that hydrogen cyanide can be added in the conjugate manner to α,β-unsaturated carbonyl compounds in which the β-carbon atom holds a mesityl radical.

Mesitalacetomesitylene (I) combines with hydrogen cyanide to give the expected keto nitrile (III) in high yield.[5]

RCOCH=CHMes

I, R = Mes
II, R = C_6H_5



$RCOCH_2\underset{\displaystyle CN}{\underset{|}{C}}HMes$

III, R = Mes
IV, R = C_6H_5

Similarly mesitalacetophenone (II) is converted to the unhindered keto nitrile, IV. Both compounds therefore behave toward hydrogen cyanide as typical chalcones.

Mesitalacetone (V) is interesting since it is a vinylog of acetomesitylene, a ketone which does not combine with hydrogen cyanide. As a methyl ketone mesitalacetone should be capable of yielding a cyanohydrin. Moreover, the mesityl group in the β-position might be expected to oppose conjugate addition. This ketone, however, was found to combine with hydrogen cyanide at 35° to give, in 63% yield, the keto nitrile (VI) corresponding to conjugate addition. No other product could be isolated.

$MesCH{=}CHCOCH_3$

V

$Mes\underset{\displaystyle CN}{\underset{|}{C}}HCH_2COCH_3$

VI

A related reaction, employed in the preparation of mesitylsuccinic acid (IX), involves conjugate addition of hydrogen cyanide to ethyl mesitalmalonate (VII). The yield of acid was low but, since the cyano ester (VIII) was not isolated, it is not possible to say whether the conjugate addition took place readily.

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[1] Atomic Energy Commission Fellow, 1949–1951.

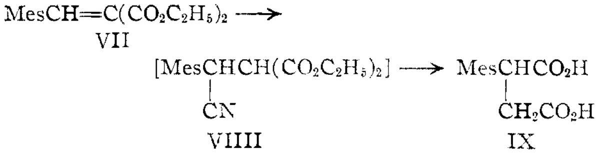
[2] E. P. Kohler and L. W. Blanchard, Jr., THIS JOURNAL, **57**, 367 (1935).

[3] R. C. Fuson and J. S. Meek, *J. Org. Chem.*, **10**, 551 (1945).

[4] R. C. Fuson and H. L. Jackson, THIS JOURNAL, **72**, 1637 (1950).

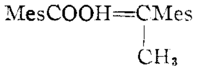
[5] It was pointed out by a Referee that the *cis* configuration for I is virtually impossible as a coplanar system, requiring nearly 90° distortion. Perpendicular attack at the olefinic bond is thus inhibited. The high yield of III accordingly requires that I have the *trans* configuration, assuming of course that the addition is initiated by attack of cyanide ion.

Attention was also called to the fact that the infrared absorption band attributable to the carbonyl function of III falls between that for the unconjugated carbonyl of VI and the "normal" aromatic carbonyl group of IV. This relationship may be taken as supporting evidence for the idea that the carbonyl joined to the mesityl radical is somewhat out of the plane of the mesityl ring and hence less highly conjugated.



$$\mathrm{MesCH{=}C(CO_2C_2H_5)_2} \longrightarrow \underset{\mathrm{VII}}{}\quad [\mathrm{Mes}\underset{\mathrm{CN}}{\mathrm{CH}}\mathrm{CH(CO_2C_2H_5)_2}]_{\mathrm{VIIII}} \longrightarrow \mathrm{Mes}\underset{\mathrm{CH_2CO_2H}}{\mathrm{CH}}\mathrm{CO_2H}_{\mathrm{IX}}$$

These results lend added support to the view that the mesityl radical alone is not a sufficiently bulky substituent to prevent addition at the end of a conjugated system. The presence of an additional substituent, however, greatly reduces the reactivity of the conjugated system: thus β-methylmesitalacetomesitylene (X) does not even undergo reaction with Grignard reagents.[3]



$$\mathrm{MesCOOH{=}}\underset{\mathrm{CH_3}}{\mathrm{C}}\mathrm{Mes}$$

X

Kadesch[6] has postulated that the inertness of acetomesitylene toward carbonyl reagents arises from the fact that the carbonyl function is forced out of the plane of the mesitylene ring by the ortho-methyl groups. Perpendicular attack toward the carbonyl function is thereby blocked very effectively by the surrounding methyl groups. According to this view the methyl groups in mesitaldehyde are not bulky enough to force the small aldehyde group from the plane of the mesitylene ring; mesitaldehyde therefore forms a cyanohydrin[7] and undergoes other carbonyl reactions.

The carbon–carbon double bond in mesitalacetomesitylene (I), by analogy with the carbonyl function in mesitaldehyde, is probably coplanar with the mesityl ring; ready attack can therefore occur in a direction perpendicular to the plane of the system. β-Methylmesitalacetomesitylene (X), on the other hand, is unreactive because the carbon–carbon double bond, like the carbonyl function in acetomesitylene, is forced into a position in which the methyl groups block attack.

Experimental[8]

β-Mesitoyl-α-mesitylpropionitrile (III).—To a solution of 27.5 g. of mesitalacetomesitylene[2,3] in 450 ml. of 95% ethanol was added 9 ml. of glacial acetic acid. A solution of 20 g. of potassium cyanide in 50 ml. of water was then added dropwise over a period of one hour. During the mixing and for 3 hours afterward the reaction mixture was stirred continuously and maintained at a temperature of 45°. The keto nitrile crystallized when the mixture was cooled. The amount, augmented by additional quantities obtained from the mother liquor, was 27.6 g. (92%). The product was recrystallized three times from absolute ethanol; m.p. 124.5°.

Anal. Calcd. for $C_{22}H_{25}NO$: C, 82.72; H, 7.89; N, 4.39. Found: C, 82.92; H, 7.70; N, 4.50.

The infrared spectrum[9] had prominent bands at 1700 and 2247 cm.$^{-1}$, assignable to a singly conjugated carbonyl function and a nitrile group, respectively.

β-Benzoyl-α-mesitylpropionitrile (IV).—A solution of 20 g. of potassium cyanide in 50 ml. of water was added drop by drop over an interval of one hour to a solution of 29 g. of mesitalacetophenone,[2,4] 500 ml. ot9 5% ethanol and 9 ml. of glacial acetic acid. The temperature of the reaction mixture was kept at 50° during the addition of the cyanide and at 45–55° for an additional 2 hours. The yield of crude nitrile was 26.7 g. (83.5%). It crystallized from absolute ethanol in white needles; m.p. 107.5–108°.

Anal. Calcd. for $C_{19}H_{19}NO$: C, 82.28; H, 6.91; N, 5.05. Found: C, 82.17; H, 7.00; N, 5.12.

The infrared spectrum contained sharp bands at 1683 and 2240 cm.$^{-1}$, assignable to a singly conjugated carbonyl group and an unconjugated nitrile group, respectively.

The 2,4-dinitrophenylhydrazone crystallized from ethyl acetate in yellow needles; m.p. 232°.

Anal. Calcd. for $C_{25}H_{23}N_5O_4$: C, 65.63; H, 5.07; N, 15.31. Found: C, 65.64; H, 5.03; N, 15.34

Mesitalacetone (V).—A solution of 2.5 g. of sodium hydroxide in 15 ml. of water was added dropwise over a period of 30 minutes to a mixture of 88.8 g. of freshly prepared mesitaldehyde, 190 ml. of acetone and 100 ml. of water. The reaction mixture was chilled during the addition of the alkali and was then allowed to warm up to room temperature. Mechanical stirring was maintained throughout the mixing and for 3 hours longer. The ketone distilled at 115–120° (0.2 mm.); m.p. 62–64°; yield 47%. It was used without further purification. This compound was reported by Kohler and Blanchard,[2] without preparative details, who gave the melting point as 67°.

α-Mesityllevulinonitrile (VI).—A solution of 40 g. of potassium cyanide in 80 ml. of water was added, dropwise and with stirring, to a solution of 58.4 g. of mesitalacetone, 300 ml. of 95% ethanol and 18 ml. of glacial acetic acid. The temperature of the reaction mixture was carefully maintained at 35°; the addition required an hour. The reaction mixture was stirred for 2 hours afterward and diluted with 300 ml. of water. The nitrile was extracted with benzene and recrystallized from ethanol; yield 41.1 g. (63%). After repeated recrystallization from this solvent it was in the form of white needles; m.p. 94°.

Anal. Calcd. for $C_{14}H_{17}NO$: C, 78.10; H, 7.96; N, 6.51. Found: C, 78.09; H, 8.10; N, 6.42.

The infrared spectrum contained bands at 1717 and 2240 cm.$^{-1}$ assignable to a carbonyl function and a nitrile group, respectively.

The 2,4-dinitrophenylhydrazone was recrystallized from ethyl acetate; m.p. 199°.

Anal. Calcd. for $C_{20}H_{21}N_5O_4$: C, 60.75; H, 5.35; N, 17.71. Found: C, 60.74; H, 5.43; N, 17.74.

Ethyl Mesitalmalonate (VII).—A solution of 151.8 g. of freshly distilled mesitaldehyde, 171.3 g. of ethyl malonate, 10 ml. of piperidine and 5.5 g. of mesitoic acid in 350 ml. of benzene was boiled under reflux for 4 days; water was drained periodically from a stopcock at the base of the condenser. At the end of 2 days 3 g. of benzoic acid and an additional 5 ml. of piperidine were added to the reaction mixture, but the rate of formation of water did not appear to increase. An additional 100 ml. of benzene was added to the reaction mixture and the whole was extracted twice with 100-ml. portions of dilute sodium hydroxide solution, and twice with 200-ml. portions of distilled water. The product was distilled twice through a Podbielniak column: b.p. 136–138° (0.4 mm.); n^{20}D 1.5103.

Anal. Calcd. for $C_{17}H_{22}O_4$: C, 70.32; H, 7.64. Found: C, 70.74; H, 7.80.

Mesitylsuccinic Acid (IX).—To a solution of 96.6 g. of ethyl mesitalmalonate in 1250 ml. of 95% ethanol was added a solution of 24 g. of potassium cyanide in 45 ml. of water. The reaction mixture was kept at 65–70° with constant stirring for 18 hours, during which time precipitation of a salt took place. The crude product was boiled under reflux with concentrated hydrochloric acid for 36 hours. The mesitylsuccinic acid was isolated by usual procedures and recrystallized three times from ethyl acetate; yield 1.7 g.; m.p. 203.5°.

Anal. Calcd. for $C_{13}H_{16}O_4$: C, 66.08; H, 6.83; neut. equiv., 118.1 Found: C, 66.15; H, 6.90; neut. equiv., 119.6.

The infrared spectrum contained a very strong band at 1709 cm.$^{-1}$, which is assignable to the carboxyl group.

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(6) R. C. Kadesch, THIS JOURNAL, **66**, 1207 (1944).

(7) A. Weissberger and D. B. Glass, *ibid.*, **64**, 1724 (1942).

(8) Microanalyses by Miss Emily Davis, Mrs. Jean Fortney and Miss Rachel Kopel.

(9) The infrared absorption spectra were observed and interpreted by Miss Elizabeth Petersen.