TABLE I

VAPOR PRESSURES IN MM.

Water		*cis*-2-Pentene		*trans*-2-Pentene		3-Methyl-1-butene	
B. p., °C.	p^a	B. p., °C.	p, calcd.	B. p., °C.	p, calcd.	B. p., °C.	p, calcd.
65	187.57	1.595	187.58	1.026	187.56		
70	233.72	6.522	233.74	5.956	233.74		
75	289.13	11.486	289.12	10.922	289.15		
80	355.22	16.494	355.21	15.927	355.22	0.218	355.25
85	433.56	21.541	433.50	20.969	433.49	5.112	433.53
90	525.86	26.633	525.81	26.055	525.78	10.053	525.86
95	633.99	31.766	633.94	31.183	633.93	15.033	633.94
100	760.00	36.944	760.03	36.354	760.03	20.061	760.00
105	906.06	42.161	906.11	41.561	906.09	25.128	906.00
110	1074.6	47.423	1074.7	46.813	1074.7	30.245	1074.6
115	1268.0	52.724	1268.1	52.100	1267.5	35.402	1268.1
120	1489.1	58.070	1489.3	57.430	1489.2	40.602	1489.2
125	1740.8	63.456	1740.8	62.803	1740.8	45.847	1740.7
130	2026.0	68.882	2025.6	68.211	2025.7	51.139	2025.9

[a] These values of the pressures corresponding to the observed boiling temperatures of water are from the tables of Osborne, Stimson and Ginnings, *J. Research Natl. Bur. Standards*, **23**, 261 (1939).

TABLE II

CONSTANTS OF ANTOINE EQUATIONS AND NORMAL BOILING POINTS

	A	B	C	N. b. p., °C.
cis-2-Pentene	6.87540	1069.466	230.786	36.94
trans-2-Pentene	6.90575	1083.987	232.965	36.35
3-Methyl-1-butene	6.82618	1013.474	236.816	20.06

The results of the measurements are presented in Table I. The data were fitted by least-squares adjustments to Antoine equations of the form, $\log_{10}p = A - B/(t + C)$, where p is the vapor pressure in mm. and t is the temperature in °C. The constants of the equations so obtained and the normal boiling points of the compounds computed from these equations are listed in Table II. Values of the vapor pressure calculated by means of the Antoine equations are given in Table I, columns 4, 6 and 8 for comparison with the experimental values in column 2.

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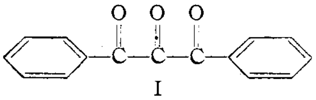
The Chemistry of Vicinal Tricarbonyl Compounds. I. Condensation Reactions of 1,3-Diphenylpropanetrione-1,2,3[1]

BY DEXTER B. SHARP AND HENRY A. HOFFMAN

Perkin–Knoevenagel type condensations have been limited largely to the use of aldehydes as carbonyl components, although a few examples[2] appear in the literature in which simple ketones have been used, most successfully by employing the Doebner[3] modification. Only minor attention has been given to condensations of vicinal polyketones with active-methylene compounds. Schmitt[4] reported a condensation of mesoxalic ester with ethyl cyanoacetate and Sachs and coworkers[5] reported similar condensations of pentanetrione-2,3,4 with pentanedione-2,4, malonic ester and p-nitrophenylacetonitrile. The latter compound was condensed also with 1-(2′-methoxyphenyl)-butanetrione-1,2,3. In no case were structure proofs reported, the structures of the products being assumed, apparently, from analytical data alone.

The present work was undertaken in order to study the condensations of active methylene compounds with 1,3-diphenylpropanetrione-1,2,3 (I),



I

the latter not having been studied in this manner. Malonic acid was employed as the principal methylene component for the twofold reason that it had not been condensed previously with vicinal tricarbonyl compounds and that structure studies of any product would be facilitated by the presence of the carboxyl functions. Structure studies were necessary to determine whether the carbon skeletons of the addenda were unchanged or had undergone rearrangement in a manner similar to that reported by Kohler and Erickson.[6] They isolated the benzoate of benzoin from the equimolar reaction of phenylmagnesium halide with I. The two reactions would be comparable if it were assumed that each involved an attack upon carbonyl carbon by the nucleophilic particles,

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[1] Abstracted in part from a thesis presented by Henry A. Hoffman to the Graduate Faculty of Kansas State College in partial fulfillment of the requirements for the degree, Doctor of Philosophy, granted in January, 1950. Supported in part by a grant-in-aid from the Frederick Gardner Cottrell funds of Research Corporation.

[2] Johnson, "Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 222.

[3] Doebner, *Ber.*, **33**, 2140 (1900); **35**, 1137 (1902).

[4] Schmitt, *Compt. rend.*, **140**, 1400 (1905).

[5] Sachs and Barschall, *Ber.*, **34**, 3047 (1901); Sachs and Rohmer, *ibid.*, **35**, 3307 (1902); Sachs and Wolff, *ibid.*, **36**, 3221 (1903); Sachs and Herold, *ibid.*, **40**, 2714 (1907).

[6] Kohler and Erickson, THIS JOURNAL, **53**, 2301 (1931).

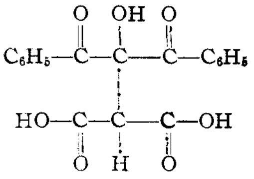
malonic acid–carbanion and phenyl–anion, respectively.

Initial attempts to obtain condensation of I with the methylene components malonic acid, acetophenone and malonic ester, in the presence of a variety of basic and acidic catalysts, either failed to yield isolable products or resulted in degradation of the triketone to benzil and benzoic acid. The degradation was predominant when strongly basic catalysts such as sodium hydroxide and sodium ethoxide were used. In addition, it was found that the same degradation products were formed when water and triketone were heated in a sealed tube at 220°.

A successful equimolar addition of *p*-nitrophenylacetonitrile to I was realized when the two were mixed and several drops of piperidine were added. This indicated that addition was not inhibited by steric factors and subsequent application of the Doebner[3] conditions finally effected an addition of malonic acid to the diphenyl triketone (I).

A pyridine solution of the triketone was mixed thoroughly with a pyridine–piperidine solution of malonic acid. The mixture was cooled and periodically stirred until small bubbles began to form. At this point (longer reaction times decreased the yield) the reaction mixture was poured into excess hydrochloric acid in order to convert the solvent and catalyst to the non-basic salts. This procedure was designed to prevent reversal of the reaction which was observed in similar cases by Kohler and Corson.[7]

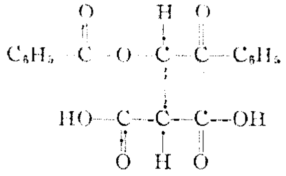
The compound obtained from this reaction was a white solid and carbon–hydrogen analysis gave values which corresponded to $C_{18}H_{14}O_7$, a one-to-one addition product. Tentatively, it was assumed that the addition involved the central carbonyl group of the triketone (I). The flanking carbonyl groups are attached to the phenyl groups which, by serving as electron sources, could diminish the positivity of these carbonyl carbons below that of the central carbonyl. Thus, the carbon of the central carbonyl group might be more susceptible to attack by a nucleophilic particle. The validity of this reasoning is supported indirectly by the structure studies of the addition product, perhaps also by the results of the Grignard reaction studied by Kohler and Erickson,[6] and from the report by Bigelow, Rule and Black[8] of the reduction of I to dibenzoylcarbinol. In addition, it has been shown[9] that *p*-nitrophenylhydrazine attacks the central carbonyl group of I. The addition product was assigned, therefore, the tentative structure II. Surprisingly, attempted dehydrations of this compound with a variety of dehydrating agents failed to produce the tetrasubstituted ethylene corresponding to II. Similarly, decarboxylation attempts resulted in no isolable monocarboxylic acid corresponding to II, although carbon dioxide was detected in such experiments.



II

Direct titration of the product with standard alkali gave a neutral equivalent which agreed with that calculated for formula II as a dicarboxylic acid. When heated with excess standard alkali saponification equivalents were obtained which corresponded to one-third of the molecular weight of II, thus a third acid function was formed by action of the alkali. From such saponifications three fragments were isolated and identified in appreciable quantities: benzoic acid, acetophenone and glyoxylic acid (the latter was isolated as the phenylhydrazone from the reaction mixture). These products accounted for all but one of the carbons of the addition product. The formation of glyoxylic acid suggested that the malonic acid portion of the molecule may have decarboxylated during saponification. However, attempts to detect the liberation of carbon dioxide in the reaction mixture by potentiometric titration were inconclusive.

An alternate structure (III) was considered possible for the addition product. III could arise by a rearrangement similar to that reported by Kohler and Erickson[6] in their Grignard study with I. Structure III could account for the failure of the dehydration attempts and the ease of cleavage to benzoic acid by dilute alkali.



III

The action of alkali upon the addition product is summarized as

$$\text{II or III (?)} \longrightarrow C_6H_5CO_2H + C_6H_5COCH_3 + CHOCO_2H + H_2O\ (?) + CO_2\ (?)$$

Work is being continued in this Laboratory to determine the structure of this product.

Experimental[10]

Starting Materials.—1,3-Diphenylpropanetrione-1,2,3 (I) was prepared by the method of Bigelow and Hanslick.[11] Distillation of the hydrate at reduced pressure gave the anhydrous ketone, m. p. 70–71° (reported,[11] 68–70°). Piperidine (Eastman Kodak Co. Yellow Label, P687) was dried and distilled before use. Pyridine (Baker and Adamson, Purified, 2165) was dried for a month over potassium hydroxide pellets and then was distilled. *p*-

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(7) Kohler and Corson, THIS JOURNAL, **45**, 1975 (1923).

(8) Bigelow, Rule and Black, *J. Chem. Soc.*, **83** (1935).

(9) Sharp, THIS JOURNAL, **71**, 1106 (1949).

(10) Each m. p. was corrected for stem exposure.

(11) Bigelow and Hanslick, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 244.

Nitrophenylacetonitrile (Eastman White Label, 1115) and malonic acid (Eastman White Label, 695) were dried eight hours in an oven kept at 60° and then were stored in tightly sealed containers.

Decomposition of 1,3-Diphenylpropanetrione-1,2,3 (I).—When freshly distilled I (14.0 g.) was refluxed for three hours in dry benzene (140 ml.) with a molar portion of ethyl sodiomalonate and the solution was acidified, there was obtained benzoic acid (4.1 g.); m. p. and mixed m. p. 120–121° with authentic benzoic acid. Also isolated was benzil (9.6 g.) which was identified as the *p*-nitrophenylhydrazone; m. p. and mixed m. p. 187–189° with authentic benzil *p*-nitrophenylhydrazone. Compound I (3.25 g.) and water (1.0 ml.) were sealed in a Carius tube and heated at 220° for fifteen hours. The tube was opened and benzoic acid (1.26 g.) and benzil (1.42 g.) were isolated and identified as above.

Condensations of 1,3-Diphenylpropanetrione-1,2,3 (I). A. With *p*-Nitrophenylacetonitrile.—Compound I (2.80 g.) and *p*-nitrophenylacetonitrile (2.75 g.) were mixed thoroughly and piperidine (2 drops) was added. Heat was evolved and the reaction mixture became yellow-green in color and solidified upon cooling. Recrystallization from alcohol yielded a white solid (2.38 g., 43%); m. p. 155–157°.

Anal. Calcd. for $C_{23}H_{16}O_5N_2$: C, 69.15; H, 4.03. Found: C, 69.09; H, 4.12.

This corresponds to a one-to-one-addition product.

B. **With Malonic Acid.**—Compound I (5.43 g.) was dissolved in dry pyridine (8.0 ml.) and was cooled to 5°. Malonic acid (2.40 g.) and dry piperidine (3.40 ml.) were mixed thoroughly and cooled to 5°. To the latter was added the pyridine solution of I and the mixture was stirred until it was homogeneous. The reaction mixture was stirred frequently while it warmed slowly to room temperature. After approximately one hour it had assumed a deep red color and small bubbles were emitted upon stirring. At this point (longer reaction times decreased the yield) the mixture was poured into water, ice and hydrochloric acid, the latter in excess over that required to react with all pyridine and piperidine. The acid solution was extracted with two portions (100 ml. each) of ethyl acetate. The ethyl acetate solution was dried over anhydrous sodium sulfate and the solvent was removed by evaporation at room temperature. The residue was dissolved in sodium carbonate (10%), filtered and reprecipitated by addition of hydrochloric acid. The resulting paste solidified after prolonged stirring (3.32 g., 44% crude). The addition product crystallized as a white solid from chloroform; m. p. 149°.

Anal. Calcd. for $C_{18}H_{14}O_7$: C, 63.16; H, 4.10; neut. equiv., 171. Found: C, 63.41; H, 4.55; neut. equiv., 171, 172.

This corresponds to a one-to-one addition product.

Structure Studies of Addition Product. A. Saponification.—Weighed samples of the malonic acid addition product were heated for one hour in excess standard alkali and the resulting solutions were back titrated to the phenolphthalein end point with standard acid. The saponification equivalents obtained were 105 (0.0658 g.), 107 (0.1217 g.) and 114 (1.4077 g.). Weights in parentheses were sample weights. The saponification equivalent of $C_{18}H_{14}O_7$ calculated as a tribasic compound is 114. A sample of addition compound (3.02 g.) was heated for fifteen minutes in sodium hydroxide solution (20%, 10 ml.). The color of the solution changed progressively from light yellow to deep red to a cloudy tan. After cooling to room temperature the alkaline reaction mixture was extracted with four portions of ether (30 ml. each) and the ether solution was dried over anhydrous sodium sulfate. The ether was removed by evaporation and gave a liquid residue (0.79 g., 74%) which was acetophenone, identified as the phenylhydrazone; m. p. and mixed m. p. 103–105° with authentic acetophenone phenylhydrazone. The alkaline aqueous solution was acidified to *p*H 2 and again extracted with four portions of ether (30 ml. each) and the ether solution was dried over anhydrous sodium sulfate. Removal of the ether gave benzoic acid (0.91 g., 85%); m. p. and mixed m. p. 120–121° with authentic benzoic acid. The acidic aqueous solution was divided into two equal parts. To the first was added 2,4-dinitrophenylhydrazine and a derivative separated from the solution; m. p. 194–197° (reported[12] 194–195° for glyoxylic acid 2,4-dinitrophenylhydrazone). To the second portion of acidic aqueous solution phenylhydrazine was added and a solid precipitated; (0.20 g., 25%) m. p. 144–145° (reported[13] 143–145° for glyoxylic acid phenylhydrazone). The neutral equivalent found was 159 and that calculated for glyoxylic acid phenylhydrazone was 164.

B. **Other Degradations.**—No pure compounds were obtained when samples of the addition product were treated with hot acetic acid, acetic anhydride, phosphorus oxychloride or concentrated sulfuric acid in experiments designed to dehydrate this compound.

When samples of the addition product were heated to and held near its m. p. carbon dioxide was detected and a deep red melt was formed. However, no compound other than starting material was isolated from these experiments.

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(12) Rabassa, *Rev. acad. cienc. Madrid*, **31**, 417 (1934).

(13) von Pechmann, *Ber.*, **29**, 2163 (1896).

MANHATTAN, KANSAS

RECEIVED MARCH 29, 1950

Cyanoethylation of Some Carbazole Derivatives

BY NATHAN L. SMITH

For lubricant additive studies it was necessary to synthesize a number of heterocyclic-substituted propionic acids as intermediates. Herein is described the preparation of β-(1,2,3,4-tetrahydro-9-carbazolyl)-propionic acid and β-(3,6-di-*t*-butyl-9-carbazolyl)-propionic acid from the corresponding substituted propionitriles, which were readily formed by the cyanoethylation of the parent heterocyclic compounds employing the method of Whitmore.[1]

Experimental[2]

3,6-Di-*t*-butylcarbazole.—The method of Buu-Hoi and Cagniant[3] provided a crystalline product melting at 228° in 76% yield.

β-(3,6-Di-*t*-butyl-9-carbazolyl)-propionitrile.—A well-stirred mixture of 17.5 g. (0.6 mole) of 3,6-di-*t*-butylcarbazole and 20.0 g. of acrylonitrile was cooled in an ice-bath and made to react by the addition of 0.5 ml. of a 40% solution of benzyltrimethylammonium hydroxide (Triton B). The reaction product was warmed on a steam-bath for an hour, cooled, taken up with acetone and allowed to crystallize. Recrystallization from aqueous acetone yielded 12.0 g. (59% yield) of fine white needles, m. p. 190–190.5°. Further recrystallization from methanol did not raise the melting point.

Anal. Calcd. for $C_{23}H_{28}N_2$: N, 8.75. Found: N, 8.98.

The product formed a picrate in alcohol which crystallized in reddish-brown needles, m. p. 184°.

β-(3,6-Di-*t*-butyl-9-carbazolyl)-propionic Acid.—A mixture of 5.0 g. (0.015 mole) of the nitrile, 5.0 g. of sodium hydroxide, and 100 ml. of 90% ethanol was heated under reflux for thirty hours, after which the solvent was removed and the residue treated with hydrochloric acid. The crude product weighed 4.5 g. (85% yield) and was recrystallized from aqueous methanol in the form of fine white needles, m. p. 193–194°; neutral equivalent 355.0 (calcd. 353.5). The sodium salt was soluble in benzene; its aqueous solution foamed freely.

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(1) Whitmore, Mosher, Adams, Taylor, Chapin, Weisel and Yanko, THIS JOURNAL, **66**, 725 (1944).

(2) Analyses performed by Oakwold Laboratories, Alexandria, Va. Melting points are uncorrected.

(3) Buu-Hoi and Cagniant, *Ber.*, **77**, 121 (1944).