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.

---

[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.

---

[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).

Anal. Calcd. for $C_{23}H_{29}O_2N$: N, 3.99. Found: N, 4.16.

The methyl ester, prepared by the method of E. Fischer, crystallized from acetone in white platelets, m. p. 116.5–117.5°.

1,2,3,4-Tetrahydrocarbazole.—The method of Rodgers and Carson[4] was used to prepare a colorless product, m. p. 113–114°.

β-(1,2,3,4-Tetrahydro-9-carbazolyl)-propionitrile.—This compound was prepared by the method described above in 53% yield, white needles, m. p. 115–116°.

Anal. Calcd. for $C_{15}H_{16}N_2$: N, 12.45. Found: N, 12.26.

β-(1,2,3,4-Tetrahydro-9-carbazolyl)-propionic Acid.—The method of hydrolysis described above was applied to prepare in 83% yield a granular product, m. p. 118–119°, neutral equivalent 242.0 (calcd. 243.2).

Anal. Calcd. for $C_{15}H_{17}O_2N$: N, 5.76. Found: N, 5.90.

---

(4) Rodgers and Carson, THIS JOURNAL, **69**, 2910 (1947).

CHEMISTRY DIVISION
NAVAL RESEARCH LABORATORY
WASHINGTON, D. C. RECEIVED MARCH 28, 1950

Dimorphic Forms of 2-Hydroxymethyl-4-*t*-butyl-6-methylphenol

BY G. SPRENGLING, S. BEATTY AND K. B. ADAMS

The methylol derivative of *p-t*-butyl-*o*-cresol was first synthesized by K. Hultzsch by alkaline reaction of the corresponding phenol with formaldehyde.[1] Hultzsch recorded the m. p. 64° for his product. An attempt to duplicate his procedure yielded a product of m. p. 73.7–74.2° (cor.), as recrystallized from a mixture of hexane and benzene. However, rapid recrystallization of the product from hexane—in which it is less soluble—gave crystals m. p. 62.9–63.4° (cor.). Recrystallization of either product from hexane with enough benzene added to delay the beginning of crystallization until the solution had cooled to near room temperature yielded the higher-melting product again. A single crystal of the higher-melting form dropped into a melt of the other at 64° caused solidification of the melt, whereafter it melted again at 73.7–74.2°. Both forms remained unchanged on standing at room temperature for over a year.

The analyses of the two products for C and H were identical, av. 74.22% C and 9.21% H (calcd. 74.19% C and 9.34% H). Infrared spectra of the two products in CCl_4 were also identical over the range 2–15μ. However, the X-ray diffraction spectra of the powdered samples were entirely different. The interplanar spacings for the principal reflections (above $2\theta = 5°$, using Cu K_α radiation) were d = 11.6, 5.9, 5.04, 4.15 and 3.98 Å. for the higher-melting, and d = 12.3, 8.2, 4.64 and 3.82 Å. for the lower-melting form.

The two substances are therefore dimorphic, and probably monotropic forms of one compound.

It is interesting to note that infrared spectra of the two forms in the crystalline state (Nujol mull) showed small but significant differences in the hydroxyl region, possibly due to differences in bonding due to different orientation of the molecules in the crystal.

CHEMICAL DEPT. RESEARCH LABS.
WESTINGHOUSE ELECTRIC CORP.
E. PITTSBURGH, PA. RECEIVED APRIL 24, 1950

---

(1) Kurt Hultzsch, *J. prakt. Chem.*, **158**, 285 (1941).

Concerning the Reaction of *o*-Chlorotoluene with Propylene Chlorohydrin

BY GUIDO H. STEMPEL, JR., AND BETTY SOBEL

The reaction of propylene chlorohydrin with *o*-chlorotoluene in the presence of BF_3 and P_2O_5 has been investigated by Bachman and Hellman.[1] They have found that dehydrohalogenation of the two chloroisopropyl compounds formed produces two new compounds which they have identified as 3-chloro-4-methyl- and 2-methyl-3-chloro-α-methylstyrene. In order to correlate their results with some obtained in this laboratory we have repeated their synthesis and carefully identified the products. We have found that their method yields instead 4-chloro-3-methyl- and 2-chloro-3-methyl-α-methylstyrene. We have found none of the other isomers although it is possible they were present in small quantity. It appears that the entering group is oriented ortho and para to the chlorine as is the case in the majority of other substitution reactions of *o*-chlorotoluene.

The identification of 4-chloro-3-methyl-α-methylstyrene rests upon the identity of the methylchlorobenzoic acid obtained by oxidation. We have found this acid to be 4-chloro-3-methylbenzoic acid because (1) mixtures of the acid in question with an authentic sample of 4-chloro-3-methylbenzoic acid melt at exactly the same temperature as the authentic sample and (2) melting point depressions result when the acid in question is mixed with an authentic sample of 3-chloro-4-methylbenzoic acid.

The identification of the 2-chloro-3-methyl-α-methylstyrene likewise rests upon the identity of the corresponding substituted benzoic acid. However, only *one* of the pertinent isomers, 3-chloro-2-methylbenzoic acid, has been reported. Its melting point has been variously recorded as 159°, and 156° and 154°.[2] It is obviously not possible to choose between the 2-chloro-3-methyl- and the 3-chloro-2-methyl- isomers by melting point alone in the absence of an authentic specimen for comparison, a comparison not reported by Bachman and Hellman.[1] We have positively identified the acid in question as 2-chloro-3-methylbenzoic acid by conversion of the acid to the amide, Hofmann rearrangement of the amide to the amine, acetylation of the amine and identification of the acetylated amine by mixed melting

---

(1) Bachman and Hellman, THIS JOURNAL, **70**, 1772 (1948).

(2) Huntress, "Organic Chlorine Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 401.