

Anal. Calcd. for $C_{20}H_{29}O_2N$: 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 Carson⁴ 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).

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

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The methylol derivative of *p-t*-butyl-*o*-cresol was first synthesized by K. Hultsch by alkaline reaction of the corresponding phenol with formaldehyde.¹ Hultsch 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 2–15 μ . However, the X-ray diffraction spectra of the powdered samples were entirely different. The interplanar spacings for the principal reflections (above $2\theta = 5^\circ$, using $Cu K_\alpha$ radiation) were $d = 11.6, 5.9, 5.04, 4.15$ and 3.98 \AA . for the higher-melting, and $d = 12.3, 8.2, 4.64$ and 3.82 \AA . 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

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

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.

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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°. 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.