The most logical explanation for these results is the preferential formation of un-ionized salts in solution, with stereochemical specificity leading to the formation of a higher concentration of un-ionized LA·*l*B. This would result in a higher concentration of DA in solution and then in the solid phase that crystallized. These results might have been predicted from the fact that such salts have long been known to be partially undissociated in concentrated solutions.[3] The preferential *retention in solution* of one optically active form of the acid is to be emphasized as the factor leading to the enrichment of the crystallized material in the other form.

It is probable that variations in such experimental conditions as relative proportions of racemic and optically active compounds used, temperature at which crystallization is allowed to occur, solvents used, repeated treatments, etc., would result in more effective resolution. However, although hypothetical cases may be constructed where a use of this method of partial resolution might be of importance, no practical use is apparent at present. For this reason no further investigation of the phenomenon has been undertaken, and it is reported here as a matter of theoretical interest.

Experimental

To a solution of 1.5 g. of S-carboxymethyl-DL-homocysteine in 15 ml. of hot water was added a solution of 2.0 g. of brucine (0.55 mole) in 15 ml. of hot absolute ethanol. The resulting solution was diluted with 15 ml. of hot absolute ethanol and was allowed to cool slowly to room temperature. It was then cooled in the refrigerator for several days, the solid was collected, washed and dried; 0.47 g. was obtained. This product was dissolved in 8 ml. of hot water, treated with Norite and filtered, and the filtrate was diluted with 16 ml. of absolute ethanol and was cooled. The solid was collected on a filter, washed and dried: 0.31 g., m.p. 227–230° dec., $[\alpha]^{25}D$ −5.1° (*c* 1, *N* HCl); (carboxymethyl-L-homocysteine, m.p. 232–234° dec., $[\alpha]^{24}D$ +21.2° (*c* 1, *N* HCl); carboxymethyl-DL-homocysteine, m.p. 224–226 dec.).[4] This product had the sour taste characteristic of carboxymethylhomocysteine and no trace of brucine could be detected.

Anal. Calcd. for $C_6H_{11}O_4NS$: N, 7.25; S, 16.59. Found: N, 7.05; S, 16.24.

The mother liquor from the first filtration was heated, 4.3 ml. of 1 *N* HCl was added, and the solution was cooled to room temperature and allowed to stand overnight. The solid that separated was collected, washed and dried; 0.77 g. was obtained. It was recrystallized from a mixture of 15 ml. of water and 30 ml. of absolute ethanol yielding 0.65 g. of analytically pure material; m.p. 226–229° dec., $[\alpha]^{25}D$ +3.5° (*c* 1, *N* HCl). A test by tasting showed brucine to be absent.

Anal. Calcd. for $C_6H_{11}O_4NS$: N, 7.25; S, 16.59. Found: N, 7.17; S, 16.71.

(3) Ref. 2, p. 295.

(4) Armstrong and Lewis, *J. Org. Chem.*, **16**, 749 (1951).

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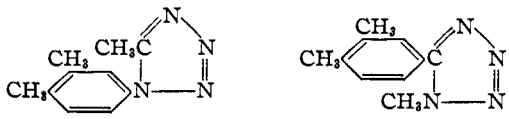
1-(3′,4′-Dimethylphenyl)-5-methyltetrazole

BY FREDERIC R. BENSON, LAWRENCE W. HARTZEL AND WALTER L. SAVELL

A by-product of the Schmidt reaction with 3,4-dimethylacetophenone was reported previously.[1] It was suggested that the substance was probably 1-(3′,4′-dimethylphenyl)-5-methyltetrazole (I) or possibly the isomer, 1-methyl-5-(3′,4′-dimethylphenyl)-tetrazole (II). Identity of the compound as I has now been established.



I II

The procedure[2] for converting N-substituted aromatic amides through the imide chlorides to 1,5-disubstituted tetrazoles recently has been improved and extended to aliphatic and mixed aliphatic-aromatic amides.[3] This modification was applied to 3,4-dimethylacetanilide producing I of unequivocal constitution. Melting points, both individual and mixed, of this compound and that isolated from the Schmidt reaction were found to be the same. Ultraviolet absorption spectra (Fig. 1) of the substances are virtually identical, with a maximum at a wave length of 231 mμ. Finally the methiodides of the compounds from the two syntheses were prepared. Both methiodides had the same melting point with no depression for their mixture.

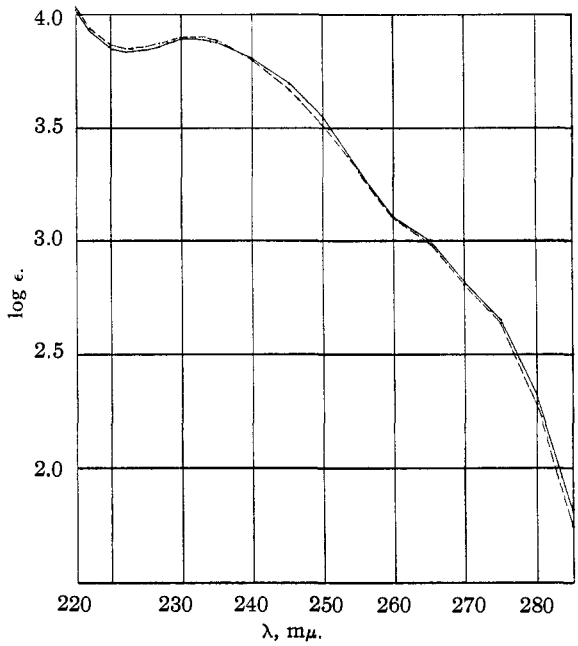


Fig. 1.—Absorption spectra of 1-(3′,4′-dimethylphenyl)-5-methyltetrazole: - - -, prepared from 3,4-dimethylacetanilide, and ——, prepared from 3,4-dimethylacetophenone.

Experimental

The isolation of the tetrazole derived from the Schmidt reaction with 3,4-dimethylacetophenone was carried out as previously described.[1]

1-(3′,4′-Dimethylphenyl)-5-methyltetrazole.—This compound was prepared in 72% yield following the method described by Harvill, *et al.*[3] The white solid after recrystallization first from heptane and then from water melted at 110.5° cor. A mixed melting point with the product isolated from the Schmidt reaction showed no depression. The

(1) F. R. Benson, L. W. Hartzel and W. L. Savell, THIS JOURNAL, **71**, 1111 (1949).

(2) J. v. Braun and W. Rudolph, *Ber.*, **74**, 264 (1941).

(3) E. K. Harvill, R. M. Herbst, E. C. Schreiner and C. W. Roberts, *J. Org. Chem.*, **15**, 662 (1950).

melting point now found for the Schmidt reaction sample (110.5° cor.) as well as that obtained from 3,4-dimethylacetanilide differs from the 111–111.5° previously reported, which was determined using a Fisher–Johns apparatus. The present melting points were obtained in capillary tubes using a Hershberg type apparatus.

Anal. Calcd. for $C_{10}H_{12}N_4$: C, 63.80; H, 6.43; N, 29.77. Found: C, 63.6; H, 6.2; N, 29.8.

The methiodides were best prepared by heating the tetrazole in a sealed tube with an excess of methyl iodide at 80–90° for 1.5 hours. The precipitate which formed was collected on a filter and recrystallized twice from ethanol. Both methiodides melted at 206° cor. The melting point of their mixture showed no depression.

Anal. Calcd. for $C_{11}H_{15}N_4I$: C, 40.01; H, 4.58; N, 16.97. Found (A) methiodide from tetrazole prepared from 3,4-dimethylacetanilide: C, 39.8; H, 4.6; N, 17.2. (B) methiodide from tetrazole from Schmidt reaction: C, 39.5; H, 4.9; N, 16.8.

The absorption spectra were determined with a Model DU Beckman quartz spectrophotometer. Absolute ethanol was used as solvent; the following concentrations of tetrazole were employed for the wave lengths in question: 7.969×10^{-5} *M* for 215–260 mμ; 1.594×10^{-4} *M* for 260–270 mμ; 1.328×10^{-3} *M* for 270–280 mμ; 1.198×10^{-2} *M* for 285 mμ.

The authors are indebted to Dr. Paul D. Sternglanz and Miss Ruth C. Thompson for the analytical and ultraviolet absorption spectra data presented in this note.

LABORATORY OF ADVANCED RESEARCH
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Some Aryloxyaliphatic Acids

BY L. F. BERHENKE, L. E. BEGIN, B. M. WILLIAMS AND F. L. BEMAN

Several aryloxyaliphatic acids, not previously reported, have been made and are reported in Table I. The aryloxyacetic acids have been proposed as identifying derivatives for phenols[1] and can be made by the method there given or by modifications thereof.[2] In addition to the purification schemes described, we have found that crystallization of the acid from chlorobenzene or of the sodium salts from water at *p*H 10–13 are also effective methods for separating the acids from unreacted phenols.

The α- and β-substituted propionic acids and the α-substituted butyric acids were similarly prepared from α- and β-chloropropionic acid and α-bromobutyric acid, respectively.

The γ-substituted butyric acid was prepared by a modification of the method previously reported.[3] Two hundred thirty-two grams of *p*-phenylphenol was neutralized with 55 g. of sodium hydroxide in 1.5 l. of water and 148 g. of γ-bromobutyronitrile added over one hour, then the mixture was refluxed for two hours. Sixty-eight grams of sodium hydroxide was added as 10 *N* solution and the nitrile hydrolyzed by refluxing overnight. The reaction mixture (*p*H about 11) was cooled, filtered, washed with water and the moist cake resuspended in 10 l. of water, acidified with concentrated hydrochloric acid, digested on the steam-bath for several hours, cooled and filtered. The crystals were dried and recrystallized from 2 l. of chlorobenzene; yield 190 g., 74%, m.p. 151–155°. Further recrystallization gives material m.p. 158.5–160°.

TABLE I

Compound	Formula	M.p., °C.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Chlorine, % Calcd.	Chlorine, % Found	Neut. equiv. Calcd.	Neut. equiv. Found
Acetic acid										
p-Acetylphenoxy-	$C_{10}H_{10}O_4$	172.5–174.5	61.84	61.77	5.19	5.18			194.2	195.5
4-*s*-Butyl-2,6-dichlorophenoxy-	$C_{12}H_{14}Cl_2O_3$	78.4–80					25.62	25.60	277.1	276.0
3-Chloro-4-biphenylyloxy-	$C_{14}H_{11}ClO_3$	158–159					13.50	13.53	262.7	263.8
5-Chloro-2-biphenylyloxy-	$C_{14}H_{11}ClO_3$	123–125					13.50	13.58	262.7	265.2
4-Chloro-*o*-cumyloxy-	$C_{11}H_{13}ClO_3$	170–171					15.50	15.37	228.7	231.7
2,6-Dichlorophenoxy-	$C_8H_6Cl_2O_3$	134.7–135					32.10	32.27	221.0	221.0
3,5-Dichlorophenoxy-	$C_8H_6Cl_2O_3$	116–116.5					32.10	32.18	221.0	221.0
2,3,6-Trichlorophenoxy-	$C_8H_5Cl_3O_3$	147–148					41.60	41.59	255.5	261.8
Butyric acid										
γ-(4-Biphenylyloxy)-	$C_{16}H_{16}O_3$	158.5–160	74.97	74.90	6.29	6.31			256.3	265.2
α-(*p*-*t*-Butylphenoxy)-	$C_{14}H_{20}O_3$	89–90.5	71.15	71.06	8.53	8.49			236.3	238.7
α-(*o*-Chlorophenoxy)-	$C_{10}H_{11}ClO_3$	80–80.5					16.53	16.43	214.6	212.3
α-(*p*-Chlorophenoxy)-	$C_{10}H_{11}ClO_3$	77.5–78							214.6	213.7
α-(2,4,5-Trichlorophenoxy)-	$C_{10}H_9Cl_3O_3$	140–141					37.52	37.36	283.5	282.3
Propionic acid										
α-(*p*-*t*-Butylphenoxy)-[a]	$C_{13}H_{18}O_3$	89–90.5	70.26	70.08	8.16	8.20			222.2	218.6
β-(2,4,5-Trichlorophenoxy)-	$C_9H_7Cl_3O_3$	143–144							269.5	269.1

[a] Preparation reported by Salminen and Weissberger, U. S. Patent 2,423,730, but no constants are given.

(1) Koelsch, THIS JOURNAL, **53**, 304 (1931).
(2) Hayes and Branch, *ibid.*, **65**, 1555 (1943).
(3) Lohman, *Ber.*, **24**, 2631 (1891).

DOW CHEMICAL CO.
MIDLAND, MICHIGAN RECEIVED FEBRUARY 23, 1951

The Conversion of Δ⁴-Cholestene-3-one to Cholesterol[1]

BY B. BELLEAU AND T. F. GALLAGHER

Because of our need for effecting the transformation of cholestenone to cholesterol in the maximum yield for partial synthesis of the isotopically labelled sterol we have investigated the action of sodium borohydride on the enol acetate of cholestenone and have obtained cholesterol in 70 to 85% yield. Dauben and Eastham[2] with lithium aluminum hydride reduced cholestenone enol acetate to

(1) This investigation was supported by grants from the Lillia Babbitt Hyde Foundation, and the National Cancer Institute, United States Public Health Service.
(2) W. G. Dauben and J. F. Eastham, THIS JOURNAL, **72**, 2305 (1950).