

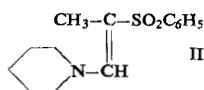
Trimethylenesulfone	M. p. [°C.]	Yield [%]
2,2-Dimethyl-3-pyrrolidino-4-phenyl-(Ib)	161 [*]	70
2-Methyl-3-piperidino-	b. p. 121/10 ⁻³ mm. Hg [**]	90
2-Ethyl-3-morpholino-	114	83
2-Ethyl-3-morpholino-4-phenyl-	170	65
2-Propyl-3-piperidino-4-ethyl-		88

[*] Mol. wt. calc. 279; found 260.

[**] Hydrochloride, m. p. 210°C., picrate, m. p. 190°C., methiodide m. p. 164°C.

The analytical, spectroscopic, and chemical findings, e.g. the correspondence of the base from 1-piperidinopentene and propane sulfochloride with that from 1-piperidinobutene and butane sulfochloride, are in harmony with the cyclic β -aminosulfone structure I. The isomeric cyclic α -aminosulfone structure and the vinylog sulfonic acid amide structure (analogous to II) are eliminated as possibilities because of the absence of reactions characteristic for these classes of substances (acid hydrolysis, reduction with formic acid, formation of immonium salts), as well as the lack of a C=C band in the infrared spectrum.

On the other hand, the vinylog sulfonic acid amide II (m. p. 107°C.), which has a strong C=C band at 1620 cm⁻¹ in the IR spectrum and a λ_{\max} value = 282 m μ (ϵ = 15300) in the ultraviolet spectrum, is formed under the same conditions



from 1-piperidinopropene and benzene sulfochloride in 66% yield. It is readily reduced to 1-piperidino-2-benzenesulfonylpropane (hydrochloride, m. p. 221°C.) with formic acid and is hydrolyzed with 2 N HCl to 2-benzenesulfonyl propion-aldehyde.

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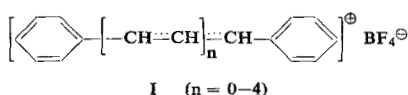
[1] Compare H. Adolph, Ph. D.-Thesis, Univ. Tübingen (Germany), 1959.

Polymethine Carbanions

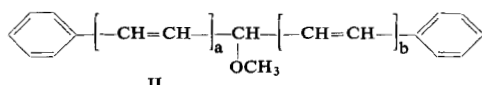
By Doz. Dr. K. Hafner and Dr. K. Goliasch

Chemisches Institut der Universität Marburg (Germany)

We reported recently on polymethine carbonium salts of type I [1]. The corresponding salts (III) of deeply colored polymethine carbanions, some of which were hitherto unknown, were prepared by splitting polyene ethers (II) with metallic sodium. These ethers are obtained by reacting secondary alcohols [1] with methanol.



I (n = 0-4)

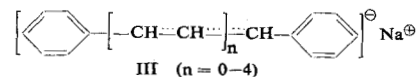


II

a = 0; b = 0 (b. p. 270-271°C [2])
a = 1; b = 0 (b. p. 178-180°C/11 mm. [3])
a = 2; b = 0 (b. p. 185-186°C/0,8 mm.)
a = 2; b = 1 (b. p. 203°C/0,8 mm.)
a = 2; b = 2 (b. p. 223-225°C/0,8 mm.)

The polyene ethers are sensitive to oxygen and light. Their thermal stability decreases with increasing chain length whereas that of the polymethine carbenate salts increases.

The salts can be prepared at room temperature under nitrogen. However, over a longer period of time, they are only stable at -60°C. They are extremely sensitive to oxygen, carbon dioxide, and atmospheric moisture [4].



III (n = 0-4)

The absorption maxima in the visible region (Table 1) are displaced bathochromically by an average of 33 m μ on lengthening the chain by one C=C-linkage (empirical rule: $\lambda_{\max} = 501 + (33 \times n)$, where n = number of C=C-double bonds).

Table 1. Color and absorption maximum of salts of carbanions (III)

n	Color of the solid substance	Color in solution	λ_{\max} [m μ] in ether at 20°C
0 [5]	yellow-orange	orange	501
1 [3]	red	wine-red	535
2	purple	red	568
3	blue, shiny green	blue	600
4	blue-black	deep blue	635

Hydrolysis of the salts leads to the unsaturated parent hydrocarbons which react with alkali metals to reform the salts (III).

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[Z 191/29 IE]

- [1] K. Hafner and H. Pelster, *Angew. Chem.* 73, 342 (1961).
[2] St. v. Konstanecki and V. Lampe, *Ber. dtsh. chem. Ges.* 39, 4019 (1906).
[3] E. Bergmann and T. Ukai, *Ber. dtsh. chem. Ges.* 66, 54 (1933).
[4] Added in Proof: Ch. Jutz and H. Amschler, *Angew. Chem.* 73, 806 (1961), reported on of salts polymethine carbanions (III) having a quasi-aromatic anion instead of the phenyl residues.
[5] K. Ziegler, *Liebigs Ann. Chem.* 473, 18 (1929).

Thin Layer Chromatography of Peptide Intermediates

By Dr. Peter Schellenberg

Institut für Organische Chemie und Organisch-Chemische Technologie der Technischen Hochschule Stuttgart (Germany)

Morin (3,5,7,2',4'-pentahydroxyflavone) [1] offers possibilities as a spray reagent for quick, convenient and reliable detection of N-protected amino acid and peptide derivatives on silica gel thin layer chromatograms. The dried chromatograms are sprayed with a 0.05% solution of morin in methanol and heated at 100°C for 2 minutes. Yellow-green fluorescent spots or dark absorption spots on a fluorescent green background can be seen in ultraviolet light. The limit of detection is about 2 μ g./spot. Since the silica gel layer has a capacity of more than 1 mg./spot with chloroform-acetone developing mixtures, impurities of down to 0.2% can be detected with certainty.

Esters of N-substituted amino acids, dipeptides and tripeptides run with characteristic R_F-values in chloroform-acetone (9:1, 8:2) or cyclohexane/ethyl acetate (1:1). Higher acyl-oligopeptide esters, as well as acyl-di- and -tripeptide esters with polar groups in the side chain (such as histidine derivatives), require stronger elution with chloroform-methanol (9:1). Compounds not protected at the carboxyl or amino end remain at the starting point in these anhydrous media. The solvent systems conventionally used in thin layer chromatography of amino acids [2] are suitable eluting agents for peptide derivatives with free carboxyl or amino groups.