methanol in methoxide[6] to form dimethyl 1-methoxy-1-methylcyclopropane-*trans*-2,3-dicarboxylate[1e] (IV, R = CH$_3$), cleaved by hot dilute methanolic hydrochloric acid to dimethyl acetosuccinate. The supposed[1g,i] anhydride of IV (R = H) is a γ-methyl-γ-methoxyitaconic anhydride, unsaturated to permanganate and decomposed by excess hot water to levulinic acid.

The diethyl ester of the Feist acid is isomerized at 240° to a substance considered[1i] as diethyl 1-butyne-1,4-dicarboxylate. However, *the isomerized ester shows no acetylenic infrared absorption:* the most probable structure is a stereoisomer of ethyl 2-carboethoxycyclopropylideneacetate (V). Further investigations[7] of these remarkable methylenecyclopropane derivatives, including reduction and reaction with diazo compounds (possible syntheses of spiropentanes), are under way.

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[6] The stability of the Feist acid and esters in *acid*[1a,b,i] evidences against α,β-unsaturation (contrast V[1j]).

[7] Dr. J. H. Sturdivant and Mr. D. R. Petersen, California Institute of Technology, are analyzing the crystal structure of the Feist acid.

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RECEIVED SEPTEMBER 2, 1952

THE EFFECT OF THE MEDIUM UPON HAMMETT'S SIGMA VALUES OF *p*-ALKYL GROUPS AND HYPERCONJUGATION

Sir:

For a number of *p*- and *m*-substituted anilines we compared the ionization constant in water (expressed as pK_a) with their catalytic constant in *n*-hexane (expressed as log k_c) on a prototropic rearrangement of a certain sulfone.[1] A linear relation exists between pK_a and log k_c, the Brønsted relation[2]; the stronger the base, the higher its catalytic effect. However, it was found that *p*-toluidine deviated; its log k_c (in *n*-hexane) is smaller than is expected from its pK_a (in water).

The effect of substitution in aniline on pK_a and on log k_c can also be expressed by means of Hammett relations.[3] Hammett's substitution constant σ for *p*-CH$_3$ derived from the pK_a of *p*-toluidine in water (−0.19) is in accordance with the one given by Hammett (−0.170),[3] the latter being derived from the ionization constant of *p*-toluic acid in water. However, a less negative value, *viz.*, −0.08, is derived from log k_c of *p*-toluidine in *n*-hexane.

That the effect of *p*-CH$_3$ in *p*-toluidine depends upon the medium[4] is, however, not restricted to this compound. With the aid of the values given by Hammett for the basic constants (log k_0 and ρ) of the recorded equilibria and reaction rates,[5] we calculated σ for the *p*-CH$_3$ group in the following media from the experimental data which Hammett used to compose his list of constants.[6]

Medium	Number of relations	σ
Water	9	−0.17
25–50% alcohol	3	−0.17
87–98% alcohol	5	−0.15
Alcohol	6	−0.14
Methanol	1	−0.11
Ether–alcohol	1	−0.105

Our own value in *n*-hexane (−0.08) fits excellently in this series and we conclude that *the σ-value for p-CH$_3$ depends upon the medium.*

Many data recorded in the literature since the publication of Hammett's list of σ-values give a better agreement when this dependence is taken into account.

The same effect is found for 3,4-xylidine. From its pK_a in water[7] as well as from the ionization constant of 3,4-xylenol in water a σ-value is found (−0.23) which is considerably more negative than the value derived from the log k_c of 3,4-xylidine in *n*-hexane (−0.10). The effect of the 3,4-dimethyl grouping is about the sum of the effect of the *m*-CH$_3$ and the medium dependent effect of the *p*-CH$_3$ group.

The fact that *p*-toluidine but not *m*-toluidine showed the deviation in the Brønsted relation, led us to suspect that the phenomenon known as hyperconjugation (Baker–Nathan effect) was involved.[8] Further evidence for this view was obtained from the observation that in the series *p*-CH$_3$, *p*-C$_2$H$_5$, *p*-*i*-C$_3$H$_7$ and *p*-*t*-C$_4$H$_9$ aniline the deviation from the Brønsted relation became smaller. In the same sequence hyperconjugation decreases.[8]

This is in accordance with recent data of Herbst and Jacox.[9] These authors derived the σ-values of *p*-alkyl groups from the rate of hydrolysis of *p*-alkyl benzoates in 87.8% alcohol and compared the values thus found with Hammett's values, derived from the ionization constants of *p*-alkylbenzoic acids in water. They found less negative values for *p*-CH$_3$ and *p*-C$_2$H$_5$, but agreeing values for *p*-*i*-C$_3$H$_7$ and *p*-*t*-C$_4$H$_9$.

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[1] For details we refer to the thesis of H. Kloosterziel, Groningen, 1952, and to papers to be published in *Rec. trav. chim.*; *cf.* Abstracts of Papers, XIIth Intern. Congress of Pure and Applied Chemistry, New York, 1951, p. 444.

[2] J. N. Brønsted and K. J. Pedersen, *Z. physik. Chem.*, **108**, 135 (1924).

[3] L. P. Hammett, "Physical Organic Chemistry," New York, N. Y., 1940, Chapt. VII.

[4] There is another indication for this in the work by J. C. James and J. G. Knox, *Trans. Far. Soc.*, **46**, 254 (1950).

[5] Ref. 3, pp. 189–190.

[6] Some data have been disregarded for obvious reasons, *cf.* L. P. Hammett, THIS JOURNAL, **59**, 96 (1937).

[7] F. Kieffer and P. Rumpf, *Compt. rend.*, **230**, 2302 (1950).

[8] For a recent monograph, see J. W. Baker, "Hyperconjugation," Oxford Press, New York, N. Y., 1952.

[9] R. L. Herbst and M. E. Jacox, THIS JOURNAL, **74**, 3004 (1952).

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RECEIVED OCTOBER 20, 1952

THE π HELIX—A HYDROGEN BONDED CONFIGURATION OF THE POLYPEPTIDE CHAIN

Sir:

In a recent letter, Dr. M. L. Huggins[1] proposed a new helical polypeptide chain configuration as a possible alternative to the Pauling-Corey α helix.[2] In the Huggins structure, the amide group is not planar and, as Pauling and Corey[3] have observed, the strain energy is great in comparison with the

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[1] M. L. Huggins, THIS JOURNAL, **74**, 3963 (1952).

[2] L. Pauling and R. B. Corey, *ibid.*, **72**, 5349 (1950).

[3] L. Pauling and R. B. Corey, *ibid.*, **74**, 3964 (1952).