of *n*-paraffins. Because the literature, recently reviewed by Kobe and Domask,[1] strongly infers that *n*-paraffin–thiourea adduct formation should not occur, a series of experiments was performed to investigate this contradiction. The results of the study show that *n*-paraffins containing fourteen or more carbon atoms can adduct with thiourea and consequently, for the separation of hydrocarbons which boil above the gasoline range, serious limitations are imposed on the previously supposed complementary selectivity of urea and thiourea.

Eight essentially pure *n*-paraffins were studied: *n*-decane, *n*-tetradecane, *n*-hexadecane, *n*-tricosane, *n*-pentacosane, *n*-octacosane and *n*-dotriacontane. Additional data were obtained with various fractions from a purified, commercial paraffin wax. Several different test methods were investigated. The most reliable procedure followed was to stir crystalline thiourea, moistened with methyl ethyl ketone, with a solution of the paraffin sample in benzene. In every case, care was taken to ensure the presence of a sufficient volume of benzene to prevent crystallization of the paraffin. The solids were filtered, washed, heated with water, and the adducted hydrocarbon recovered and identified.

From the results of the tests, certain conclusions are apparent. A *n*-paraffin containing twelve or less carbon atoms does not form an adduct with thiourea at 0° or above. *n*-Tetradecane (*n*-$C_{14}H_{30}$) forms an adduct at 0° but not at 25°. Paraffins containing sixteen or more carbon atoms can form thiourea adducts at either temperature. Obviously, modification of various conditions and techniques could shift the minimum chain length somewhat in either direction. The ease of formation and the "stability" of the adducts become greater as the molecular weight of the paraffin increases. However, even the higher molecular weight paraffins tested gave very poor yields of adduct at 45° due to the great change of adduct "stability" with temperature. Washing the adducts with one to three volumes of cold (5 to 10°) hydrocarbon solvents does not cause significant decomposition. It is advisable to allow adduct formation to proceed for about one hour in qualitative work. Quantitative recovery can be obtained only by successive treatments, each of about forty-eight hours duration, using in excess of 25 g. of thiourea per gram of *n*-paraffin.

At our request, certain of the above generalizations have been confirmed independently by another laboratory.[2] Professor Schiessler also determined that if the *n*-paraffin chain were coiled into a multiturn helix containing five methylene groups per turn, its dimensions would fall within the limits predicted for a molecule which will adduct with thiourea.[3]

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[1] K. A. Kobe and W. G. Domask, *Petroleum Refiner*, **31**, no. 3, 106–113; no. 5, 151–157; no. 7, 125–129 (1952).

[2] R. W. Schiessler, Am. Petroleum Institute Project 42, Pennsylvania State College, State College, Pa., private communication.

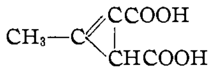
[3] R. W. Schiessler and D. Flitter, THIS JOURNAL, **74**, 1720–1723 (1952).

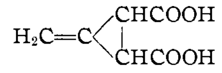
## STRUCTURE OF FEIST'S METHYLCYCLOPROPENEDICARBOXYLIC ACID

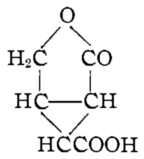
*Sir:*

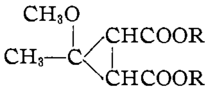
In 1893, Feist[1a] discovered that the reaction of 3-bromo-5-carboethoxy-4,6-dimethyl-2-pyrone with alkali furnished a dicarboxylic acid $C_6H_6O_4$, to which subsequent investigators[1] have ascribed the structure of 1-methylcyclopropene-2,3-dicarboxylic acid (I). Although my work on this most accessible supposed derivative of cyclopropene is not completed, current interest[1j] suggests publication of the conclusions, which differ from all advanced hitherto.

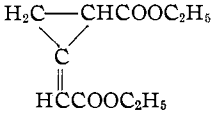
The Feist acid must be reformulated as 1-methylenecyclopropane-*trans*-2,3-dicarboxylic acid[2] (II). *The acid contains no C-methyl group.*[3] On bromination there are formed a dibromo diacid,[1a] reconverted to the unsaturated acid by zinc[1c] or sodium amalgam,[1e] and a bromo lactone monoacid,[1a] inert to neutral permanganate or hot silver nitrate. The bromo lactone may be reversibly hydrated to a hydroxy diacid, obtained also by hydrolysis of the dibromo acid.[1b] Reduction of the bromo lactone by sodium amalgam[1a] or over palladium gives a lactone monoacid, which may be reversibly hydrolyzed[4] and has a lactone carbonyl band at the same position as the bromo lactone (5.55 μ). *On oxidation with permanganate in bicarbonate the lactone gives trans-cyclopropane-1,2,3-tricarboxylic acid,*[5] m. p. 213.5–217.5°, neutr. equiv. 59.7, trimethyl ester m. p. 55–57°. *The lactone must therefore be 1-hydroxymethylcyclopropane-trans-2,3-dicarboxylic acid lactone* (III), and the bromo lactone and dibromo acid are respectively the 1-bromo derivative of III and 1-bromo-1-bromomethylcyclopropane-*trans*-2,3-dicarboxylic acid.

I


II


III


IV


V


The dimethyl ester[1c] of the Feist acid adds

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[1] (a) F. Feist, *Ber.*, **26**, 747 (1893); (b) *Ann.*, **436**, 125 (1924); (c) D. T. Jones, *J. Chem. Soc.*, **87**, 1062 (1905); (d) C. K. Ingold, *ibid.*, **121**, 2676 (1922); (e) F. R. Goss, C. K. Ingold and J. F. Thorpe, *ibid.*, **123**, 327 (1923); (f) *ibid.*, 3342 (1923); (g) *ibid.*, **127**, 460 (1925); (h) F. R. Goss and C. K. Ingold, *ibid.*, **127**, 2776 (1925); (i) G. A. R. Kon and H. R. Nanji, *ibid.*, 2557 (1932); (j) K. B. Wiberg, Abstracts of the 122nd National Meeting of the American Chemical Society, September 14–19, 1952, p. 38M.

[2] The stereochemistry is fixed by resolution.[1b,g]

[3] Determined by Mr. S. M. Nagy, Massachusetts Institute of Technology. The lactone III also possessed no C-methyl, whereas oxidations of citraconic anhydride and IV ($R = CH_3$) gave 0.82 and 0.7 equivalents of acetic acid.

[4] The reported[1a,e] reversion of lactone to unsaturated acid in alkali proved erroneous.

[5] Compare the reported[1b] oxidation of bromo lactone to a triacid $C_6H_5O_6Br$.

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 $\gamma$-methyl-$\gamma$-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.

[6] The stability of the Feist acid and esters in *acid*[1a,b,i] evidences against $\alpha,\beta$-unsaturation (contrast V[1i]).

[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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## 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 $\sigma$ 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 $\rho$) of the recorded equilibria and reaction rates,[5] we calculated $\sigma$ 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 | $\sigma$ |
|---|---|---|
| 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 $\sigma$-value for p-CH$_3$ depends upon the medium.*

Many data recorded in the literature since the publication of Hammett's list of $\sigma$-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 $\sigma$-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 $\sigma$-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$_9$.

[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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## THE $\pi$ 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 $\alpha$ 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

[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).