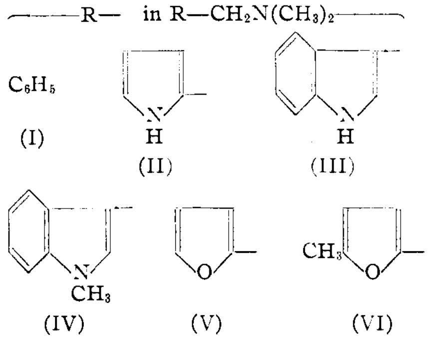
[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

Alkylations with Substituted Furfurylamines

BY ERNEST L. ELIEL AND PAUL E. PECKHAM[1]

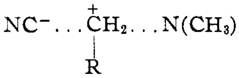
It has been known for some time that alkylations with tertiary amines of the type $RCH_2N(CH_3)_2$ and their quaternary salts proceed much more readily when R is 2-pyrryl[2] (II) or 3-indolyl[3] (III) than when R is phenyl[4] (I). The hypothesis that the enhanced reactivity of the heterocyclic amines is due to the operation of an elimination–addition mechanism[5] is inadequate, since 1-methylgramine (IV) which cannot react by such a mechanism also shows enhanced reactivity,[4b,5,6] which thus seems to be due to the presence of the hetero-atom. It was thought that a comparison of the reactivity of furfuryldimethylamine (V) with 1-methylgramine (IV) would throw some light on the exact nature of the alkylation mechanism.



This paper describes alkylations of sodium cyanide and piperidine with the methiodides of furfuryldimethylamine (V) and 5-methylfurfuryldimethylamine (VI) and some attempted alkylations with the hydrochlorides of these amines. It was found that the salts of the oxygen heterocycles V and VI are considerably less reactive than those of the nitrogen heterocycles II, III and IV. Their reactivity in the alkylations studied is no greater than that of salts of benzyldimethylamine (I).

The alkylation of sodium cyanide with the methiodide of furfuryldimethylamine (V) is of special interest since furfuryl chloride reacts with sodium cyanide to yield principally a rearrangement product, 2-methyl-5-cyanofuran[7] (VII) and only minor quantities of the expected 2-furylacetonitrile[7b] (VIII) while, on the other hand, the methiodide of 1-methylgramine (IV) yields small amounts of the rearranged 1,3-dimethyl-2-cyanoindole[6a] (IX) in addition to the normal 1-methylindole-3-acetonitrile[5] (X). Furfuryltrimethylammonium iodide was found to react with sodium cyanide at temperatures above 180° to give principally the normal nitrile (VIII) and only minor quantities of the rearranged product (VII). It seems, then, that the alkylation of sodium cyanide with this quaternary salt to form (VIII) does not proceed through a furfuryl carbonium ion intermediate to any great extent; for if a carbonium ion were the intermediate, *about* as much of the rearranged nitrile (VII) should result from the quaternary salt as does from the corresponding chloride.[8,8a]

The experimental data may be satisfactorily interpreted on the assumption that the reaction involves the transition state



$$NC^{-}\ldots\underset{\displaystyle R}{\overset{+}{C}H_2}\ldots N(CH_3)_3$$

which resembles the one involved in the bimolecular nucleophilic displacement (S_N2) reactions of alkyl halides. Distribution of the positive charge on the central carbon atom by resonance involving the radical R would be expected to stabilize this structure, thus lowering the activation energy in the alkylation reaction. This effect should be most marked in the nitrogen heterocycles where one of the canonical forms has the positive charge on the nitrogen atom.[6a] The small amounts of rearranged products may have been formed either by an S_N2' mechanism[8] or by cleavage of the carbon–amino nitrogen bond (S_N1) followed by rearrangement of the resulting carbonium ion *prior to* incipient formation of the new carbon–carbon bond.

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[2] (a) Herz, Dittmer and Cristol, THIS JOURNAL, **70**, 504 (1948); (b) Albertson, *ibid.*, **70**, 669 (1948).

[3] (a) Snyder, *et al.*, *ibid.*, **66**, 200 (1944); **66**, 350 (1944); **67**, 38 (1945); **69**, 3140 (1947); **70**, 3770 (1948); U. S. Patent 2,447,544 (1948), *C. A.*, **43**, 2643d (1949). (b) THIS JOURNAL, **71**, 663 (1949). (c) Albertson, *et al.*, *ibid.*, **66**, 500 (1944); **67**, 36 (1945); **67**, 502 (1945); **70**, 1150 (1948); U. S. Patent 2,451,310 (1948), *C. A.*, **43**, 1442d (1949). (d) Lyttle and Weisblat, THIS JOURNAL, **69**, 2118 (1947); **71**, 3079 (1949). (e) Salzer and Andersag, U. S. Patent 2,315,661 (1943), *C. A.*, **37**, 5418 (1943).

[4] (a) von Meyer and Schwabe, *Abhandl. mathem.-phys. Klasse sächs. Ges. Wisse.*, **31**, 179 (1908), *C. A.*, **5**, 887 (1911). (b) Snyder, *et al.*, THIS JOURNAL, **61**, 2895 (1939); **66**, 200 (1944); **71**, 291 (1949). (c) *ibid.*, **61**, 668 (1939). (d) Wittig, *et al.*, *Ann.*, **560**, 116 (1948). (e) von Braun, *et al.*, *Ber.*, **59**, 2330 (1926).

[5] Snyder and Eliel, THIS JOURNAL, **70**, 1703 (1948).

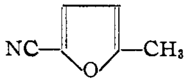
[6] (a) Snyder and Eliel, *ibid.*, **70**, 1857 (1948); (b) **70**, 3855 (1948); (c) **70**, 4233 (1948).

[7] (a) Runde, Scott and Johnson, *ibid.*, **52**, 1284 (1930); (b) Reichstein, *Ber.*, **63**, 749 (1930).

[8] This assumes that the chloride reacts through a carbonium ion intermediate. If the chloride reacts by an S_N2' mechanism [Kepner, Young and Winstein, THIS JOURNAL, **71**, 115 (1949)] a carbonium ion intermediate on the part of the quaternary salt presumably ought to yield *more* of the rearranged product than the chloride does, which again is contrary to the observed fact.

[8a] This interpretation and the following conclusion were criticized by one of the referees who believes that both the chloride and the quaternary amine salt may react *via* the carbonium ion, the difference in the products being due to the difference in the reaction conditions.

In the course of this investigation, improved syntheses of 5-methylfurfuryldimethylamine and N-(5-methyl)-furfurylpiperidine have been developed by the use of amine acetates instead of amine hydrochlorides in the Mannich reaction leading to these compounds.[9] Unlike 2-methylfuran, furan was found not to yield a Mannich base when heated with formaldehyde and dimethylamine in aqueous acetic acid, but furfuryldimethylamine under the same conditions yielded a small amount of 2,5-bis-dimethylaminomethylfuran (XI). A synthesis of furfurylmethylaniline is described in the experimental part.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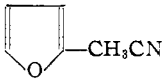
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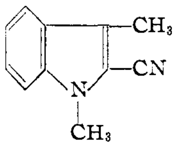
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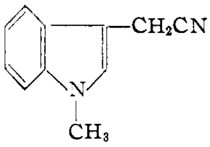
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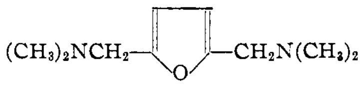
(XI)

Experimental[10]

Furfuryldimethylamine (V).—Dimethylformamide was obtained from 85% aqueous formic acid and 40% aqueous dimethylamine[11] and was converted into furfuryldimethylamine by interaction with furfural.[12]

The product was collected at 140-142° (lit.[11] 140-145°, lit.[12] 142-145°). The methiodide, prepared by adding a slight excess of methyl iodide to a *ca.* 20% solution of the amine in absolute alcohol, melted at 117-118° (lit.[12] 116-117°, lit.[13] 118-120°).

5-Methylfurfuryldimethylamine (VI).—To 180 ml. of glacial acetic acid, cooled in an ice-bath, was slowly added 128.5 g. (1 mole) of 35% aqueous dimethylamine, followed by 61.0 g. (0.75 mole) of 37% aqueous formaldehyde and 41.0 g. (0.5 mole) of 2-methylfuran. The mixture was heated on a steam-bath in a flask equipped with a reflux condenser for four hours and left at room temperature for an additional twenty-four hours. It was then poured into a cold solution of 250 g. of sodium hydroxide in 800 ml. of water. After the heat of neutralization had been dissipated, the mixture was extracted three times with ether. The combined ether extracts were dried over solid potassium hydroxide and the solution fractionated. A small amount (1.5 g.) of unreacted 2-methylfuran was recovered after the ether had distilled. The product (VI) was collected at 161-164° and weighed 60.0 g. (86% as compared with the 65% yield previously[9] reported). The picrate crystallized in slender yellow prisms from ethanol and melted at 116-116.5°.

Anal. Calcd. for $C_{14}H_{16}N_4O_8$: C, 45.64; H, 4.38. Found: C, 45.70; H, 4.54.

5-Methylfurfuryltrimethylammonium Iodide.—To an ice-cold solution of 116.5 g. (0.84 mole) of 5-methylfurfuryldimethylamine (VI) in 450 ml. of absolute alcohol 140,0 g. (0.99 mole) of methyl iodide was added portionwise with good swirling. The methiodide crystallized from the solution and was collected after thorough chilling. The crystals were washed with three portions of absolute ether and weighed 220.5 g. when dry. An additional 9.0 g. were obtained by combining the ether wash with the alcoholic filtrate. The total yield of material melting at 161-162° (dec.) was 229.5 g. (97%). Two recrystallizations from absolute ethanol did not affect the melting point.

Anal. Calcd. for $C_9H_{16}INO$: C, 38.45; H, 5.74. Found: C, 38.41; H, 5.67.

N-(5-Methyl)-furfurylpiperidine.—This compound was prepared in a manner similar to that described above for VI from 30 ml. of glacial acetic acid, 8.5 g. (0.1 mole) of piperidine, 12.2 g. (0.15 mole) of 37% aqueous formaldehyde and 9.0 g. (0.11 mole) of 2-methylfuran. The product was collected at 102-103° (10 mm.) and weighed 16.4 g. (92%). Its hydrochloride melted at 147.5-148.5° (lit.[9] 147-148°). It is essential to avoid an excess of piperidine in this reaction, since otherwise methylene-bis-piperidine is formed as a by-product which is hard to eliminate since its boiling point is close to that of 5-methylfurfurylpiperidine.

2,5-Bis-dimethylaminomethylfuran (XI).—When the above described variation of the Mannich reaction was applied to 12.5 g. (0.1 mole) of furfuryldimethylamine (V), 30 ml. of glacial acetic acid, 12.2 g. (0.15 mole) of 37% aqueous formaldehyde and 25.7 g. (0.2 mole) of 35% aqueous dimethylamine, 7.0 g. of furfuryldimethylamine boiling at 140-146° was recovered. Fractionation of the distillation residue *in vacuo* yielded 0.7 g. of a liquid boiling at 107-109° (10 mm.), n^{20}_D 1.4728. The picrate melted at 202-205° (dec.) after two recrystallizations from acetone-alcohol and gave the correct analysis for a dipicrate of XI.

Anal. Calcd. for $C_{22}H_{24}N_8O_{15}$: C, 41.25; H, 3.78; N, 17.50. Found: C, 41.05; H, 3.86; N, 17.74.

Application of the Mannich reaction as described above to furan yielded no liquid amine.

Furfurylaniline.—To an ice-cold solution of 19.2 g. (0.2 mole) of furfural in 175 ml. of 95% ethanol, 18.6 g. (0.2 mole) of redistilled aniline was added portionwise with cooling. The resulting red solution of furfuralaniline was placed in a hydrogenation bottle and *ca.* 10 g. of Raney nickel was added. Hydrogenation was effected at an initial pressure of 60 lb., the theoretical amount of hydrogen being absorbed in about one hour The colorless reduced solution was fractionated *in vacuo*, furfurylaniline being collected at 146-147° (10 mm.) (lit.[14] 147-148° (10 mm.)). The yield was 29.1 g. (84%).

N-Methyl-N-furfurylaniline.—Sodamide was prepared[15] from 12.5 g. (0.55 mole) of sodium in *ca.* 450 ml. of liquid ammonia, and the ammonia was replaced by 400 ml. of ether in the usual way. To the well-stirred ethereal suspension of sodamide, a solution of 86.5 g. (0.5 mole) of furfurylaniline in an equal volume of dry ether was added dropwise from a separatory funnel; soon after the addition of this solution had been initiated, a solution of 90.0 g. (0.63 mole) of methyl iodide in an equal volume of ether was simultaneously added in a similar fashion and at about the same rate as the amine solution. A white precipitate of sodium iodide formed and the ether refluxed gently without the application of external heat as the reaction proceeded. Addition of the reagents was complete in about one hour; the suspension was then refluxed for another thirty minutes and finally the excess sodamide was destroyed by the addition of 95% ethanol followed by ice. Four hundred milliliters of water was added, the top layer was separated and the aqueous layer was extracted once with ether. The combined organic layer and ether extract were dried over potassium hydroxide and the ether was distilled. Fractionation of the residue *in vacuo*

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[9] Holdren and Hixon, THIS JOURNAL, **68**, 1198 (1946).

[10] All melting and boiling points are uncorrected. Microanalyses by Micro-Tech Laboratories, Skokie, Ill.

[11] Nabenhauer, U. S. Patent 2,185,220 (1940); *C. A.*, **34**, 3023 (1940).

[12] Weilmuenster and Jordan, THIS JOURNAL, **67**, 415 (1945).

[13] Beilstein, 4th ed., Vol. XVIII, p. 585.

[14] Umnova, *J. Gen. Chem.* (*U. S. S. R.*), **10**, 569 (1940); *Chem. Zentr.*, **111**, II, 2014 (1940).

[15] Vaughn, Vogt and Nieuwland, THIS JOURNAL, **56**, 2120 (1934).

yielded 77.2-81.0 g. (83-87%) of N-methyl-N-furfurylaniline collected at 142-145° (10 mm.), $n^{20}D$ 1.5760.

Anal. Calcd. for $C_{12}H_{13}NO$: C, 76.97; H, 7.00; N, 7.48. Found: C, 77.21; H, 7.17; N, 7.85.

The methiodide was desired for studying its reaction with aqueous sodium cyanide. When the amine was refluxed with an excess of methyl iodide in acetone, a white solid separated in rather poor yield (about 10%). It was thought to be the desired methiodide, but resisted purification as evidenced by the fact that even after repeated recrystallizations from absolute alcohol its analytical data were unsatisfactory.

Anal. Calcd. for $C_{13}H_{16}INO$: C, 47.42; H, 4.89. Found: C, 45.47; H, 5.61.

Amine Exchange Reactions. N-Furfurylpiperidine.—A mixture of 13.35 g. (0.05 mole) of furfuryltrimethylammonium iodide and 50 ml. of piperidine was boiled under reflux for three hours. The mixture became homogeneous and trimethylamine was evolved. The solution was cooled (crystals, presumably piperidine hydriodide, separated at this point) and poured into a solution of 5 g. of sodium hydroxide in 800 ml. of water. The resulting emulsion was extracted with three portions of ether and the combined ether extracts were washed with three portions of water. The ether solution was then dried over potassium hydroxide and distilled. The residue was fractionated *in vacuo*, N-furfurylpiperidine being collected as a colorless liquid at 93-94° (11 mm.). The yield was 4.0 g. (48%).

The picrate was crystallized from 95% ethanol and melted at 107-108°.

Anal. Calcd. for $C_{16}H_{18}N_4O_8$: N, 14.21. Found: N, 14.10.

The methiodide was crystallized from absolute ethanol and melted at 172.5-173.5°.

Anal. Calcd. for $C_{11}H_{18}INO$: C, 43.01; H, 5.91. Found: C, 43.01; H, 6.04.

Amine Exchange Reactions. N-(5-Methyl)-furfurylpiperidine.—A mixture of 14.05 g. (0.05 mole) of 5-methylfurfuryltrimethylammonium iodide and 50 ml. of piperidine was boiled under reflux for six hours. The crystals which separated on cooling were collected and rinsed with ether and the rinsings were combined with the remainder of the filtrate, which was then dried over solid potassium hydroxide. The solid material was dissolved in a solution of 12 g. of sodium hydroxide in 100 ml. of water and the organic bases extracted with ether. This ether extract was also dried over potassium hydroxide and the combined ether solutions were then fractionated, first at atmospheric pressure and then *in vacuo*. N-(5-Methyl-2-furfuryl)-piperidine was collected at 105-107° (11 mm.), it weighed 6.2 g. (69%). The hydrochloride melted at 147.5-148.5° and did not depress the melting point of an authentic specimen (see above). von Braun[16] obtained dibenzylamine from benzyltrimethylammonium bromide and benzylamine under similar conditions.

Attempted Alkylation Reactions with Amine Hydrochlorides.—When 13.0 g. of 5-methylfurfuryldimethylamine hydrochloride (prepared by mixing an ether solution of the amine with a solution of hydrogen chloride in isopropyl ether, m. p., after crystallization, 160.5-161°—lit.[9] 158-158.5°), 35 g. of piperidine and 200 ml. of *n*-hexanol were refluxed for twenty-four hours, fractionation of the basic reaction products led to an 85% recovery of 5-methylfurfuryldimethylamine (VI), identified by its hydrochloride, m. p. and mixed m. p. 159-160.5°. No basic material boiling above 60° at 10 mm. was obtained.

Furfuryldimethylamine hydrochloride (a very hygroscopic solid) similarly yielded only furfuryldimethylamine (V) identified by its methiodide which melted at 117-118°; no N-furfurylpiperidine was obtained.

It is known that the hydrochloride of 1-methylgramine (IV) under similar conditions yields 3-piperidinomethyl-1-methylindole.[6a]

When 5-methylfurfuryldimethylamine hydrochloride was boiled under reflux with piperidine in 2-ethylhexanol as a solvent, an amine boiling at 91-92° (13 mm.) or 208-209° (743 mm.) having $n^{25}D$ 1.5010 was obtained.[16] The hydrochloride of this amine was oily; its picrate formed yellow crystals from ethanol which melted at 148-149° (dec.) and whose analysis suggests that it is an isomer of 5-methylfurfuryldimethylamine picrate.

Anal. Calcd. for $C_{14}H_{16}N_4O_8$: C, 45.64; H, 4.38; N, 15.22. Found: C, 46.00; H, 4.45; N, 14.88.

The mixed melting point with 5-methylfurfuryldimethylamine picrate was 94-120°. Since 17.8 g. of the hydrochloride of VI yielded 8.5 g. of this amine (whose structure is under study) the yield is 60%, if the product is isomeric with VI.

Reaction of Furfuryltrimethylammonium Iodide and Sodium Cyanide.—Furfuryltrimethylammonium iodide (26.7 g., 0.1 mole) and sodium cyanide (30.0 g., 0.6 mole) were ground together in a mortar and the mixture was then heated in a 500-ml. distilling flask equipped with a condenser and receiver at a temperature of 180-200° and a pressure of 100 mm. An oily distillate (7.2 g.) was collected and submitted to fractionation at 18 mm. pressure. Three fractions resulted. The first one, collected at 46-47° was basic, had $n^{25}D$ 1.4609 and was identified as furfuryldimethylamine (V) by its methiodide, melting point and mixed melting point 117-118°. It weighed 1.2 g. (10%). The second fraction was collected at 54-55° and had[17] $n^{25}D$ 1.4732. It was identified as 5-cyano-2-methylfuran (VII) by hydrolysis[18] to the corresponding acid which melted at 108.5-109.5° and did not depress the melting point of an authentic specimen.[18,7] This fraction weighed 0.5 g. (5%). A third fraction was collected at 82-84°; it had[17] $n^{25}D$ 1.4700 and weighed 2.9 g. (27%). Saponification[7a] yielded furylacetic acid, melting point and mixed melting point[19] 67.5-68°, thus the third fraction was furfuryl cyanide (VIII).

The conditions of the above reaction were varied in several ways: (1) The pyrolysis was conducted at a pressure of 10 mm. (2) The starting materials were employed in the form of an aqueous paste and the reaction products were swept out by superheated steam at about 210°. (3) The reaction was performed in aqueous triethylene glycol as a solvent. These changes slightly affected the over-all yield of products but did not materially change the ratio in yield of the isomeric nitriles VII and VIII.

In the case of the reaction in aqueous triethylene glycol, an appreciable amount of the furylacetonitrile (VIII) was hydrolyzed to the corresponding acid during the reaction and recovered as such.

Reaction of 5-Methylfurfuryltrimethylammonium Iodide and Sodium Cyanide.—A paste of 28.1 g. (0.1 mole) of 5-methyl-2-furfuryltrimethylammonium iodide and 30.0 g. (0.6 mole) of sodium cyanide with a small amount of water was heated to 200° and steam superheated to 225° was passed over it. The distillate was collected as long as it appeared turbid. It was then extracted four times with ether and the combined ether extracts were dried over sodium sulfate and distilled. Fractionation of the residue *in vacuo* yielded 4.5 g. (37%) of 5-methyl-2-furylacetonitrile collected at 82-85° (12 mm.). This nitrile was identified by hydrolysis to the corresponding acid[20] which melted at 60.5-61.5° (lit.[20] 57-58°, lit.[21] 61-62°).

Attempts to effect the reaction of furfuryltrimethylammonium iodide or 5-methylfurfuryltrimethylammonium iodide with sodium cyanide in refluxing aqueous solution yielded only traces of the expected nitriles. It is known that quaternary salts of benzylamine will alkylate cyanides

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(16) 5-Methylfurfuryldimethylamine has $n^{25}D$ 1.4620 (ref. 9).

(17) The authentic data are $n^{20}D$ 1.4833 for 2-methyl-5-cyanofuran (ref. 18) and $n^{25}D$ 1.4715 for furfuryl cyanide (ref. 7a), thus the rearranged product obtained in this investigation in such small amounts was apparently quite impure.

(18) Kirner and Richter, THIS JOURNAL, **51**, 3131 (1929).

(19) The authors are indebted to Mr. Frank X. Werber, Department of Chemistry, University of Illinois, for an authentic specimen of 2-furylacetic acid.

(20) Scott and Johnson, THIS JOURNAL, **54**, 2549 (1932).

(21) Reichstein and Zschokke, *Helv. Chim. Acta*, **15**, 249 (1932).

under pyrolytic conditions[4a] but not in refluxing aqueous solution[4c] while 1-methylgramine methiodide reacts rapidly with aqueous sodium cyanide at the reflux temperature to yield a mixture of the isomeric nitriles IX and X.[5,6a]

Acknowledgment.—The authors are indebted to the Electrochemicals Department of the du Pont Company for gratuitous supplies of furan and 2-methylfuran.

Summary

1. An improved method is described for the synthesis of Mannich bases derived from 2-methylfuran.

2. Furfuryltrimethylammonium iodide and the corresponding 5-methyl compound have been found to undergo amine exchange with piperidine, but the hydrochlorides of furfuryldimethylamine and the corresponding 5-methyl compound do not react with piperidine in refluxing *n*-hexanol differing in this respect from analogous indole compounds.

3. Furfuryltrimethylammonium iodide and the corresponding 5-methyl compound react with sodium cyanide to yield nitriles only at temperatures above 180° thus distinguishing themselves again from the indole Mannich bases. Furfuryltrimethylammonium iodide unlike furfuryl chloride with sodium cyanide yields mainly furfuryl cyanide and only traces of 2-methyl-5-cyanofuran.

4. The synthesis of N-furfurylaniline has been improved and N-methyl-N-furfurylaniline has been synthesized.

NOTRE DAME, INDIANA RECEIVED AUGUST 18, 1949

[CONTRIBUTION OF THE RESEARCH AND DEVELOPMENT BRANCH, OFFICE OF SYNTHETIC LIQUID FUELS, BUREAU OF MINES]

Composition of Synthetic Liquid Fuels. I. Product Distribution and Analysis of C_5–C_8 Paraffin Isomers from Cobalt Catalyst[1]

BY R. A. FRIEDEL[2] AND R. B. ANDERSON[2]

The composition of synthetic liquid fuels, such as are obtained in the Fischer–Tropsch process, are of interest both in studying reaction mechanism and in determining applicability as fuels. Little quantitative work on these products has been reported; general product-distribution studies have been reviewed by Storch.[3] The first comprehensive information on the isomeric composition of Fischer–Tropsch hydrocarbons was published by von Weber.[4] By determining boiling points and molecular weights of fractions, von Weber estimated that the mole fractions of branched hydrocarbons were 0.15, 0.27 and 0.40 for the C_6, C_8 and C_{10} ranges, respectively. Later, Koch and Hilberath[5] determined isobutane content and showed qualitatively the presence of the various monomethyl paraffin isomers in the C_5–C_7 range. Traces of more highly-branched paraffins were reported, but none involving a quaternary carbon atom were claimed to exist. The present paper deals principally with the product distribution from C_1 to C_{20} and with the quantitative analysis of paraffin isomers in the C_5–C_8 range.

Product Distribution, C_1 to C_{20}

The distribution of hydrocarbon products from tests of precipitated cobalt catalysts in small reactors with 2 hydrogen to 1 carbon monoxide gas at atmospheric pressure, space velocity of 100 and about 190°, was obtained by fractional distillation of the liquids and mass spectrometer analysis of the gases. The liquid products were fractionated in a 6-foot, 25 mm. diameter, Podbielniak column, at atmospheric pressure up to C_{13} and at 40-mm. pressure from C_{13} to C_{20}. Plate values for the atmospheric distillation varied between about 50–80 theoretical plates. Fractionations were carried out on both the original sample and on a hydrogenated portion. The molecular weight distributions obtained from the boiling point curves were identical for the two distillations. Estimated accuracies for the distribution vary from 5% at C_6 to 25% at C_{20}. Qualitative tests by ferrox paper, 2,4-dinitrophenylhydrazone, and spectrometric methods showed the presence of oxygenated compounds in various fractions. For the over-all distribution to C_{20} no further separation or analysis was undertaken.

The distribution according to carbon number fraction is given in Fig. 1a. The yield of methane was large followed by a minimum at C_2, a broad maximum from C_5 to C_{11}, and a gradual decrease to C_{20}. Ten per cent. of the products was above C_{20}, the average molecular weight of this residue being 309. This distribution is similar to that reported by Craxford[6] for C_1 to C_{13}, but differs considerably from those reported by Underwood[7] for C_1 to C_{32} and by Herington[8] for C_5 to C_{11} in which the weight fraction decreased continually with increasing carbon number above C_5.[9]

Herington[8] considered the formation of hydro-

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(1) Not subject to copyright.

(2) Research and Development Branch, Office of Synthetic Liquid Fuels, Bureau of Mines, Bruceton, Pennsylvania.

(3) H. H. Storch, *Chem. Eng. Progress*, **44**, 469 (1948).

(4) U. von Weber, *Angew. Chem.*, **52**, 607 (1939).

(5) H. Koch and F. Hilberath, *Brennstoff-Chem.*, **22**, 135, 145 (1941); **23**, 67 (1942).

(6) S. R. Craxford, *Fuel*, **26**, 119 (1947).

(7) A. J. V. Underwood, *Ind. Eng. Chem.*, **32**, 449 (1940).

(8) E. F. G. Herington, *Chem. and Ind.*, **65**, 347 (1946).

(9) C. W. Montgomery and E. B. Weinberger, *J. Chem. Phys.*, **16**, 424 (1948), calculated the distribution curve of paraffin hydrocarbons in terms of temperature, methane to ethane ratio and carbon to hydrogen ratio assuming thermodynamic equilibrium, and were able to satisfactorily approximate the distribution data of Underwood.