ethanol was refluxed 5 minutes with 9.2 g. of 1:1 aqueous potassium hydroxide solution. After diluting with an equal volume of water the *p*H was adjusted to 2.0 with hydrochloric acid and the solution extracted five times with ether. The ether solution was dried and the ether removed by distillation. The residue was distilled at atmospheric pressure. A small fraction (*ca.* 1 ml.) was collected at 140°, n^{25}_D 1.5000.

Reaction of 2-Methylfuran with Ammonia.—Ammonia gas was bubbled through 2-methylfuran (du Pont) and the vapor passed through a 22 × 600 mm. Pyrex tube packed with 4–8 mesh alumina. The tube was heated to 420–430° in a resistance combustion furnace. The exit vapors were condensed in a water-cooled spiral condenser and formed two layers. The lower water layer was extracted with ether and the extract was combined with the upper layer. After drying the ether solution, the ether was removed by distillation and the green residue was distilled under reduced pressure. The infrared spectrum of the distillate which was collected below 60° (30 mm.) showed the presence of pyrrole and 3-methylpyrrole in addition to 2-methylpyrrole.

Reaction of 2,5-Dimethoxytetrahydro-2-methylfuran with Ammonia.—Ammonia was bubbled through boiling 2,5-dimethoxytetrahydro-2-methylfuran (obtained from Dr. N. Elming) and the vapors passed through a 14 × 300 mm. Pyrex tube heated to 250°. The exit vapors were condensed in a trap cooled in Dry Ice. After allowing the ammonia to evaporate, the residue was vacuum distilled. The infrared spectrum of the material collected at 80–82° (72 mm.) showed it to be pure 2-methylpyrrole.

[Contribution from the Department of Chemistry, The Pennsylvania State University, University Park, Penna.]

The Stereochemistry of the Alkylation of Pyrrylmagnesium Bromide

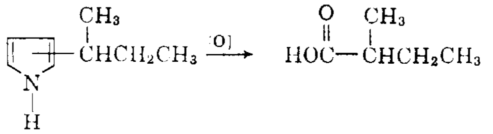
By P. S. Skell and G. P. Bean

Received July 16, 1962

Alkylation of pyrrylmagnesium bromide with (−)-2-bromobutane gave optically active 2- and 3-*sec*-butylpyrroles. Oxidation of the pyrroles to (+)-2-methylbutyric acid indicated that the alkylation at both the 2- and 3-positions had proceeded with complete inversion of configuration.

In the previous paper[1] it was shown that the alkylation of pyrrylmagnesium halides in every case produced both the 2- and 3-alkylpyrroles in addition to pyrrole and polyalkylpyrroles. Also the nature of the alkyl halide appeared to have little effect on the position of substitution, as the ratio of 2- to 3-substitution changed only by a factor of 2 within the range of halides studied.

Since information about the steric course of the alkylation of pyrrylmagnesium halides is essential for understanding the mechanism of this substitution reaction, the alkylation with optically active 2-bromobutane was studied. No optically active alkylpyrroles have been reported; therefore the alkylation of pyrrylmagnesium bromide with an optically active halide would only indicate whether or not complete racemization had occurred unless the configuration and optical purity of alkylpyrroles can be related to a compound of known configuration and optical purity. Fortunately, the oxidation of alkylpyrroles with cold sodium permanganate produces the corresponding carboxylic acids. Therefore in the sequence PyMgBr + R*X → R*Py → R*COOH the configuration of the asymmetric carbon atom is affected only in the alkylation step.

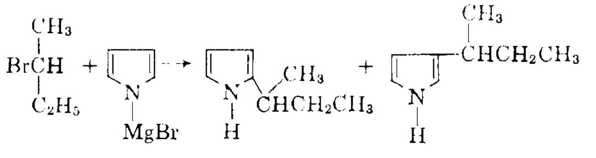


The alkylation of pyrrylmagnesium bromide with (−)-2-bromobutane gave optically active 2- and 3-*sec*-butylpyrrole. These isomeric pyrroles were separated and oxidized to the (+)-2-methylbutyric acid (see Chart I). Since the optical purity of the two acids were identical, it follows that the steric course in both the 2- and 3-positions must be identical.

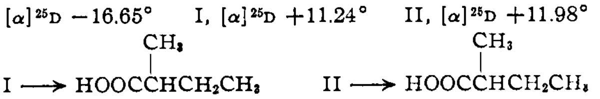
The relation of the configuration of the alkyl halide and the acid has been determined by Kenyon, Phillips and co-workers[2] (Chart II). Displacement of the tosyl group of the tosyl ester of (+)-2-butanol by cyanide ion and subsequent hydrolysis gave (−)-2-methylbutyric acid, which is a reaction which proceeds with inversion of configuration. Since 2-bromobutane and 2-butanol of the same configuration have the same sign of rotation,[3] it follows that in the alkylation of pyrrylmagnesium bromide with (−)-2-bromobutane the configuration of the asymmetric carbon must have been inverted.

Chart I

Alkylation of Pyrrylmagnesium Bromide with (−)-2-Bromobutane



$[\alpha]^{25}_D$ −16.65° I, $[\alpha]^{25}_D$ +11.24° II, $[\alpha]^{25}_D$ +11.98°

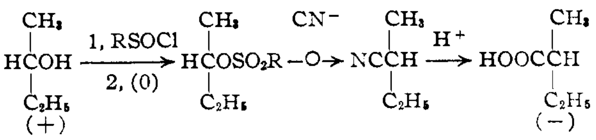


$$\text{I} \longrightarrow \text{HOOC}\overset{\text{CH}_3}{\text{C}}\text{HCH}_2\text{CH}_3 \qquad \text{II} \longrightarrow \text{HOOC}\overset{\text{CH}_3}{\text{C}}\text{HCH}_2\text{CH}_3$$

$[\alpha]^{25}_D$ +8.83° $[\alpha]^{25}_D$ +8.80°

Chart II

Stereochemical Relationship of 2-Butanol and 2-Methylbutyric Acid



$$\underset{(+)}{\mathrm{H\overset{CH_3}{C}OH}}\atop{\scriptstyle C_2H_5} \xrightarrow[2,\ (0)]{1,\ \mathrm{RSOCl}} \mathrm{H\overset{CH_3}{\underset{C_2H_5}{C}}OSO_2R} \xrightarrow{\mathrm{CN^-}} \mathrm{NC\overset{CH_3}{\underset{C_2H_5}{C}}H} \xrightarrow{\mathrm{H^+}} \underset{(-)}{\mathrm{HOOC\overset{CH_3}{\underset{C_2H_5}{C}}H}}$$

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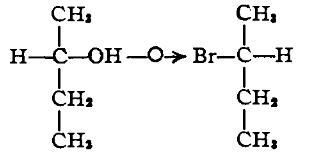
[1] P. S. Skell and G. P. Bean, *J. Am. Chem. Soc.*, **84**, 4655 (1962).

[2] A. J. Houssa, J. Kenyon and H. Phillips, *J. Chem. Soc.*, 1700 (1929); J. Kenyon, H. Phillips and V. P. Pittman, *ibid.*, 1072 (1935).

[3] W. A. Cowdrey, E. D. Hughes, C. K. Ingold, S. Masterman and A. D. Scott, *ibid.*, 1252 (1937)

It is, however, more difficult to calculate the amount of racemization that occurred during the alkylation step. Such a value must depend upon the correctness of the values assumed for the rotation of the optically pure compounds. For the over-all reaction using the highest value reported for the rotation of 2-butanol ($[\alpha]^{25}D$ 13.63°)[4] and 2-methylbutyric acid ($[\alpha]^{25}D$ 20.5°)[5] there appears to have been a 55.3% retention of activity. In this sequence, only in the preparation of the alkyl halide and the subsequent reaction with pyrrylmagnesium bromide was the asymmetric center involved. Skell, Allen and Helmkamp[6] have demonstrated the following relationship between optically pure 2-butanol and 2-bromobutane by inversion of configuration at the optically active center



$$H-\overset{CH_3}{\underset{\underset{CH_3}{CH_2}}{C}}-OH \longrightarrow Br-\overset{CH_3}{\underset{\underset{CH_3}{CH_2}}{C}}-H$$

$[\alpha]^{25}D$ −13.65° $[\alpha]^{25}D$ + 39.4°

Thus, the starting 2-bromobutane was 16.65/39.4 or 42.3% resolved and the recovered 2-methylbutyric acid was 8.81/20.5 or 43.0% resolved. Since these calculations are based on specific rotation values from three different laboratories and complex experimental relationships, the apparent 0.7% discrepancy is not significant. *Thus the alkylation at both the 2- and 3-positions occurs with complete inversion of configuration.*

A general method for determining the optical purity of alkyl halides with the halogen at the asymmetric center may be the conversion to alkylpyrroles and oxidation to the corresponding carboxylic acid, as indicated above. This method should prove particularly valuable with secondary, tertiary and benzyl-type halides.

Experimental

(+)-2-Butanol.—2-Butanol was resolved through the brucine salt of the half-ester of phthalic acid by the method of Hauser and Kantor.[7] The (+)-2-butanol prepared had $[\alpha]^{25}D$ + 10.6°.

(−)-2-Bromobutane.—Hydrogen bromide was bubbled through 31.05 g. of (+)-2-butanol, $[\alpha]^{25}D$ + 10.6°, cooled in an ice-bath until the theoretical weight had been taken up. The product was sealed in several tubes and heated to 110° for 3 hours. After the tubes were cooled in ice, they were opened and the product separated from the heavy acid layer. The upper layer was extracted with a concentrated solution of calcium chloride to remove unreacted alcohol and then dried over calcium chloride. The bromide was distilled to give a yield of 42.7 g. (73%), $[\alpha]^{25}D$ −16.65°.

Reaction of (−)-2-Bromobutane with Pyrrylmagnesium Bromide.—To 0.5 mole of pyrrylmagnesium bromide, prepared from 33.5 g. of pyrrole and methylmagnesium bromide, was added 41,4 g. of (−)-2-bromobutane, $[\alpha]^{25}D$ −16.65°, and 19.6 g. of (±)-2-bromobutane. After refluxing for 33 hours, the reaction was hydrolyzed with dilute phosphoric acid and worked up as usual. The product was distilled under reduced pressure and the distillate carefully fractionated through a Podbielniak Mini-Cal column to give 6.15 g. of pyrrole, b.p. 49° (36 mm.), $n^{25}D$ 1.5070; 16.95 g. of 2-*sec*-butylpyrrole, b.p. 96° (36 mm.), $n^{25}D$ 1.4900, $[\alpha]^{25}D$ +7.63°; and 7.20 g. of 3-*sec*-butylpyrrole, b.p. 100° (36 mm.), $n^{25}D$ 1.4878, $[\alpha]^{25}D$ + 8.13°.

Oxidation of (+)-2-*sec*-Butylpyrrole to 2-Methylbutyric Acid.—(+)-2-*sec*-butylpyrrole (5.10 g.) was slowly added with stirring to a cold solution of 51 g. of sodium permanganate in 500 ml. of water. The temperature was kept below 10° by cooling the reaction in ice. After all of the pyrrole had been added, the reaction was stirred an additional hour and, while still in an ice-bath, sulfur dioxide was bubbled through the solution to destroy the manganese dioxide. The solution was acidified and extracted ten times with ether to remove the organic acid. The combined ether extracts were dried over sodium sulfate and then over Drierite. The ether was removed by distillation through a short glass-helices packed column, and the residue (about 3 ml.) distilled. The fraction boiling between 160 and 180° was collected, $n^{25}D$ 1.4020. The specific rotation of the 2-methylbutyric acid was $[\alpha]^{25}D$ +5.99°.

Oxidation of (+)-3-*sec*-Butylpyrrole to 2-Methylbutyric Acid.—The (+)-3-*sec*-butylpyrrole (5.10 g.) was oxidized as above. The product had a specific rotation of $[\alpha]^{25}D$ + 5.97°.

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[4] R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, **99**, 45 (1911); **103**, 1923 (1913); see P. J. Leroux and H. J. Lucas, *J. Am. Chem. Soc.*, **73**, 41 (1951).

[5] K. B. Wiberg and T. Hutton, *ibid.*, **78**, 1640 (1956); see footnote 6.

[6] P. S. Skell, R. G. Allen and G. K. Helmkamp, *ibid.*, **82**, 410 (1960).

[7] C. R. Hauser and S. W. Kantor, *J Chem. Soc.*, **75**, 1744 (1953).

[CONTRIBUTION FROM THE DIVISION OF PURE CHEMISTRY, NATIONAL RESEARCH COUNCIL, OTTAWA, CANADA. ISSUED AS NRC No. 7050]

Free Radicals by Mass Spectrometry. XXVIII. The HS, CH_3S, and Phenyl-S Radicals: Ionization Potentials and Heats of Formation

BY T. F. PALMER[1] AND F. P. LOSSING

RECEIVED MAY 12, 1962

The vertical ionization potentials of the HS, CH_3S and phenyl-S radicals have been measured by electron impact to be 10.50 ± 0.1, 8.06 ± 0.1 and 8.63 ± 0.1 volt, respectively. From appearance potentials of the radical ions from derivatives, these estimates for the heats of formation of the radicals and ions (in kcal./mole) were obtained: $\Delta H_f(HS^+) \leq 276$, $\Delta H_f(HS) \leq 33.7$, $\Delta H_f(CH_3S^+) \leq 218$, $\Delta H_f(CH_3S) \leq 31.8$. A calculation of $I(CH_3S)$ from the appearance potentials of CH_3S^+ ion from CH_3SCH_3 and CH_3SSCH_3 is in good agreement with the directly measured value. No heats of formation for C_6H_5S ion or radical were obtained.

Introduction

The HS radical has been investigated by a number of workers using spectroscopic methods. It has been observed in absorption in a radio frequency discharge through H_2S[2] and in emission in Schüler-type discharges containing H_2S.[3,4] It has also been observed in emission in flames

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[1] National Research Council of Canada Postdoctorate Fellow 1960–1962.

[2] M. N. Lewis and J. U. White, *Phys. Rev.*, **55**, 894 (1939).

[3] S. Leach, *Compt. rend.*, **230**, 2181 (1950).

[4] S. Leach, *Discussions Faraday Soc.*, **9**, 81 (1950).