done in 25 ml of ice-cold dry methanol was poured into 69 ml of 0.29 *N* ethereal diazomethane[17] (20.0 mmoles) (precooled to 0°). The system was protected from light and maintained at 0° for 45 min. Unreacted diazomethane was then destroyed with a few drops of glacial acetic acid. The product was extracted with 15% aqueous sodium hydroxide and then with water. The aqueous layers were combined, saturated with sodium chloride, and extracted exhaustively with methylene chloride. The organic extracts were combined, dried over annydrous magnesium sulfate, and concentrated to a final volume of *ca.* 25 ml by distillation at atmospheric pressure through a 2-ft tantalum-packed column. (Vacuum evaporation of solvents results in some loss of 2-methoxypyridine.) Vpc analysis[11] showed 0.53 g (4.86 mmoles) of 2-methoxypyridine and 0.73 g (6.70 mmoles) of N-methyl-α-pyridone.

The aqueous extract was acidified with sulfuric acid and exhaustively extracted with chloroform. The dried extract was concentrated by rotary evaporation under reduced pressure; this gave 0.70 g (7.37 mmoles) of pale yellow crystals of α-pyridone, mp 104–106°. The infrared spectrum in chloroform is identical with that of authentic α-pyridone. (In a number of instances comparison was also made with the mercuric chloride adduct of α-pyridone, mp 196.5–197.5° when recrystallized from toluene.)

The amount of unreacted α-pyridone corresponds to a 37% recovery. Thus, the maximum number of millimoles of alkylated products is 0.63(20.0) or 12.6. The per cent yield of 2-methoxypyridine is 4.86/12.6 or 39%. The per cent yield of N-methyl-α-pyridone is 6.70/12.6 or 53%. The material balance is (4.86 + 6.70 + 7.37)/20.0 or 95%.

Stability of 2-Methoxypyridine and N-Methyl-α-pyridone to Diazomethane in Methanol–Diethyl Ether.—A methanolic solution of 2-methoxypyridine and an equivalent amount of ethereal diazomethane were allowed to stand together at 0° for 48 hr. Analysis by vpc showed 95% recovery of 2-methoxypyridine after appropriate work-up. No dialkylation was detected with sodium tetraphenylboron[18] and no N-methyl-α-pyridone was found. N-methyl-α-pyridone could have been detected to the extent of 2% by the vpc analysis. In the same way, equivalent amounts of methanolic N-methyl-α-pyridone and ethereal diazomethane were allowed to stand together for 48 hr at 0°. Vpc analysis, after work-up, showed 98% recovery of N-methyl-α-pyridone. No dialkylation[18] could be detected, and vpc could detect no 2-methoxypyridine; if present, it could have been detected to the extent of 0.4%.

Reaction of α-Pyridone with Diazomethane in Ethanol–Ethyl Ether.—A 100-ml aliquot of 0.20 *N* ethereal diazomethane (20.0 mmoles) was diluted with ether to a final volume of 167 ml. A solution containing 1.90 g (20.0 mmoles) of α-pyridone dissolved in 94 ml of absolute ethanol was cooled to 0° and poured into the cold (0°) ethereal diazomethane. After 45 min in the cold, with protection from light, the product was treated with a few drops of glacial acetic acid and divided into two parts. Part A (130 ml) was worked up in the usual way and analyzed by vpc (*vide supra*). In this way 0.11 g (29% yield) of 2-methoxypyridine, 0.19 g (50% given) of N-methyl-α-pyridone, and 0.64 g of α-pyridone were obtained. Part B (125 ml) was brominated (*vide supra*) to yield 0.52 g of light yellow crystals which, when chromatographed on alumina, gave 0.40 g (45% yield, of 3,5-dibromo-N-methyl-α-pyridone) of white crystals, mp 181.5–182.5°. A mixture melting point with authentic 3,5-dibromo-N-methyl-α-pyridone of mp 182.5–183° was 181.5–182.5°. The infrared spectrum was identical with that of an authentic sample of the dibromo derivative.

The reaction was repeated in order to isolate N-methyl-α-pyridone; it was conducted and worked up as usual. The internal standard was not added. Instead, the solvent was removed by rotary evaporation to yield an oil which was pumped at 1 mm for 1 hr at 60° to remove 2-methoxypyridine. The residual 0.44 g of oil had the infrared spectrum of N-methyl-α-pyridone.

Reaction of α-Pyridone with Diazoethane in Ethanol–Diethyl Ether.—A 1.90-g sample (20.0 mmoles) of α-pyridone was dissolved in 94 ml of abolute ethanol, cooled to 0°, and poured into 167 ml of precooled 0.12 *N* ethereal diazoethane[19] (20 mmoles). After 45 min in the cold, the product was treated with a few drops of glacial acetic acid and was divided. Part A (130 ml) was treated as usual (*vide supra*) to yield 0.17 g (23% yield) of N-ethyl-α-pyridone, 0.51 g (68% yield) of 2-ethoxypyridine, and 0.41 g of α-pyridone, mp 105–106°. Part B (65 ml) was brominated (*vide supra*) to yield 0.42 g of light yellow solid (I). On chromatographing a benzene solution of I on Merck basic alumina, 0.18 g (21% yield of 3,5-dibromo-N-ethyl-α-pyridone) of white crystals, mp 109–110°, was obtained. The infrared spectrum was identical with that of an authentic sample of dibromo compound. Part C (54 ml) was poured into 300 ml of water and the ethereal layer was separated. The aqueous phase was saturated with sodium chloride and extracted with seven 50-ml portions of benzene. The organic phases were combined, washed with two 10-ml portions of water, and dried over anhydrous magnesium sulfate. The extract was filtered and 6 ml of mercuric chloride in absolute ethanol (*vide supra*) was added. Rotary evaporation of the solvent under vacuum yielded white crystals which were transferred to a sintered-glass funnel and washed with 200 ml of water.[20] The crystals were dried under slight vacuum. By this procedure, 0.64 g (64% yield) of the 1:1 adduct of 2-ethoxypyridine and mercuric chloride, mp 151–152°, was obtained. The infrared spectrum in a Nujol mull was identical with that of an authentic sample of the adduct.

Reaction of the Sodium Salt of α-Pyridone with Triethyloxonium Fluoroborate in Ethanol.—To a dry flask equipped with a nitrogen inlet tube was added 3.16 g (27.0 mmoles) of the sodium salt of α-pyridone dissolved in 90 ml of absolute ethanol. The solution was cooled to *ca.* 12° and 2.01 g (10.6 mmoles) of triethyloxonium fluoroborate[21] was added; only part of the oxonium salt dissolved. Sodium fluoroborate precipitated shortly after the oxonium salt was added. The ice bath was removed and the mixture was stirred for 30 min during which the temperature rose to *ca.* 20°. Using two 1-ml aliquots, no dialkylation[18] could be detected. The mixture was then filtered and diluted to 100 ml with absolute ethanol. A 50-ml aliquot was poured into 75 ml of water, saturated with sodium chloride, and exhaustively extracted with methylene chloride. The combined extract was dried over anhydrous magnesium sulfate and concentrated (*vide supra*). Vpc analysis showed 0.12 g (19% yield) of 2-ethoxypyridine and 0.49 g (77% yield) of N-ethyl-α-pyridone.

A 25-ml aliquot was brominated as described above. Work-up yielded 0.57 g of yellow crystals which were chromatographed to yield 0.48 g (66% yield of 3,5-dibromo-N-ethyl-α-pyridone) of white crystals, mp 108.5–109.5°. A mixture melting point with authentic 3,5-dibromo-N-ethyl-α-pyridone, mp 109.5–110°, was 108.5–109.5°. The infrared spectrum was identical with that of the authentic dibromo derivative.

Acknowledgment.—It is a pleasure to thank the Explosives Department of the du Pont Company and the Purdue Research Foundation for financial support.

(17) Th. J. de Boer and H. Backer, *Org. Syn.*, **36**, 16 (1956).

(18) N. Kornblum and G. P. Coffey, *J. Org. Chem.*, **31**, 3449 (1966).

(19) The procedure employed by A. McKay, W. Ott, G. Taylor, M. Buchanan, and J. Crooker [*Can. J. Res.*, **28B**, 683 (1950)] for diazomethane was used.

(20) Both 2-ethoxypyridine and N-ethyl-α-pyridone form adducts with mercuric chloride. However, the adduct of the latter is extremely water soluble; it can be preferentially dissolved by washing the combined adducts. Care must be exercised since too much water will cause partial solubilization of the adduct of 2-ethoxypyridine.

(21) N. Kornblum and R. A. Brown, *J. Am. Chem. Soc.*, **86**, 2681 (1964).

The Reaction of Triethyloxonium Fluoroborate with the Sodium Salt of α-Pyridone[1]

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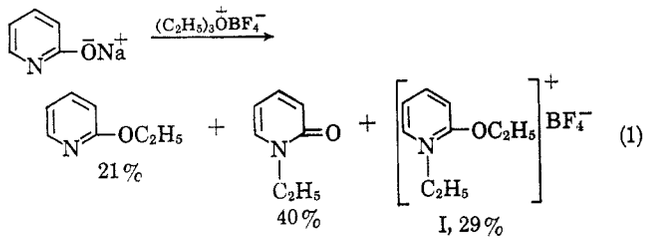
Received June 10, 1966

As part of a study of the alkylation of the salts of α-pyridone, we have examined the reaction of the sodium salt of α-pyridone with triethyloxonium fluoroborate.

(1) Paper IX in the series "The Chemistry of Ambident Anions." Paper VIII: N. Kornblum and G. P. Coffey, *J. Org. Chem.*, **31**, 3447 (1966).

(2) Purdue Research Foundation Fellow 1963–1965.

When a cold suspension of the pyridone salt in methylene chloride is treated with 1 equiv of triethyloxonium fluoroborate dissolved in methylene chloride the oxonium salt is consumed within 5 min and three products are formed (eq 1).



(1)

The dialkylate (I)[3] arises from further alkylation of *both* 2-ethoxypyridine and N-ethyl-α-pyridone for each of these readily reacts with triethyloxonium fluoroborate under the conditions employed to form I; 2-ethoxypyridine does so about three times faster than N-ethyl-α-pyridone.[4]

When the reaction of eq 1 is conducted at room temperature for 5 min, 2 days, and 4 days, a change in the proportions of products is observed (Table I), the increase in yield of N-ethyl-α-pyridone and the decrease in yield of the dialkylate (I) being especially noteworthy. Since all the triethyloxonium fluoroborate is consumed in 5 min (or less) it is clear that the subsequent change in product distribution cannot involve the triethyloxonium salt.

TABLE I

ALKYLATION OF THE SODIUM SALT OF α-PYRIDONE WITH TRIETHYLOXONIUM FLUOROBORATE[a,b]

	Yield, %			Material
Reacn time	N-Ethyl-α-pyridone[c]	2-Ethoxy-pyridine[c]	Dialkylate-I[d]	balance, %[e]
5 min[f]	40	21	29	93
5 min	36	27	28	90
48 hr	52	22	16	85
96 hr	57	20	8	82

[a] Equivalent amounts of sodium salt and triethyloxonium fluoroborate. [b] In methylene chloride at 25° except where otherwise noted. [c] By vpc. [d] Isolated as the tetraphenylboron salt. [e] This takes into account unreacted sodium salt of α-pyridone. [f] At 2°.

It transpires that, when the reaction mixture is allowed to stand, a relatively slow alkylation of unreacted α-pyridone sodium salt by the dialkylate (I) occurs and that this is the process which gives rise to the enhanced proportion of N-ethyl-α-pyridone with time. This is demonstrated by treating a suspension of the sodium salt of α-pyridone in methylene chloride with a solution of the dialkylate (I) in methylene chloride; a reaction occurs which goes 40% to completion in 2 days at room temperature and produces N-ethyl-α-pyridone in 79% yield and 2-ethoxypyridine in 9% yield. In other words, the dialkylate (I) is an ethylating agent. It is noteworthy that neither 2-ethoxypyridine nor N-ethyl-α-pyridone in methylene chloride solution is affected by a solution of the dialkylate (I) in methylene chloride after 4 days at room temperature.[5] Thus, while the dialkylate (I) is an ethylating agent it is a much more selective one than triethyloxonium fluoroborate.

In the reaction between the sodium salt of α-pyridone and triethyloxonium fluoroborate in methylene chloride, the insolubility of the sodium salt reduces its rate of reaction with the oxonium salt to the point where the products of the initial ethylation process (2-ethoxypyridine and N-ethyl-α-pyridone) are able to compete for the highly reactive, relatively nonselective triethyloxonium fluoroborate. As a consequence, when equivalent amounts of reactants are employed a portion of the sodium salt of α-pyridone fails to react with the oxonium salt.

Experimental Section[6]

Sodium Salt of α-Pyridone.—To a solution of 19 g (200 mmoles) of α-pyridone in 50 ml of absolute methanol was added 78.6 ml of 2.54 *N* methanolic sodium methoxide (200 mmoles). The solution was concentrated by rotary evaporation under vacuum until the salt just started to precipitate and then the mixture was poured into anhydrous ether. The salt was isolated, washed thoroughly with ether and with methylene chloride, and then dried by evaporation at 60° (1 mm) 95% yield.

Anal. Calcd for C_5H_4NNaO: C, 51.29; H, 3.44; N, 11.96; Na, 19.64; neut equiv, 117.1. Found: C, 50.97; H, 3.68; N, 11.80; Na, 19.33; neut equiv 118.0, 118.4.

N-Ethyl-2-ethoxypyridinium Fluoroborate (I).—To a dry flask containing 9.51 g (77.3 mmoles) of 2-ethoxypyridine dissolved in 50 ml of methylene chloride was added 14.64 g of triethyloxonium fluoroborate (77.3 mmoles) dissolved in 50 ml of methylene chloride in the course of 10 min (room temperature). After stirring for 2 hr the reaction product was worked up by removing the solvent under reduced pressure (ultimately 1 mm). The residual oil crystallized at 0° (yield 97%). Recrystallization from a nitrobenzene–ether mixture gave crystals melting at 47.5–48.5°.

Anal. Calcd for $C_9H_{14}BF_4NO$: C, 45.22; H, 5.90; F, 31.79; N, 5.86. Found: C, 45.36; H, 5.56; F, 31.90; N, 6.03.

The same compound is obtained on substituting N-ethyl-α-pyridone for 2-ethoxypyridine.

N-Ethyl-2-ethoxypyridiniumtetraphenylboron was obtained by adding a solution of 2.0 g of sodium tetraphenylboron in 20 ml of water to 1.0 g of N-ethyl-2-ethoxypyridinium fluoroborate dissolved in 20 ml of water. The white precipitate was collected by filtration, 100% yield. For analysis a sample was recrystallized from 95% ethanol (protect from light), mp 153–154° dec when bath is preheated to 145°.

Anal. Calcd for $C_{33}H_{34}BNO$: C, 84.07; H, 7.27; N, 2.97. Found: C, 84.38; H, 7.46; N, 3.26.

Reactions of N-Ethyl-2-ethoxypyridinium Fluoroborate (I). A. With Sodium Hydroxide.—To a flask containing 25.00 ml

(3) The structure of the dialkylate (I) is established by elemental analysis, infrared and nmr spectra, and by its reactions. With aqueous sodium hydroxide it produces N-ethyl-α-pyridone and ethanol and with sodium iodide in acetone it yields N-ethyl-α-pyridone and ethyl iodide. No 2-ethoxypyridine is observed in either of these reactions. Sodium ethoxide in dimethyl sulfoxide also produces only N-ethyl-α-pyridone.

(4) The formation of N-methyl-2-ethoxyquinolinium fluoroborate from N-methyl-α-quinolone and triethyloxonium fluoroborate is known: H. Meerwein, W. Florian, N. Schön, and G. Stopp, *Ann.*, **641**, 1 (1961).

(5) Also relevant are results obtained in N-methylpyrrolidone and in absolute ethanol. In these solvents the sodium salt of α-pyridone, the dialkylate (I), 2-ethoxypyridine, and N-ethyl-α-pyridone are all soluble. In N-methylpyrrolidone the reaction between the dialkylate (I) and the sodium salt of α-pyridone is 99% complete after 28 hr at 25°; under these conditions 2-ethoxypyridine and N-ethyl-α-pyridone are completely unaffected by I. In absolute ethanol the reaction between I and the sodium salt of α-pyridone is 90% complete after 65 hr at 25°; under these conditions 2-ethoxypyridine and N-ethyl-α-pyridone are completely unaffected: G. P. Coffey, Ph.D. Thesis, Purdue University, 1966.

(6) All melting and boiling points are uncorrected. Microanalyses are by Dr. C. S. Yeh, Purdue University. Quantitative gas chromatographic analyses were carried out with a Perkin-Elmer Model 154 vapor fractometer with printing integrator using a 5 ft × 0.25 in. 10% Dow 710 on Fluoropak column at 160° and 30 psi of helium. The internal standard was 1-bromo-4-chlorobenzene. Relative response determinations were performed before each analysis using known mixtures of 2-ethoxypyridine and N-ethyl-α-pyridone. For the preparation of triethyloxonium fluoroborate, 2-ethoxypyridine, and N-ethyl-α-pyridone, see N. Kornblum and G. P. Coffey, ref 1.

of 0.6301 N aqueous sodium hydroxide (15.73 mmoles) was added a solution of 3.70 g (15.48 mmoles) of N-ethyl-2-ethoxypyridinium fluoroborate in 20 ml of water. Water was then added to bring the volume to 100 ml and the system was stirred, under nitrogen, at 27° for 11 hr. The product was saturated with sodium chloride and exhaustively extracted with methylene chloride, and the extracts were dried. After concentrating by distillation the residue was subjected to gas chromatographic analysis;[6] 1.37 g (89% yield) of N-ethyl-α-pyridone was found and no 2-ethoxypyridine could be detected.

B. With Sodium Iodide.—A solution of 3.34 g of I in 50 ml of acetone was treated with 2.10 g of sodium iodide. The resulting light yellow solution was protected from light and stirred under nitrogen at 27°. After 119 hr the reaction was 84% complete. Vpc analysis[6] revealed the presence of N-ethyl-α-pyridone; no 2-ethoxypyridine could be found even though as little as 0.2% could readily be detected. On working up the product 0.86 g (68% yield) of a colorless oil, bp *ca.* 90° (1 mm), was isolated; its infrared spectrum was identical with that of authentic N-ethyl-α-pyridone.

C. With Sodium Ethoxide.—To 55 ml of 0.023 N sodium ethoxide in DMSO was added 0.303 g of I dissolved in 25.0 ml of DMSO. Additional DMSO was added until the final volume was 100 ml and the system was stirred, under nitrogen, at 29° for 1.5 hr. On working up the product and analyzing by vpc, methylene chloride, DMSO, and N-ethyl-α-pyridone were found, but 2-ethoxypyridine could not be detected.

Reaction of the Sodium Salt of α-Pyridone and Triethyloxonium Fluoroborate.—The following is a typical example of the reactions described in Table I. A three-necked, round-bottom flask was equipped with a Trubore stirrer, a pressure equalizing funnel, and an adapter containing a gas inlet tube and thermometer; the assembly was flamed under nitrogen. To the flask was added 2.72 g (23.20 mmoles) of the sodium salt of α-pyridone and 60 ml of methylene chloride. The slurry was stirred and cooled to −3.5° with an ice–salt bath. In 20 ml of methylene chloride was dissolved 4.42 g (23.20 mmoles) of triethyloxonium fluoroborate; the solution was cooled to −5° and added rapidly to the sodium salt. Within 1 min the temperature rose to 2°. After 5 min at 2° the mixture was filtered into 10 ml of water. Titration with aqueous sodium hydroxide showed no acid; the oxonium salt had all reacted. The salts were thoroughly washed with methylene chloride, dissolved in water, and titrated for unreacted sodium salt of α-pyridone using 0.100 N hydrochloric acid (53.30 ml of acid required). To the resulting neutral, aqueous solution was added 50 g of potassium acetate in 20 ml of water. After 12 hr at 0° 2.07 g (16.4 mequiv) of potassium fluoroborate was collected by filtration.

The methylene chloride solution was extracted with 75 ml of water and four 25-ml portions of water, dissolved methylene chloride was removed by evaporation, and the aqueous extract (cooled to 0°) was treated with a freshly prepared solution of 2.5 g of sodium tetraphenylboron in 25 ml of water. After 10 min at 0°, 2.48 g (29% yield) of N-ethyl-2-ethoxypyridinium tetraphenylboron, mp 148.5–149.5°, was obtained. Recrystallization from 95% ethanol gave white crystals, mp 153–154°; the infrared spectrum was identical with that of an authentic sample. To the aqueous filtrate was added a solution of 5 g of potassium chloride in 25 ml of water and the resulting precipitate of potassium tetraphenylboron was removed by filtration. The clear, aqueous filtrate was saturated with sodium chloride and exhaustively extracted with methylene chloride. These extracts were combined with the original methylene chloride solution, dried, and concentrated by distillation at atmospheric pressure to a volume of *ca.* 25 ml. Analysis[6] by vpc gave 0.47 g (21% yield) of 2-ethoxypyridine and 0.88 g (40% yield) of N-ethyl-α-pyridone.

Reaction of the Sodium Salt of α-Pyridone with N-Ethyl-2-ethoxypyridinium Fluoroborate (I).—A solution of 3.59 g of I in 20 ml of methylene chloride was added to a slurry of 1.76 g of the sodium salt of α-pyridone in 60 ml of methylene chloride. The mixture was stirred under nitrogen at 25° for 48 hr with protection from light. The solid was isolated by filtration, dissolved in water, and titrated with 0.100 N hydrochloric acid, requiring 72.40 ml. Treatment with sodium tetraphenylboron (*vide supra*) yielded 4.21 g of white crystals, mp 152–153°; thus the reaction was 40% complete. Recrystallization from 95% ethanol gave crystals, mp 154–155°, having an infrared spectrum identical with that of authentic N-ethyl-2-ethoxypyridinium tetraphenylboron.

Further work-up (*vide supra*) yielded a concentrate which by vpc analysis[6] was found to contain 0.14 g (9% yield) of 2-ethoxypyridine and 1.18 g (79% yield) of N-ethyl-α-pyridone.

Stability of 2-Ethoxypyridine and of N-Ethyl-α-pyridone to N-Ethyl-2-ethoxypyridinium Fluoroborate (I).—2-Ethoxypyridine (0.90 g, 7.30 mmoles) was dissolved in 50 ml of methylene chloride and treated with a solution of 1.75 g of I in 30 ml of methylene chloride. The solution (protected from light) was stirred under nitrogen at 25° for 4 days. At the end of this time the dialkylate I was recovered quantitatively as the tetraphenylboron salt (3.43 g, mp 152–153°). Recrystallization from 95% ethanol gave white crystals, mp 154–155°; the infrared spectrum was the same as that of authentic tetraphenylboron salt of I. The remainder of the product gave a concentrate (*vide supra*) which by vpc analysis[6] was found to contain 0.82 g (91% recovery) 2-ethoxypyridine. No N-ethyl-α-pyridone was found; 1.5% could readily be detected.

In the same way, equivalent amounts of N-ethyl-α-pyridone and I were allowed to react for 4 days at 25°; the reactants were quantitatively recovered and no 2-ethoxypyridine could be detected by vpc.

Acknowledgment.—Support of this work by a grant from the Explosives Department of E. I. du Pont de Nemours and Company is gratefully acknowledged. G. P. C. thanks the Purdue Research Foundation for a Fellowship for 1963–1965.

The Absolute Configuration of *trans*-2,6-Dimethylpiperidine[1]

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Received May 25, 1966

Among the naturally occurring simple piperidine derivatives are (−)-2,6-dimethylpiperidine (I) and its N-methyl derivative, (−)-1,2,6-trimethylpiperidine (II), whose isolation from *Nanophyton erinaceum* was reported by Kuzovkov and Menshikov[2] in 1950. These simple compounds possess many of the structural features common to more complex piperidine alkaloids, such as pinidine, carpaine, cassine, and the hemlock and lobelia alkaloids. As part of our continuing study of the stereochemistry of natural piperidines,[3] we have determined the absolute configurations of I and II.

The configurations were established by Hofmann degradation of both enantiomers of II to 2-dimethylaminoheptane, whose configuration was then related to that of 2-heptanol.

A mixture of *cis*- and *trans*-(±)-I, prepared by sodium–alcohol reduction of 2,6-lutidine, was carefully separated by fractional distillation. The pure *trans*-I obtained was methylated under Eschweiler–Clark conditions to *trans*-II, and this was partially resolved[4] with *d*-tartaric acid to give dextrorotatory II. Hofmann elimination of the methiodide of (+)-II yielded 2-dimethylaminohept-6-ene (III), which was hydrogenated to (+)-2-dimethylaminoheptane (IV), characterized as its crystalline levorotatory methiodide.

(1) This research was supported by a research grant (GM-06568) from the Public Health Service, to whom the authors express their appreciation.

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(4) R. Lukeš and J. Jizba, *Collection Czech. Chem. Commun.*, **19**, 930 (1954).