and crystallized from methanol, yielding yohimbane, *d,l*-alloyohimbane, and ajmalicine, each from its corresponding 3-dehydro product, as identified by m.p., mixture m.p., and infrared spectra. The yields were 91, 52, and 71%, respectively.

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The Base-Catalyzed Alkylation of Fluorene with Secondary Alcohols

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Recently, the successful alkylation of fluorene with primary alcohols and their alkoxides was reported, and the general subject was reviewed.[2] It was the purpose of this investigation to determine whether the reaction could be extended to secondary alcohols as could be predicted from the postulated mechanism for the reaction.[2,3]

TABLE I

9-ALKYLFLUORENES

Alkyl Group	Method	M.P. of Product, °C.	Yield, %	M.P. of Analytical Sample, °C.	Analyses C Calc'd	Analyses C Found	Analyses H Calc'd	Analyses H Found
Cyclohexyl	I	110.0–115.6	60.5	115.3–115.7[a]	91.88	91.98	8.12	7.83
Cyclohexyl	II	112.0–116.0	69.0					
Cyclohexyl	III	113.0–116.6	74.2					
Cyclopentyl[b]	I	60.0–62.4	24.4	62.0–62.4	92.26	92.24	7.74	7.84
Cycloheptyl	III	63.0–68.8	40.0	65.6–66.8	91.55	91.32	8.45	8.49
Isopropyl	I	53.9–54.5	<1	53.9–54.5[c]				
Isopropyl	IV	50.0–54.5	52.3	53.8–54.8[c]	92.26	91.94	7.74	8.08
Neopentyl	I	79.0–79.8	35.2	79.4–79.8	91.47	91.51	8.53	8.45

[a] W. G. Brown and B. A. Bluestein, *J. Am. Chem. Soc.*, **65,** 1082 (1943), report, m.p. 116°. [b] Decomposed upon standing exposed to air for one month. [c] Footnote (*a*) reports 54–55°.

It has now been found that cyclopentanol and cyclohexanol together with their respective sodium salts at 220–230° do alkylate fluorene in from 24–60% yield (see Table). Furthermore, isopropyl alcohol together with its sodium salt alkylates fluorene, but in only about 1% yield. These yields are generally lower than those for primary alcohols previously reported under comparable conditions.[2,3]

Recently a number of investigators[4-8] have reported for a related reaction, the N-alkylation of aniline, that the temperature for alkylation may be lowered by the use of U. O. P. nickel or Raney nickel. In the present reaction, these results were corroborated: 9-cyclohexylfluorene was obtained in 69% yield using U. O. P. nickel and in 74% yield with Davison sponge nickel catalyst. When the use of the latter catalyst was combined with the technique of returning the refluxing solvent through a Soxhlet thimble containing calcium hydride, the yield of 9-isopropylfluorene was raised from below 1% to 52%.

The alkylation of fluorene was also attempted with one primary alcohol — neopentyl alcohol. It was hoped that the bulky *tert*-butyl group on the postulated intermediate fulvene would prevent further reduction.[2,3,9] However, a colorless compound corresponding in all respects to those expected for a fluorene and not a fulvene was obtained. Absorption bands at 1368 cm.$^{-1}$ and 1390 cm.$^{-1}$ are characteristic of a neopentyl group[10] and preclude the possibility of rearrangement during alkylation.

EXPERIMENTAL

Cycloheptanol. Cycloheptanone (49.0 g., 0.44 mole) was added dropwise to a stirred suspension of 5.0 g. (0.13 mole) of lithium aluminum hydride in 200 ml. of dry ether. After the addition was complete, the mixture was refluxed for three hours. Ten percent sulfuric acid then was added with stirring until a clear solution was obtained. The aqueous layer was separated, washed twice with ether, and the combined organic layers were washed with sodium carbonate solution and then with water until neutral. After drying over sodium sulfate, the ether and then the cycloheptanol distilled to give 38.8 g. (0.34 mole, 80%), b.p. 184–187°, n_D^{25} 1.4742.[11]

Alkylation reactions. Method I. Sodium (2 g., 0.087 g.-atom) was added in small pieces to 40 ml. of the required alcohol contained in a Carius tube to which a condenser had been temporarily attached. An oil-bath hastened reaction of the sodium. Upon cooling the solution to room tempera-

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[1] To whom inquiries should be sent.

[2] K. L. Schoen and E. I. Becker, *J. Am. Chem. Soc.*, **77,** 6030 (1955).

[3] See also Y. Sprinzak, *J. Am. Chem. Soc.*, **78,** 466 (1956).

[4] E. F. Pratt and E. J. Frazza, *J. Am. Chem. Soc.*, **76,** 6174 (1954).

[5] R. C. Rice and E. J. Kohn, *J. Am. Chem. Soc.*, **77,** 4052 (1955).

[6] C. Ainsworth, *J. Am. Chem. Soc.*, **78,** 1635 (1956).

[7] B. B. Corson and H. Dressler, *J. Org. Chem.*, **21,** 474 (1956).

[8] J. Horyna and O. Černý, *Chem. Listy*, **50,** 381 (1956).

[9] S. M. Linder, E. I. Becker, and P. E. Spoerri, *J. Am. Chem. Soc.*, **75,** 5972 (1953).

[10] L. Bellamy, *The Infra-red Spectra of Complex Molecules*, John Wiley and Sons, Inc., New York, 1954, p. 13.

[11] P. A. S. Smith and D. R. Baer [*J. Am. Chem. Soc.*, **74,** 6135 (1952)] reported 50% yield with the same reagent but without heating, b.p. 87–88.5° (15 mm.), n_D^{20} 1.4757.

ture, the alkoxide solution generally solidified. Then 10 g. (0.060 mole) of fluorene was added to the cooled solution and the tube was sealed. After heating the tube for from 15 to 24 hours at 220–230°, the tube was cooled, opened, and extracted with benzene, water, and finally benzene. Neutralization of the mixture with 10% hydrochloric acid was followed by separating the aqueous layer and extracting it with benzene. The organic layers were combined, distilled to remove benzene and residual alcohol, and then distilled at reduced pressure (about 0.5 mm.). The product solidified in the receiver and was recrystallized from methanol.

Method II. To a 500 ml., 3-necked flask equipped with a Dean-Stark trap filled with xylene, a thermometer reaching almost to the bottom of the flask, and a gas-inlet tube, and holding a mixture of 25 ml. of cyclohexanol and 25 ml. of xylene was added in pieces 1.56 g. (0.040 atom) of potassium. The addition was carried out under nitrogen and at such a rate as to maintain the temperature below 50°. The nitrogen-inlet tube then was replaced by a stopper and a mixture of 1 g. of U. O. P. nickel with 20.75 g. (0.125 mole) of fluorene was added in one portion, along with 250 ml. of xylene, and the mixture was refluxed for 24 hours. At this point 1.6 ml. (71%) of water had been collected. After cooling, filtering, and washing until neutral with water, the xylene and excess alcohol were distilled and finally the residue was collected at 142–148° (0.1 mm.). Recrystallization from methanol gave 21.4 g. (0.086 mole, 69%) of colorless product, m.p. 112–116°.

Method III. In this procedure the U. O. P. nickel was replaced by Davison sponge nickel catalyst. The latter was prepared for use by washing it six times with anhydrous methanol and then with the alcohol to be used.

Method IV. The Dean-Stark trap was replaced by a Soxhlet extraction apparatus in which the thimble was filled with calcium hydride.

Attempted preparation of molecular addition compounds. Tetranitrofluorenone, chloranil, trinitrofluorene, picrolonic acid, picric acid, 1,3,5-trinitrobenzene, styphnic acid, and picric acid in a variety of solvents failed to give molecular addition compounds. The first two gave evidence of some reaction as evidenced by the appearance of a blood-red color in acetonitrile, but all attempts to isolate a pure material were fruitless.

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The Reduction of Perfluoroalkyl Isocyanates with Lithium Aluminum Hydride

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The reduction of alkyl isocyanates to methylalkylamines by means of lithium aluminum hydride has been reported by Finholt, Anderson, and Agre.[2] The present work was undertaken to determine whether a similar reduction of perfluoroalkyl isocyanates would be of value as a novel synthesis of methylfluoroalkylamines.

Treatment of perfluoropropyl and perfluoroheptyl isocyanate with excess lithium aluminum hydride has now been found to produce the corresponding methyl-1,1-dihydroperfluoroalkylamines in yields of 74% and 61%, respectively. The reactivity of fluorine atoms *alpha* to the nitrogen atom in amines has been noted before.[3] In the present work this reactivity has resulted in a reduction at these positions in addition to the desired reaction with the isocyanate group.

To avoid the reduction of the *alpha* fluorine atoms, an obvious modification is the use of limited quantities of the lithium aluminum hydride. This proved unsuccessful since the reaction of perfluoropropyl isocyanate with a one-half mole-ratio of the hydride gave a small yield (2.4%) of N-1,1-dihydroperfluoropropyl formamide together with high molecular weight materials. Therefore, the replacement of the *alpha* fluorine atoms of the isocyanate by hydrogen precedes the complete reduction of the isocyanate group.

Since the fluorine atoms *alpha* to a nitrogen atom are so susceptible to reducing agents, the treatment of either N-perfluoroalkyl urethans or perfluoroalkyl isocyanates with lithium aluminum hydride does not offer much promise as a possible synthesis of perfluoroalkylamines.

EXPERIMENTAL

Reagents. Perfluoropropyl and perfluoroheptyl isocyanates were prepared from the corresponding acid chlorides by the Curtius reaction.[4] Since the boiling point of the perfluoropropyl isocyanate (27–28°) is very close to that of the acid chloride (38–39°), in order to obtain a pure sample it was necessary to distil through a helices-packed column. Great care must be observed in this distillation. In one experiment, while dismantling the equipment after removal of the product, a violent explosion of the column hold-up completely destroyed the apparatus. This explosion was due to a higher-boiling fraction composed of either the acid azide or hydrazoic acid.

Ethereal solutions of lithium aluminum hydride were prepared by extracting commercial hydride with dry ether in a Soxhlet apparatus to eliminate insoluble material. The ethereal solution was standardized by measuring the volume of hydrogen liberated when 1 ml. of the solution was added to butanol.

Perfluoropropyl isocyanate reduction with excess lithium aluminum hydride. To a solution of 0.2 mole of lithium aluminum hydride in 150 ml. of ether, kept below 5°, was added dropwise 22 g. (0.10 mole) of perfluoropropyl isocyanate dissolved in 30 ml. of anhydrous ether. Upon completion of the addition, stirring was continued at room temperature for two hours. After a small quantity of water

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(1) From the thesis to be submitted by Robert G. Taborsky to the Graduate School of Western Reserve University in partial fulfillment of the requirements for the doctor's degree. Presented at the Atlantic City meeting of the American Chemical Society, September, 1956.

(2) Finholt, Anderson, and Agre, *J. Org. Chem.*, **18**, 1338 (1953).

(3) Pruett, Barr, Rapp, Bahner, Gibson, and Lafferty, *J. Am. Chem. Soc.*, **72**, 3646 (1950).

(4) Albrecht and Husted, U. S. Patent 2,617,817 (1952).