TABLE I

PREPARATION OF *n*-BUTYLLITHIUM

Run	Time of addition, min.	Temp. during addition, °C.	Type of lithium	G. atoms lithium	Moles *n*-butyl bromide	Final concn., molar	Yield[a] %	Stirring after addition Hr.	Stirring after addition Temp., °C.
1	30	−20	Cut[b]	2.2	1.0	0.835	77.7	1.25	0–20
2	25	− 5	Cut	1.0	0.5	1.20	82.9	1	0
3	35	0	Sand[c]	1.0	0.5	1.47	77.3	2	0
4	35	−10	Cut	1.14	0.5	1.25	85.4[d]	2	0
5	35	−10	Wire	1.23	0.5	1.14	83.7[e]	2	0
6	15	−10	Cut	3.3	1.5	0.89	80.0	3	4

[a] Yield after filtration as determined by double-titration. [b] Prepared as described in THIS JOURNAL, **63**, 2327 (1940). [c] Supplied by the Metalloy Corp., Minneapolis, Minn. [d] In this run helium was used in place of nitrogen and double-titrations were made five minutes, one hour, and two hours after addition; yields were 78.5, 83.9, and 85.4%, respectively. [e] Yield determined by double-titration before filtration was 90%; the above yield was determined after storing sixteen hours at 10° following filtration.

mined by double-titration[1] was 90% before filtration and 83.7% after filtering and storing sixteen hours at 10°. After four days at 10°, the yield was 82.5%.

CHEMICAL LABORATORY
IOWA STATE COLLEGE
AMES, IOWA

RECEIVED NOVEMBER 17, 1948

Fluorene Analog of Amidone

BY DAVID GINSBURG[1] AND MANUEL M. BAIZER

Present interest in amidone analogs and derivatives[2,3] prompts us to report on the synthesis of a fluorene analog of amidone. This work was completed about a year ago but we have had no opportunity to establish the structure[4] of the isomer which was characterized.

Blicke and Zambito[5] state that the related "1,1-biphenylene-1-(β-dimethylaminoethyl)-butanone-2" is in the process of preparation. No details have appeared to date.

Experimental[6]

9-Formylfluorene.—This compound was prepared in 74% yield by the procedure of Von and Wagner.[7]

9-Formylfluorene Oxime.—A 78% yield was obtained by the procedure of Vorländer.[8]

9-Cyanofluorene.—A 90% yield was obtained in the dehydration of 9-formylfluorene oxime by thionyl chloride in absolute ether.[8]

Condensation of 9-Cyanofluorene with 1-Dimethylamino-2-chloropropane.—The procedure followed was similar to the one used in the condensation of diphenylacetonitrile with the chloroamine to yield the precursors of the amidones.[9]

In a 250-ml., three-necked flask, equipped with thermometer, mercury-sealed stirrer and reflux condenser, 19.1 g. (0.1 mole) of 9-cyanofluorene and 12.2 g. (0.1 mole) of 1-dimethylamino-2-chloropropane were dissolved in 100 ml. of dry benzene at 25°. Sodium amide (4.3 g., 0.11 mole) was added, portionwise, with continuous stirring in the course of thirty minutes. The temperature rose spontaneously to 40° in one hour; ammonia was evolved. The mixture was refluxed for thirty minutes, cooled and 50 ml. of water added. The benzene layer was separated and shaken with 50 ml. of 20% hydrochloric acid. The benzene layer on evaporation left 2.5 g. of unchanged 9-cyanofluorene. The acid extract was made alkaline by the addition of 33% sodium hydroxide, and the oil which separated was extracted with 200 ml. of ether. The ethereal solution was dried and the solvent removed by distillation. The residual oil, presumed by analogy to be mixture (I) of 9-cyano-9-(β-dimethylaminopropyl)-fluorene and 9-cyano-9-(α-methyl-β-dimethylaminoethyl)-fluorene, weighed 25.5 g. Upon distillation a yellow oil was obtained; b. p. 195–199° (8 mm.).

Reaction of I with Ethylmagnesium Bromide.—A Grignard reagent was prepared from 9.7 g. (0.40 mole) of magnesium turnings and 44 g. (0.38 mole) of ethyl bromide in 100 ml. of dry ether. To the ethereal solution was added, in one portion, a solution of 29 g. (0.11 mole) of I in 35 ml. of dry xylene. A greenish precipitate formed after a few minutes of heating under reflux in an oil-bath at 95–100°. The heating was continued for three and one-half hours; the mixture was then decomposed, while still hot, by the careful addition of 40 ml. of concentrated hydrochloric acid dissolved in 100 ml. of water. After the addition of benzene three layers were formed. The two upper layers were removed together and heated on a steam-bath until the solvents had been vaporized. The residual oily hydrobromide was moistened with alcohol and chilled briefly in an acetone–solid carbon dioxide-bath, whereupon crystallization occurred. The solid was filtered and recrystallized from ethanol. The yield of II,[10] m. p. 232–234°, was about 75% based upon one-half the input of I.

Anal. Calcd. for $C_{21}H_{26}BrNO$: C, 64.94; H, 6.75; N, 3.61. Found: C, 64.43; H, 7.02; N, 3.77.[11]

The melting point of the base, liberated from II, is 57–60° and of the hydrochloride 262–263°.

THE NEW YORK QUININE AND CHEMICAL WORKS, INC.
BROOKLYN, N. Y.

RECEIVED DECEMBER 6, 1948

---

[1] Present address: Daniel Sieff Research Institute, Rehovoth, Israel.

[2] Gardner, *et al.*, THIS JOURNAL, **70**, 2906 (1948).

[3] May and Mosettig, *J. Org. Chem.*, **13**, 459 (1948).

[4] Schultz, Robb and Sprague, THIS JOURNAL, **69**, 2454 (1947), outline a structure proof for the isomeric nitriles which are the precursors of the amidones.

[5] Abstracts of American Chemical Society meeting April, 1947, p. 3K.

[6] Melting points and boiling points are not corrected.

[7] Von and Wagner, *J. Org. Chem.*, **9**, 162 (1944).

[8] Vorländer, *Ber.*, **44**, 2468 (1911).

[9] O. P. B. Report PB 981, p. 97.

[10] By analogy with the findings in the amidone synthesis,[9] we consider it probable that II is 9-propionyl-9-(β-dimethylaminopropyl)-fluorene hydrobromide and that the by-products remain in the mother liquors.

[11] Microanalyses by Schwarzkopf Laboratories, Elmhurst, L. I., N. Y.

The Configuration at the 20-Position in Certain Steroids

BY W. KLYNE AND D. H. R. BARTON

Isomeric C_{21} steroids bearing a secondary hydroxyl group at C_{20} are commonly distinguished