[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

Attempted Rearrangement of 9-Bromomethylenefluorene into 9-Bromophenanthrene

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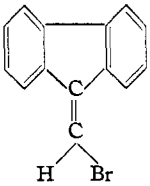
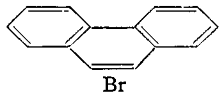
Most of the rearrangement reactions of aliphatic compounds are known in both a nitrogen series and in a carbon series. For example, the Hofmann,[1] Curtius,[2] and Lossen[3] rearrangements have their carbon analog in the Wolff[4] rearrangement of diazoketones. The Stieglitz[5] rearrangement of N-bromotriphenylmethylamine is the nitrogen analog of the Wagner–Meerwein,[6] Demjanov,[7] and pinacol[8] rearrangements. No unambiguous example of a carbon analog of the Beckmann rearrangement seems to be known although the transformation of 2,2-dimesitylvinyl alcohol into a 1,2-dichloro-1,2-dimesitylethane by the action of phosphorus pentachloride may be interpreted as such an example.[9] Since the Beckmann rearrangement of fluorenone oxime into phenanthridone takes place in high yield,[10] we have studied the reaction of 9-bromomethylenefluorene (I), which in the presence of Lewis acids might be expected to rearrange into 9-bromophenanthrene (II). Under reaction conditions mild enough to permit recovery of 9-bromophenanthrene but vigorous enough to cause reaction of the 9-bromomethylenefluorene we were unable to obtain any evidence of the rearrangement. The product of the reaction of 9-bromomethylenefluorene with aluminum bromide appeared to be polymeric.



I



II

Experimental[11,12]

9-Bromomethylenefluorene.—Ethyl fluorenylideneacetate was prepared from fluorenone by the method of Sielitz and Jassoy.[13] The ester was hydrolyzed in 96% yield by dissolving 2.65 g. in 20 ml. of 95% ethanol, adding a solution of 1 g. of potassium hydroxide in 3 ml. of water and heating for ten minutes. Most of the alcohol was evaporated, 50 ml. of water added, the solution clarified and acidified. The dried and powdered acid (2.19 g.) was suspended (floated) in 25 ml. of dry carbon tetrachloride, the theoretical amount of bromine added, and the flask placed in contact with a 100-watt light bulb for three hours. During this time the suspension was stirred occasionally and the suspended solid gradually sank to the bottom. The 3.61 g. of dibromoacid was boiled for thirty minutes with 30 ml. of 0.5 *N* sodium hydroxide leading to dehydrobromination and decarboxylation[14] and the formation of 2.12 g. (87%) of crude 9-bromomethylenefluorene. This was recrystallized from a mixture of benzene and petroleum ether (b. p. 60–70°) in which it is quite soluble, giving bright yellow prisms, m. p. 72.5–73°. When crystallized from nitrobenzene on a microscope slide, it formed parallelograms with a 60° angle, extinction parallel to the long edge, and the slow ray parallel to the long edge. Wieland and Krause[15] report a m. p. of 78° for this compound.

Anal. Calcd. for $C_{14}H_9Br$: C, 65.39; H, 3.58; Br, 31.08. Found: C, 65.6; H, 4.0; Br, 31.0.

9-Bromomethyl-9-bromofluorene.—This compound was prepared by the method of Wieland and Krause[15] from fluorenone via 9-methyl-9-fluorenol and 9-methyl-9-chlorofluorene. The m. p. observed for 9-bromomethyl-9-bromofluorene in the range 130–140° depends on the time of heating since it decomposes below its m. p.

Dehydrobromination of 9-Bromomethyl-9-bromofluorene.—Attempts to prepare 9-bromomethylenefluorene by dehydrobromination of 9-bromomethyl-9-bromofluorene gave rise to various mixtures which were difficult to resolve. When refluxed with sodium acetate in acetic acid,[15] 1.2 to 1.3 moles of sodium bromide was formed from each mole of dibromide within three minutes. The usual reaction product was a yellow oil which would not crystallize, but in several experiments it was possible to isolate a substitution product which is probably 9-bromomethyl-9-acetoxyfluorene obtained in the form of colorless needles from petroleum ether, m. p. 106–106.5°. Recrystallization from nitrobenzene on a microscope slide gave rectangular crystals with parallel extinction.

Anal. Calcd. for $C_{16}H_{13}O_2Br$: C, 60.58; H, 4.13. Found: C, 60.19; H, 4.03.

It was possible to separate 9-bromomethylenefluorene from the various by-products by chromatographic adsorption from 60–70° petroleum ether on an adsorbent consisting of equal parts by volume of Celite 535 and silicic acid (Merck).

Attempted dehydrobromination by means of calcium carbonate in isopropyl alcohol gave colorless crystals, m. p. 114.5–115°. This compound is probably 9-bromomethyl-9-isopropoxyfluorene.

Anal. Calcd. for $C_{17}H_{17}OBr$: Br, 25.19. Found: Br, 24.9, 25.0.

Pyridine, piperidine, alcoholic potassium hydroxide, and heat alone also failed to lead to simple reaction products.

Stannic Bromide.—This is easily prepared by a modification of the method of Lorenz.[16] In a 250-ml. round-bottom flask with a ground joint and fitted with an efficient condenser is placed 59 g. of mossy tin. Bromine (160 g.) is run in from a separatory funnel with a stem extending into the condenser. The reaction is highly exothermic and the rate of addition of the bromine is limited by the capacity of the condenser. The crude

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[1] Wallis and Lane, "Organic Reactions," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1946, p. 267.

[2] Peter A. S. Smith, *ibid.*, p. 337.

[3] Yale, *Chem. Rev.*, **33**, 242 (1943).

[4] Bachmann and Struve, "Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 38.

[5] Stieglitz and Vosburgh, *Ber.*, **46**, 2151 (1913).

[6] Bartlett and Gill, THIS JOURNAL, **63**, 1273 (1941).

[7] Ruzicka and Brugger, *Helv. Chim. Acta*, **9**, 399 (1926).

[8] Bartlett and Pöckel, THIS JOURNAL, **59**, 820 (1937).

[9] Fuson, Southwick and Rowland, *ibid.*, **66**, 1109 (1944).

[10] Moore and Huntress, *ibid.*, **49**, 2618 (1927).

[11] All melting points are corrected.

[12] Carbon-hydrogen microanalyses by Mrs. Priscilla J. Bohrer.

[13] Sielitz and Jassoy, *Ber.*, **54**, 2133 (1921).

[14] *Cf.* Adams and Johnson, "Laboratory Experiments in Organic Chemistry," The Macmillan Company, New York, N. Y., third edition, 1945, p. 309.

[15] Wieland and Krause, *Ann.*, **443**, 129 (1925).

[16] Lorenz, *Z. anorg. Chem.*, **9**, 365 (1895).

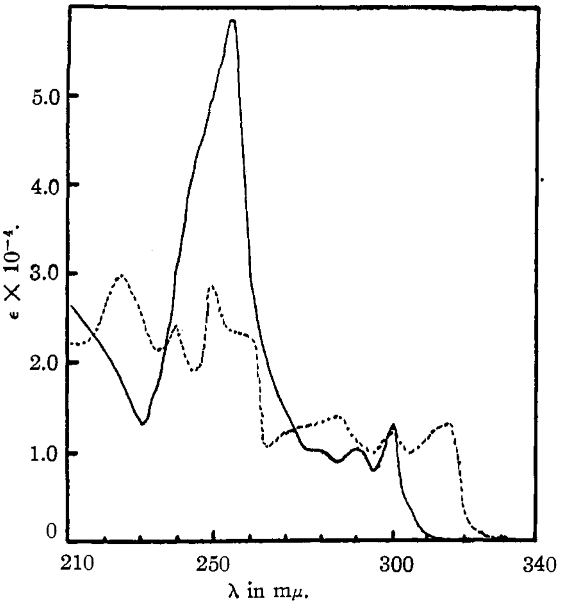

Fig. 1.—Ultraviolet absorption spectrum of 9-bromophenanthrene —— and of 9-bromomethylenefluorene - - - - in Phillip's *Spectro* grade "iso-octane": readings were taken every multiple of 5 mμ; ε was calculated from the equation $\log (I/I_0) = \epsilon cl$ where l = 1 cm. and c = concn. in moles/l.

product is transferred to an ordinary cork-stoppered distilling flask and distilled. Most of the bromine distils in the forerun (20 g.) and the almost colorless product is then collected in sealing bottles (about 195 g.). The distillate is allowed to solidify to the extent of about 90%, and the colored melt is poured off leaving a residue of colorless crystals. The reported[17] m. p. is about 30°.

Attempted Rearrangement of 9-Bromomethylenefluorene.—These experiments (Table I) were carried out by dissolving the compound in the solvent and adding a solution of anhydrous aluminum bromide in the same solvent. The absorption spectra of 9-bromomethylenefluorene and 9-bromophenanthrene (Fig. 1) are sufficiently different to permit the detection of less than 5% of 9-bromophenanthrene in a mixture of the two. Both 9-bromophenanthrene and 9-bromomethylenefluorene are easily soluble in "iso-octane."

TABLE I

THE REACTION OF 9-BROMOPHENANTHRENE AND 9-BROMOMETHYLENEFLUORENE WITH ALUMINUM BROMIDE AND WITH STANNIC BROMIDE AT ROOM TEMPERATURE[a]

Cpd.	μ moles	Cat.	μ moles	Solvent	Result
P[b]	78	$AlBr_3$	7	CS_2	92% P recovered
P	78	$AlBr_3$	38	CS_2	70% P recovered
P	78	$AlBr_3$	156	CS_2	No P recovered[c,d]
P	80	$AlBr_3$	150	$C_6H_5NO_2$[e]	Much P recovered
P	78	$SnBr_4$	5000	None[f]	No reaction
F	2200	$AlBr_3$	5	CS_2	Some F recovered No P
F	78	$AlBr_3$	21	CS_2	No F, no P[d,g]
F	78	$AlBr_3$	106	CS_2	No F, no P[d]
F	80	$AlBr_3$	150	$C_6H_5NO_2$[e]	No F, no P[d]
F	78	$SnBr_4$	1500	None[f]	No reaction

[a] Time varied from thirty minutes to twelve hours but was the same for any two corresponding runs with P and F. The reaction was probably complete within a few minutes in CS_2. [b] P = 9-bromophenanthrene; F = 9-bromomethylenefluorene. [c] Clar[18] reports the formation of dibenzo[b,k]perylene by dimerization from the action of an excess of aluminum chloride on 9-bromophenanthrene. [d] No material soluble in "iso-octane." [e] Twelve hours at room temperature followed by one hour at 90°. [f] P and F are soluble in $SnBr_4$. [g] Repeated on 2.0 millimole scale. Product consisted of pale yellow powders which decomposed without melting. One fraction was insoluble in chloroform (less than 1 mg. in 10 ml.) and contained 16.4, 16.5% Br. Another more soluble fraction contained 27.4% Br. A total of 85% of the starting material was recovered.

Summary

In an attempt to find a carbon analog of the Beckmann rearrangement, 9-bromomethylenefluorene was treated with aluminum bromide and with stannic bromide. None of the expected rearranged product, 9-bromophenanthrene, was obtained, however.

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(17) Mellor "Inorganic and Theoretical Chemistry," Vol. VII, Longmans, Green and Company, New York, N. Y., 1927, p. 455.

(18) "Elsevier's Encyclopedia of Organic Chemistry," Elsevier Publishing Company, Inc., New York, N. Y., 1946, Vol. 13, p. 815.

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