[Contribution from the Department of Chemistry, Duke University]

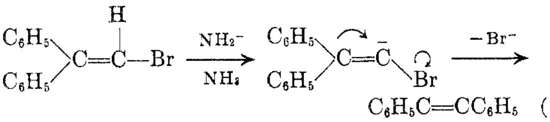
Reaction of 9-Bromomethylenefluorene with Potassium Amide in Liquid Ammonia. Dimerization[1]

CHARLES R. HAUSER and DANIEL LEDNICER

Received June 17, 1957

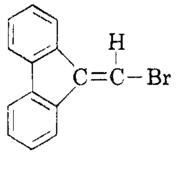
9-Bromomethylenefluorene reacted with potassium amide in liquid ammonia to form a brick-red cumulene and a white product, both of which still contained the fluorene nucleus. No phenanthrene derivative which might have been produced through α-elimination and rearrangement, was found. Mechanisms are considered. An improved method of synthesis is described for the α,β-unsaturated acid employed in the preparation of the 9-bromomethylenefluorene.

Coleman and coworkers[2] have shown that 1,1-diaryl-2-haloethenes undergo with potassium amide in liquid ammonia the α-elimination of hydrogen halide accompanied by the rearrangement of an aryl group to form tolanes. The mechanism has been considered to involve the ionization of the α-hydrogen of the halide by the amide ion, and rearrangement of the resulting carbanion as illustrated below for the bromoethene (Equation 1).[3,4]

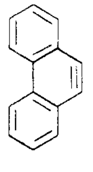


$$(C_6H_5)_2C{=}C(H){-}Br \xrightarrow[NH_3]{NH_2^-} (C_6H_5)_2C{=}\overset{-}{C}{-}Br \xrightarrow{-Br^-} C_6H_5C{=}CC_6H_5 \quad (1)$$

In the present investigation a study was made of the reaction of the analogous compound in the fluorene series, bromide I, with this reagent. The corresponding rearrangement of bromide I would involve ring enlargement to form a phenanthrene derivative, possibly through intermediate II which would be the phenanthrene analog of benzyne.[5]

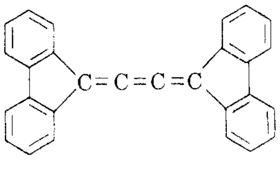


I

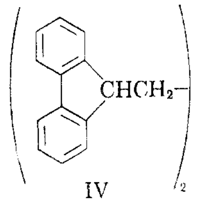


II

However, no phenanthrene derivative was found. Instead, the brick-red solid, cumulene III, and a white solid were obtained. The cumulene (III), which has previously been prepared in other ways,[6,7] was readily identified by its melting point,[6] visible spectrum,[7] and by reduction to IV.[6]



III

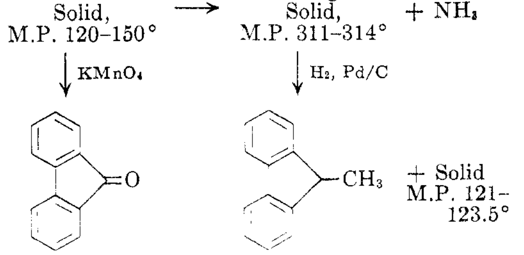


IV

The white solid, which contained nitrogen but no halogen, exhibited an infrared absorption peak due to the N—H group and apparently also one due to a C=N group. It decomposed slowly at room temperatures and rapidly at its melting point, about 120–150°, eliminating ammonia to form a higher-melting orange solid. The latter product showed the same infrared absorption peak assumed for the C=N group but the peak for the N—H group was absent. The analytical values for the orange product, as well as the "neutralization equivalent" of the ammonia eliminated in its formation, suggests that it has the molecular formula $C_{70}H_{47}N_3$ (a pentamer).

Although neither the white solid nor the orange solid derived from it were identified, they both evidently contained the fluorene nucleus since oxidation of the former and reduction of the latter produced fluorenone and 9-methylfluorene, respectively. Also, another product was formed in the latter reaction. These results are summarized in Scheme A.

Scheme A



The yield of cumulene III from bromide I, as well as that of the white product, was dependent on the mode of addition of the reactants. Thus, III was obtained in 95% yield when the potassium amide in liquid ammonia was added slowly to the

---

(1) Supported by the Office of Ordnance Research, U. S. Army.

(2) G. H. Coleman and R. D. Maxwell, *J. Am. Chem. Soc.*, **56**, 132 (1934); G. H. Coleman, W. H. Holst, and R. D. Maxwell, *J. Am. Chem. Soc.*, **58**, 2310 (1936).

(3) C. R. Hauser, *J. Am. Chem. Soc.*, **62**, 933 (1940).

(4) A. A. Bothner-By, *J. Am. Chem. Soc.*, **77**, 3293 (1955).

(5) See J. D. Roberts, C. W. Vaughan, L. A. Carlsmith, and D. A. Semenow, *J. Am. Chem. Soc.*, **78**, 611 (1956).

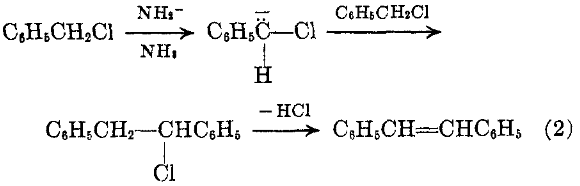
(6) D. Lavie and E. D. Bergman, *J. Org. Chem.*, **18**, 367 (1953).

(7) R. Kuhn and G. Platzer, *Ber.*, **73B**, 1410 (1940).

bromide whereas the yield of this compound was decreased to only 12% when the bromide was added slowly to the reagent. The white solid was the main product under the latter conditions, in which the amide ion was always present in excess. Also, under these conditions some of the cumulene III appeared to be destroyed since, in a blank experiment, only 52% of this compound was recovered after it had been treated with potassium amide in liquid ammonia for one hour.

While potassium amide produced a 95% yield of cumulene III under the most suitable conditions, sodium amide gave only a 51% yield of this product under similar conditions. In a single experiment, lithium amide produced mainly tar.

The conversion of bromide I to cumulene III appears to be analogous to that of α-phenylalkyl halides to dimeric olefins which has been shown to involve a self-alkylation β-elimination mechanism[8,9] as illustrated below with benzyl chloride (Equation 2). In fact, intermediate dimeric halides, such as V, have been isolated.[9]

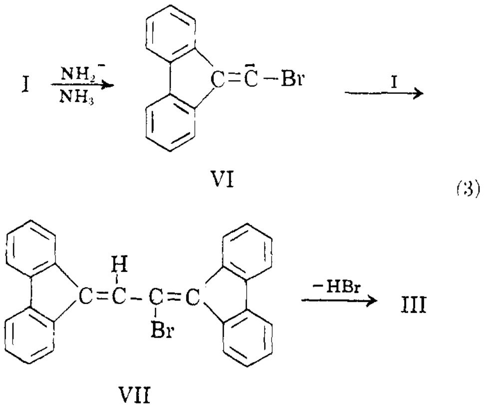


$$C_6H_5CH_2Cl \xrightarrow[NH_3]{NH_2^-} C_6H_5\underset{\displaystyle H}{\overset{-}{C}}—Cl \xrightarrow{C_6H_5CH_2Cl}$$

$$C_6H_5CH_2—\underset{\displaystyle Cl}{C}HC_6H_5 \xrightarrow{-HCl} C_6H_5CH{=}CHC_6H_5 \quad (2)$$

V

The analogous self-alkylation of bromide I to produce cumulene III, which may be regarded as a dimeric olefin, would involve the intermediate formations of carbanion VI and dimeric halide VII (Equation 3).

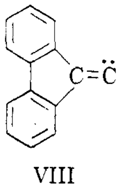


VI

VII

Whereas the addition of one half of an equivalent of sodium amide to benzyl chloride produced dimeric halide V in good yield,[9] these conditions failed to yield dimeric halide VII, the only isolable material being cumulene III (23%) and recovered bromide I (43%). However, this does not necessarily mean that dimeric halide VII is not an intermediate since its dehydrohalogenation (β-elimination) might be expected to proceed faster than the self-alkylation of bromide I which is a vinyl type halide.

An alternative mechanism would involve the loss of bromide ion from intermediate carbanion VI to form carbene VIII which undergoes dimerization to give cumulene III. This mechanism of formation of cumulene III appears less likely than that involving self-alkylation (Equation 3) since such a carbene as VIII might be expected to add the elements of ammonia, which is present in large excess, more readily than undergo dimerization. On the other hand, the formation of the white product mentioned above might have involved the addition of ammonia or the amide ion to carbene VIII to form an enamine which underwent further reaction. Thus, not only did the white product contain nitrogen but its formation was favored when the amide ion was present in excess and the halide in minimum amounts.

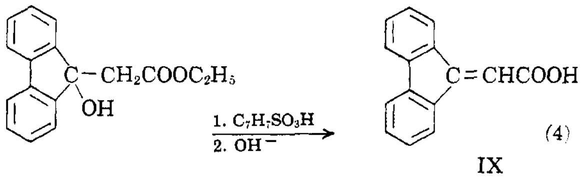


VIII

It is of interest that, regardless of the mechanisms, the formations of cumulene III and of the white product did not involve the type of rearrangement exhibited by 1,1-diphenyl-2-bromoethene to which bromide I is structurally analogous. Apparently the energetics that would be involved in the enlargement of the five-membered ring within carbanion VI to form the phenanthryne (II) are unfavorable.

Finally, it should be mentioned that α,β-unsaturated acid IX from which bromide I was prepared was synthesized more conveniently than previously.[10] This was accomplished in an over-all yield of 72% from 9-fluorenone by an adaptation of the method developed recently in this laboratory[11] employing two equivalents of lithium amide to one of ethyl acetate and one of the ketone (Equation 4). α,β-Unsaturated acid IX was converted to bromide I by the method of DeTar and co-workers.[10]

$$CH_3COOC_2H_5 \xrightarrow{2\ LiNH_2} LiCH_2COOC_2H_5 \xrightarrow{\text{fluorenone}}$$



IX

---

[8] M. S. Kharasch, W. Nudenberg and E. K. Fields, *J. Am. Chem. Soc.*, **66**, 1276 (1944).

[9] C. R. Hauser, W. R. Brasen, P. S. Skell, S. W. Kantor and A. E. Brodhag, *J. Am. Chem. Soc.*, **78**, 1653 (1956).

[10] See D. R. F. DeTar, E. Broderick, G. Foster and B. D. Hilton, *J. Am. Chem. Soc.*, **72**, 2183 (1950).

[11] C. R. Hauser and J. K. Lindsay, *J. Am. Chem. Soc.*, **77**, 1055 (1955).

EXPERIMENTAL[12]

9-Fluorenylideneacetic acid (IX). Ethyl acetate (17.6 g., 0.20 mole) in 80 ml. of ether was added to a suspension of 0.44 mole of lithium amide (from 3.0 g. of lithium), in 600 ml. of liquid ammonia.[11] After stirring for 10 min., a solution of 36.0 g. (0.20 mole) of 9-fluorenone in 400 ml. of ether was added to the grey suspension. When all the ketone had been added the ammonia was displaced by 160 ml. of ether and the greenish grey suspension stirred under reflux for 2 hr. The mixture was allowed to cool and treated with 200 ml. of cold dilute hydrochloric acid; the organic layer was separated, washed with water, with saturated sodium bicarbonate solution, and again with water. The ethereal solution was then dried over sodium sulfate and the solvent was removed to leave behind 51.0 g. of an amber oil.

The product of the above reaction and 2.5 g. of *p*-toluenesulfonic acid in 500 ml. of benzene was brought to reflux. After the evolution of water had ceased (70 min.) solid sodium bicarbonate was added, the solution was washed with water, and the solvent was removed *in vacuo.* On cooling, the residue formed a crystalline mass.

This solid was dissolved in 180 ml. of ethanol containing 20 g. of sodium hydroxide and 20 ml. of water. The resulting blue solution was heated under reflux for 2.5 hr. At the end of this time the solution was poured into 1.2 l. of water, and this was washed with ether. Acidification of the alkaline aqueous solution afforded a yellow precipitate. The acid thus obtained was collected by filtration, dried, and recrystallized from ethanol to yield 32.0 g. (72%) of acid IX, m.p. 223.5–224.5°, lit.[13] 227–228°.

Conversion of acid IX *to bromide* I. Acid IX (5.56 g., 0.025 mole) was dibrominated and then the dibromide treated with aqueous base in the manner described by DeTar and co-workers[10] to afford 3.80 g. of (I), m.p. 73.5–74.5°, and a second crop of 1.23 g., m.p. 71–73° (total yield, 78%).

Reaction of bromide I *with potassium amide. A. Inverse addition procedure.* Potassium amide (0.011 mole) was prepared from 0.42 g. of potassium and 100 ml. of liquid ammonia in an inverse addition flask. Over a period of 25 min. the base was added to a solution of 2.44 g. (0.010 mole) of bromide I in 30 ml. of ether and 100 ml. of liquid ammonia. A brick-red solid precipitated as the addition proceeded. After a total reaction time of 40 min., 5 g. of ammonium chloride was added to the mixture and the ammonia allowed to evaporate. The residual solid was washed with water and then ether. After drying, 1.60 g. (95%) of red solid remained. This was recrystallized from anisole to yield 1.37 g. (80%) of cumulene III (red crystals), m.p. 309° (charring) lit.[6] 302°; λ_{max}, 488, 453 mμ (pyridine), lit.[7] λ_{max} 488, 454 mμ.

A suspension of 0.30 g. of the red compound (III) and 0.15 g. of 10% palladium on charcoal in 75 ml. of ethyl acetate was stirred under hydrogen until the theoretical amount (58 ml.) of gas had been taken up. The catalyst was removed by filtration and the solvent evaporated. The residual solid was recrystallized from benzene ethanol to yield 197 mg. of IV, m.p. 228–229°; lit.[8] 223–224°.

B. Addition of bromide I *to potassium amide.* A solution of 5.0 g. (0.02 mole) of the halide in 200 ml. of ether was added to 0.045 mole of potassium amide (from 1.8 g. of potassium) in 400 ml. of liquid ammonia with vigorous stirring over 1.5 hr. After an additional hour ammonium chloride was added and the ammonia allowed to evaporate. The reddish residue was washed with 500 ml. of ether in portions. After the solid was washed with water and dried, 0.42 g. (12%) of the red cumulene III remained.

The ether extracts were then washed with water and taken to dryness under vacuum at room temperature. A white (sometimes yellowish) solid remained, m.p. 125–150° (dec.); λ_{max} 2.90, 3.00, 6.05 μ. Since this solid darkened on standing at room temperature, and more quickly in solution, it could not, in the authors' hands, be further purified, either by crystallization or chromatography. All further reactions of this were undertaken with the material as obtained from the reaction.

Oxidation of white product. A solution of 2.1 g. of the white solid in 50 ml. of acetone was added to a hot solution of 10 g. of potassium permanganate in 100 ml. of water. The reaction was stirred under gentle reflux as in the course of 8 hr. 40 g. of additional potassium permanganate was added. When the reaction had cooled the manganese dioxide was removed by filtration and washed well with water. Concentration of the alkaline washes to 30 ml. and subsequent acidification failed to yield any organic material.

The air dried manganese dioxide was washed well with ether. When this solution was taken to dryness 0.95 g. of reddish gum remained. This was chromatographed on an alumina column to afford 0.50 g. of orange crystals m.p. 82–84°, and 60 mg. m.p. 80–83°. A mixed melting point of the first fraction with an authentic sample of 9-fluorenone was 82–84°.

Deammoniation of white product to form orange compound. A carefully weighed sample (0.7660 g.) of the white solid was heated to 160° under a stream of nitrogen and the exit gas bubbled through water. At the end of 1 hr. the evolution of ammonia had ceased. The "neutralization equivalent" of the water in the trap was 442; calcd. for $C_{70}H_{47}N_3$, 465, (assuming loss of two molar equivalents of ammonia).

The dark solid was recrystallized from anisole to afford 0.51 g. of dark needles, m.p. 304–310° (dec.).

A small sample was recrystallized to constant m.p. 311–314° (dec.); λ_{max} 6.05 μ (red in presence of base and yellow in acid).

Anal. Calcd. for $C_{70}H_{47}N_3$: C, 90.43; H, 5.10; N, 4.52. Found:[14] C, 90.46, 90.39; H, 5.14, 5.04; N, 4.52, 4.57.

Catalytic reduction of orange compound. A suspension of 380 mg. of V and 200 mg. of 10% palladium on charcoal in 20 ml. of ethyl acetate was stirred under hydrogen for 4 hr., with the uptake of 78 ml. of gas (3.4 mmole). The oily gum which remained when the solvent was removed partly crystallized on standing. Recrystallization from methanol afforded 120 mg. of solid m.p. 100–120°. A sample was recrystallized to constant m.p. 121–123.5°.

Anal. Found: C, 89.87; H, 6.23; N, 4.05.

Chromatography of the gums obtained from the mother liquors of the first crystallization afforded 80 mg. of crystals m.p. 41–43°, whose ultraviolet absorption spectrum is identical with that of 9-methylfluorenone.

Attempted isolation of dimeric halide VII. A solution of sodium amide prepared from 0.12 g. (0.0052 mole) of sodium and 100 ml. of liquid ammonia was added to 2.57 g. (0.010 mole) of the bromide I, over 30 min. The red solid came out almost immediately. The reaction mixture was then worked up in the usual manner to afford 0.40 g. (22.5%) of cumulene, m.p. 298°.

The ether washes were taken to dryness to leave behind a tarry partially crystalline residue. This was dissolved in chloroform and passed through a short alumina column to yield 1.10 g. (43%) of starting material, m.p. 68–72°.

In one run where a full equivalent of sodium amide was added to the bromide I, the yield of cumulene obtained was 52%.

DURHAM, N. C.

---

[12] All melting points are uncorrected. Analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

[13] A. Sieglitz and H. Jassoy, *Ber.*, **54**, 2133 (1921).

[14] The two values represent different samples.