tion was refluxed two hours, 30 ml. of water added, and the solution refluxed two more hours. After hydrolysis the solvent was removed at the vacuum of the water pump. The product was dissolved in 200 ml. of water with the aid of a few drops of hydrochloric acid, the benzoic acid extracted with benzene and the compound precipitated by addition of dilute sodium hydroxide to a pH of 5.5. The product was dissolved in 200 ml. of dilute sodium hydroxide, filtered, and precipitated by addition of hydrochloric acid to pH 5.5. Yields from the benzamido derivative were 80 to 90%. The compound crystallized as small, predominantly hexagonal plates, melting with decomposition at 250°.

Anal. Calcd. for $C_{11}H_{13}O_2NSe$: N, 5.15; Se, 29.01. Found: N, 5.13; Se, 28.8.

α,α'-**Diamino-γ,γ'-diseleno-dibutyric Acid, IV. A. By Reduction with Sodium in Liquid Ammonia.**—II was reduced with sodium in liquid ammonia by following the procedure used for the reduction of β-(benzylseleno)-alanine[2] to obtain the diselenide. The recovery of IV is about 90% of the theoretical. Less selenium is cleaved in the reduction and subsequent aeration than in the preparation of the selenium analog of cystine. The compound crystallized as sheets or plates mostly as parallelograms decomposing at 260°.

Anal. Calcd. for $C_8H_{16}O_4N_2Se_2$: N, 7.74; Se, 43.61. Found: N, 7.71; Se, 43.3.

B. By the Reaction of I with Sodium Hydrogen Selenide.—When I reacted with sodium hydrogen selenide by a procedure similar to that described for the preparation of the selenium analog of cystine from methyl α-amino-β-chloropropionate hydrochloride,[2] the yield of IV was less than 20%. Apparently yields are low because prolonged heating in acid solution is necessary to hydrolyze the ester and benzoyl group.

α-**Amino-γ-(methylseleno)-butyric Acid, V.**—To 4 g. of IV in about 150 ml. of liquid ammonia, small pieces of sodium were added until the blue color persisted for ten minutes, then 4 ml. of methyl iodide was added. The last of the ammonia was driven off by warming on the steam-bath. Ten ml. of 10% sodium hydroxide was added and the solution heated to boiling. The volume was increased to about 150 ml. and the solution neutralized (pH of 6) with hydriodic acid. A small amount of free iodine was present (by starch test) so the solution was extracted three times with ether. The volume was reduced to about 75 ml., and 1.5 volumes of methyl alcohol added. After cooling overnight in the refrigerator 2.6 g. of the selenium analog of methionine was obtained. The filtrate was evaporated to 20 ml. and an additional 1.1 g. (6.88% N) obtained. The amino acid can be recrystallized by dissolving in hot water and adding one volume of methyl alcohol. Yields of 80% have been obtained from IV. With II yields have been slightly less. The compound crystallizes in transparent, hexagonal sheets or plates. It is pure white and has a metallic luster. It melted with decomposition at 265°.

Anal. Calcd. for $C_5H_{11}O_2NSe$: N, 7.14; Se, 40.26. Found: N, 7.09; Se, 39.8.

Summary

The selenium analog of S-benzylhomocysteine has been prepared and this compound has been reduced with sodium in liquid ammonia to give, after oxidation in air, the selenium analog of homocystine (α,α'-diamino-γ,γ'-diseleno-dibutyric acid). When methyl iodide is added to the reduced form in liquid ammonia, the selenium analog of methionine (α-amino-γ-(methylseleno)-butyric acid) is formed.

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Photochemical Bromination of Fluorene[1]

BY JOHN R. SAMPEY AND E. EMMET REID

Introduction

The photochemical bromination of fluorene has not been studied. The similarity of the 9-bromofluorene to a side-chain bromo compound suggested that it might be prepared by the photochemical bromination of fluorene instead of *via* the fluorenol.[1a] We have found this to be the case.

Experimental

9-Bromofluorene.—To a solution of 8.3 g. of fluorene in 100 ml. of carbon tetrachloride in a 20-cm. evaporating dish under a strong mercury arc, or in direct sunlight,[2] 50 ml. of a molar solution of bromine in carbon tetrachloride was added dropwise, the rate of addition being

(1) Presented before the Organic Division of the American Chemical Society at the 109th meeting, April 10, 1946, Atlantic City, N. J.

(1a) W. E. Bachmann and J. C. Sheehan, THIS JOURNAL, **62**, 2687-2690 (1940).

(2) The 2-bromofluorene is formed slowly even in the absence of illumination. *Cf.* C. Courtot and C. Vignati, *Bull. soc. chim.*, **41**, 58-64 (1927), and P. C. Clarkson and M. Gomberg, THIS JOURNAL, **52**, 2886 (1930).

adjusted to the disappearance of the brown color. The solvent is evaporated under an air blast, and the residue is recrystallized from hot 78% alcohol; yield 60–64% white needles of 9-bromofluorene, melting 104–105°.

Alcohol of 78% strength was found to be the best solvent for the separation of the 9-bromoisomer from the other products of bromination. The compound is soluble in hot carbon tetrachloride and hot petroleum ether, and fairly insoluble in the cold solvents, but neither solvent gives as good separation from the impurities as does alcohol. By working fast with the alcoholic solution, there was little apparent formation of the ether.

The bromination takes place with equal ease in carbon disulfide (sulfur free), care being taken to keep the inflammable vapors away from the mercury arc. There is less discoloration when the bromination is carried out in a thin-walled Erlenmeyer flask under anhydrous conditions; the flask is equipped with a dropping funnel and a calcium chloride tube; the solution is agitated a few mm. above the mercury arc, the quantity of solvent being cut to 40–50 ml. in the anhydrous bromination.

Hydrolysis of 9-Bromofluorene.—Refluxing 1.0 g. of 9-bromofluorene with 125 ml. of water for 30 minutes, and titrating for bromide ion, showed better than 90% hydrolysis.

Formation of Tetraphenylene-ethylene.—A solution of 4.5 g. of 9-bromofluorene, dissolved in 25 ml. acetone, is

treated with 10 ml. of an alcoholic solution of potassium hydroxide in the cold; allow about half the acetone to evaporate, and add 20 ml. of water to dissolve the potassium bromide and precipitate the red tetraphenylene-ethylene; crystallize from hot carbon tetrachloride; m. p. 185–187°; yield 62%.

Factors Affecting the Rate of Bromination.—The photochemical bromination of fluorene shows the marked negative catalytic effect of sulfur, which has been found to characterize side-chain brominations.[3] A solution of 1.66 g. of fluorene and an equivalent amount of bromine in 30 ml. of carbon bisulfide in a glass-stoppered flask was discolorized within thirteen seconds under the mercury arc. A similar solution to which 0.1 g. of sulfur had been added was exposed for 195 seconds; titration showed that only 35% of the bromination had taken place.

The photochemical bromination of fluorene does not show the pronounced negative catalytic effect of moisture, which has been observed in the bromination of ketones.[4] When the experiments in the preceding paragraph were repeated, after adding 1.0 ml. of water to each, the results in both were the same as without the water.

Summary

1. 9-Bromofluorene may be prepared in 60–64% yields by the photochemical bromination of fluorene.

2. 9-Bromofluorene is readily hydrolyzed in hot aqueous solution.

3. The photochemical bromination shows the pronounced negative catalytic effect of sulfur, which characterizes side-chain brominations.

(3) J. R. Sampey, F. S. Fawcett and B. A. Morehead, THIS JOURNAL, **62**, 1869 (1940).

(4) J. R. Sampey and E. M. Hicks, *ibid.*, **63**, 1098 (1941).

Higher Hydrocarbons.[1] IV.[2] Six Phenyleicosanes and Six Cyclohexyleicosanes

BY FRANK C. WHITMORE, ROBERT W. SCHIESSLER, C. S. ROWLAND[3] AND J. N. COSBY[4]
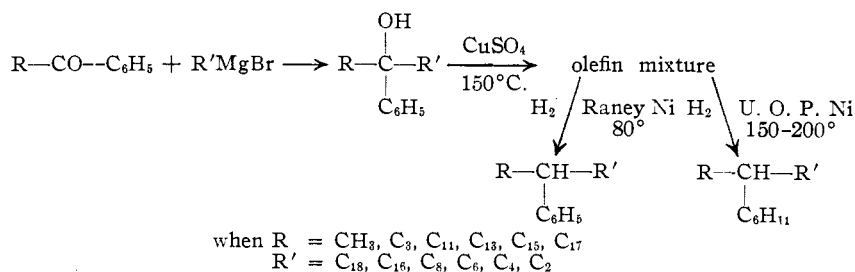
In the continuation of our work on the synthesis and properties of high molecular weight hydrocarbons, the preparations of twelve new monocyclic hydrocarbons are now reported. As pointed out in the second paper[2] of this series, the large variations in physical properties of lubricating oil fractions in a given range of molecular weight is probably primarily due to differences in molecular type; nevertheless, it is important to have a knowledge of the property variations which may be attributed to positional isomers. The present work is aimed at clarifying the latter problem, at least as regards monocyclic derivatives of the paraffins.

Each of the hydrocarbons reported herein consists of a normal twenty-carbon paraffinic chain, with a phenyl or cyclohexyl group attached to one of the chain carbon atoms. They are the 2-, 3-, 4-, 5-, 7- and 9-phenyleicosanes, and the 2-, 3-, 4-, 5-, 7- and 9-cyclohexyleicosanes. The isomers containing the phenyl and cyclohexyl groups in the 1-position, 1-phenyleicosane and 1-cyclohexyl-eicosane, were reported in the third paper[2] of the series.

The phenyleicosanes were synthesized by adding the appropriate phenone to excess of the appropriate alkylmagnesium bromide. For example, the preparation of 7-phenyleicosane involved the addition of myristophenone to excess n-hexylmagnesium bromide. The resulting tertiary carbinols were dehydrated by heating with copper sulfate, and the purified olefins selectively hydrogenated over Raney nickel to the final hydrocarbon (Figs. 1 and 2).

GENERAL METHOD OF SYNTHESIS

$$R\text{—}CO\text{—}C_6H_5 + R'MgBr \longrightarrow R\text{—}\underset{\underset{C_6H_5}{|}}{\overset{\overset{OH}{|}}{C}}\text{—}R' \xrightarrow[150°C.]{CuSO_4} \text{olefin mixture}$$

$$R\text{—}\underset{\underset{C_6H_5}{|}}{CH}\text{—}R' \qquad R\text{—}\underset{\underset{C_6H_{11}}{|}}{CH}\text{—}R'$$

H₂ / Raney Ni 80°   H₂ \ U. O. P. Ni 150–200°

when R = CH₃, C₃, C₁₁, C₁₃, C₁₅, C₁₇
R' = C₁₈, C₁₆, C₈, C₆, C₄, C₂

The cyclohexyleicosanes were prepared by complete hydrogenation at 150–200° over U. O. P. nickel[5] of the phenyl olefins synthesized as above.

Table I summarizes the important properties of the hydrocarbons. The methods of determining the properties listed and their precision and accuracy were discussed in the first paper.[2] Numerous other properties have been determined and will be reported in the appropriate journals.

Experimental

Intermediates.—As emphasized in our earlier papers,[2] great care has been exercised in obtaining pure intermedi-

(1) American Petroleum Institute Project No. 42: Advisory Committee: L. C. Beard, Jr. (Chairman), J. R. Bates, L. M. Henderson, L. A. Mikeska, H. Ramser and S. Tymstra. Presented before the Organic Division, American Chemical Society, New York, 1944.

(2) Whitmore, Sutherland and Cosby, THIS JOURNAL, **64**, 1360 (1942); Whitmore, Cosby, Sloatman and Clarke, *ibid.*, **64**, 1801 (1942); Whitmore, Herr, Clarke, Rowland and Schiessler, *ibid.*, **67**, 2059 (1945).

(3) Present address: Interchemical Corporation, New York, N. Y.

(4) Present address: Allied Chemical Corporation, Morristown, N. J.

(5) Supplied by the Universal Oil Products Co., Chicago, Ill.