diphenylselenium dibromide, the identity of which was confirmed by a mixed melting point with some known diphenylselenium dibromide.[20]

In an entirely similar manner, triphenylselenonium bromide yielded two liquids boiling at 153–156 and 300–304°. The last was obviously diphenyl selenide, the first, bromobenzene (b. p. 156°). The chloride gave the selenide and a liquid boiling at 130–140°, which appeared to be chlorobenzene (b. p. 132°).

Summary

1. A method has been described for the synthesis of triphenylselenonium chloride, $(C_6H_5)_3SeCl$, by the action of benzene upon diphenylselenium dichloride in the presence of aluminum chloride.

2. From triphenylselenonium chloride the following salts have been prepared by metathesis: the bromide, iodide, dichromate, picrate and nitrate. Triphenylselenonium hydroxide appears to be a base of moderate strength.

3. The chloride, bromide and iodide have been shown to decompose with heat to give diphenyl selenide and chloro-, bromo- or iodobenzene, respectively.

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[CONTRIBUTION FROM THE PEARSON MEMORIAL LABORATORY OF TUFTS COLLEGE]

THE BROMINATION OF DESYLACETOPHENONE

BY CHARLES F. H. ALLEN AND ERNEST F. HERRMANN

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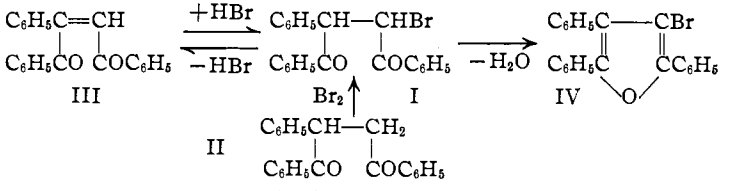
In an earlier paper[1] in which it was shown that bromofurans are produced when diacylstyrenes are treated with hydrogen bromide, the assumption was made that an open-chain addition product containing bromine was an intermediate product. Such a substance could form the ring compound by a loss of water from its enolic modification. Although the reaction undoubtedly took this course, unfortunately we were unable to isolate this bromo ketone (I)



In an attempt to prepare the latter substance, desylacetophenone (II), the saturated diketone corresponding to phenyldibenzoylethylene (III), was treated with bromine. In both chloroform and acetic acid solutions a quantitative yield of the bromofuran (IV) was obtained. Since the pri-

[20] Krafft and Vorster, *Ber.*, **26**, 2818 (1893).

[1] Allen and Rosener, THIS JOURNAL, **49**, 2110 (1927).

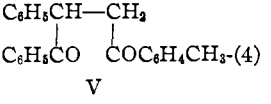
mary reaction was one of substitution, as evidenced by the copious evolution of hydrogen bromide, it was indicated that such a bromo ketone was undoubtedly formed. The closing of the ring doubtless was brought about by the dehydrating action of the hydrogen bromide. Acting upon this assumption, the bromination was carried out in acetic acid solution in the presence of a large amount of potassium acetate, a reagent which has previously been shown to be efficacious in removing hydrogen bromide as rapidly as formed.[2] Under these conditions and using small amounts it was found possible to isolate an open-chain bromo ketone (I) from the mixture. It was found that if large quantities were used, most of the product was the bromofuran, even when a considerable excess of potassium acetate was present. Evidently the acetic acid, acting as a dehydrating agent on a part of the bromo ketone first formed, brought about ring closure during the slow bromination.

We hoped that by selecting a solvent such as ethyl acetate, which was not a dehydrating agent, and using a limited amount of hydrogen bromide, it might be possible to isolate the open-chain bromo compound, starting with phenyldibenzoylethylene. This procedure was unsuccessful, a nearly quantitative yield of bromofuran being obtained.

On treatment with dehydrating agents the open-chain bromo compound loses the elements of water and forms the bromofuran (IV). Alcoholic potash, however, removes hydrogen bromide with consequent production of phenyldibenzoylethylene (III). The relation between these various compounds is shown in the outline above.

Experimental

The desylacetophenone was made by Smith's method.[3] Two homologs, using *p*-methylacetophenone and methyl α-thienyl ketone, were also prepared in the same way.



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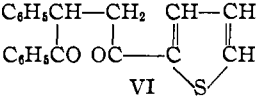

VI

	Substance	M. p., °C.	Analysis Calcd. C	Calcd. H	Found C	Found H
V	$C_{23}H_{20}O_2$	122	84.1	6.1	83.8	6.3
VI	$C_{20}H_{16}O_2S$	126	75.0	5.0	74.8	5.2

Bromination.—Five grams of desylacetophenone was dissolved in 25 cc. of warm glacial acetic acid, a little of the solution transferred to a test-tube and 3.1 g. of pulverized dry potassium acetate added to the remainder, the whole being in a flask fitted with a stirrer, condenser and dropping funnel, the end of which was drawn out into a fine capillary. A little bromine was added to the sample in the test-tube, and once hydrogen bromide was evolved the whole was introduced into the flask. A solution of 2.5 g. of bromine in 6 cc. of acetic acid was admitted, drop by drop, while stirring vigor-

[2] Kohler, Graustein and Merrill, THIS JOURNAL, **44**, 2549 (1922).

[3] Smith, *J. Chem. Soc.*, **57**, 649 (1890).

ously and refluxing in bright sunlight. The red bromine color was still present after boiling for two and a half hours. The mixture was poured into 200 cc. of water containing 5 g. of sodium bisulfite and the oily gum formed removed. The accumulated product from several runs was combined and after a tedious process of fractional crystallization, an open-chain bromo compound (I) and unchanged desylacetophenone (II) were separated in crystal form. The average yield of solid from several runs was 50%, only half of which was the desired bromine compound.

1,2,4-Triphenyl-3-bromobutandione-1,4 (I) crystallizes in long white needles that melt at 119° and decompose at 130°. It is readily soluble in all the usual organic solvents except petroleum ether.

Anal. Calcd. for $C_{22}H_{17}O_2Br$: Br, 20.4. Found: Br, 20.2.

When 30 g. of ketone was brominated in a similar way, the only solid containing halogen that could be isolated was 2,3,5-triphenyl-4-bromofuran (IV). This was doubtless owing to the dehydrating action of the acetic acid on the open-chain bromoketone, since it took several hours to add all the bromine.

Bromination in both chloroform and acetic acid in the absence of potassium acetate gave practically quantitative yields of the bromofuran. Thus 5 g. of desylacetophenone in 25 cc. of hot chloroform reacted instantly with the calculated amount of bromine in the same solvent, with copious evolution of hydrogen bromide. After evaporating about one-half and washing with sodium bisulfite, addition of two volumes of methyl alcohol caused the bromofuran to crystallize. This was filtered and a further amount obtained by partial evaporation of the filtrate. The total amount was 5 g. or 85%; it was identified as triphenylbromofuran by comparison with an authentic specimen.

The difference in the results of the two methods indicates that the hydrogen bromide formed must be involved in some way. Since it is known to accelerate the rate of enolization of ketones and because bromine combines rapidly with enolic forms in the absence of potassium acetate, the apparent substitution reaction is much faster; part of the hydrogen bromide may act as a dehydrating agent on the bromo ketone, which by loss of water forms the bromofuran. In the absence of hydrogen bromide, bromination is so slow that other reactions take place, accounting for the large amount of oily product and small amount of bromo ketone. If the treatment with bromine was prolonged until all of the desylacetophenone had disappeared, then the bromofuran appeared, formed by dehydration of the open-chain compound.

Hydrogen Bromide on Phenyldibenzoylethylene in Ethyl Acetate.—To 2 g. of phenyldibenzoylethylene in 25 cc. of hot ethyl acetate was added 2 g. of hydrogen bromide gas and the yellowish solution allowed to evaporate in a current of air. The only product was the bromofuran.

Alcoholic Potash on the Open-Chain Bromo Ketone.—Two-tenths gram of bromo ketone was added to 10 cc. of hot alcoholic potash; it rapidly dissolved. After five minutes the solution was cooled and acidified with acetic acid; 0.14 g. of yellow crystals of phenyldibenzoylethylene (III) slowly separated and was identified by comparison with an authentic specimen. The bromofuran is unaffected by prolonged boiling with alkalies.[1]

Dehydrating Agents on the Bromo Ketone.—A solution of 0.2 g. of bromo ketone in 10 cc. of glacial acetic acid was refluxed for two hours, poured into water and the precipitated gum taken up in a small amount of chloroform. On adding two volumes of alcohol, white, fluffy needles of the bromofuran crystallized in a quantitative yield. Acetic anhydride acted in a similar manner.

This work has been assisted by a grant from the Cyrus M. Warren Fund of the American Academy of Arts and Sciences,

Summary

1. Desylacetophenone reacts with bromine to form a monosubstitution product, which can be isolated only if the reaction is carried out in the presence of potassium acetate. In the absence of the latter reagent, ring closure takes place with formation of triphenylbromofuran.

2. The structure of the bromo ketone has been determined.

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THE MOLECULAR WEIGHT OF BENCE-JONES PROTEIN

BY THE SVEDBERG AND BERTIL SJÖGREN

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Certain diseases, especially myelomas, are characterized by the appearance in the urine of a peculiar protein called after its discoverer Bence-Jones protein.[1] The question of the origin of this abnormal product of cell life has caused much discussion. The comparative rareness of cases which are accompanied by the appearance of this protein has hampered the study of its properties. Recently such a case was reported from the Academic Hospital in Upsala and by courtesy of Professor G. Bergmark we received a sufficient quantity of urine for an ultracentrifugal investigation. In view of the fact that one of the theories about the origin of Bence-Jones protein considers it to be a product of protein cleavage, the determination of its molecular weight seemed to us to be of great interest. From analytical data Cohn has calculated a minimal molecular weight of 24,500,[2] but judging from the results of similar computations compared with the results of ultracentrifugal determinations no certain conclusion as to *the actual molecular weight in aqueous solution* can be drawn from his calculation.

Preparation of Material.—To 2400 cc. of urine were added 4800 cc. of saturated ammonium sulfate solution and some toluene as a preservative. After standing for twenty-four hours at 0° the precipitate was centrifuged off and washed repeatedly with a mixture of two parts of saturated ammonium sulfate and one part of water. The precipitate was then dissolved in the smallest possible volume of water and reprecipitated with ammonium sulfate solution to a saturation degree of 60%. After standing for twenty-four hours at 0°, the precipitate was filtered off and washed with ammonium sulfate solution of 60% saturation. This material was divided in two parts. One portion was dissolved in phosphate buffer of P_H 5.5 (0.095 *M* in KH_2PO_4 and 0.005 *M* in Na_2HPO_4) and dialyzed at 0° against the same buffer for six days, after which time the SO_4-reaction was negative; volume of solution, 50 cc., concentration 1.19% (Ma-

[1] See Wells, "Chemical Pathology," Saunders Co., Philadelphia and London, 5th ed., 1925, p. 596.

[2] Cohn, Hendry and Prentiss, *J. Biol. Chem.*, 63, 764 (1925).