place at that temperature, and that it is reasonable to assume that none took place during the process of distillation, at a lower temperature.

In conclusion, the helpful criticism of Dr. A. A. Noyes and of Dr. M. L. Huggins is gratefully acknowledged.

Summary

1. The action of alcoholic potassium hydroxide on 2-bromobutane results in the formation of butenes consisting of approximately 86% of *cis*-2-butene and 14% of *trans*-2-butene and no 1-butene.
2. The action of alcoholic potassium hydroxide on 2-bromopentane results in the formation of pentenes consisting of approximately 71% of 2-pentene and 29% of 1-pentene.
3. An explanation of these phenomena is offered from the standpoint of electron displacement.
4. A new hypothesis of the mechanism of substitution processes is offered, which states that substitution takes place most easily at the point where electrons are least firmly held by carbon.
5. A new type of valence bond is proposed, by means of which the direction of electron displacements can be readily indicated.

Pasadena, California

[Contribution from the Chemical Laboratory of the University of Michigan]

THE PREPARATION OF TRIARYLMETHYL ACETATES

By C. S. Schoepfle

Received March 5, 1925 Published May 5, 1925

The only method which has been available for the preparation of triarylmethyl acetates is the reaction of silver acetate upon the triarylmethyl halides.[1] Acetic anhydride does not react with triaryl carbinols, and acetyl chloride or acetyl bromide gives the triarylmethyl chloride or bromide, respectively. It has now been found that silver acetate can be replaced to advantage by ammonium acetate. Triphenyl-bromomethane when shaken for ten hours with dry, finely divided ammonium acetate in benzene gives an almost quantitative yield of triphenylmethyl acetate (triphenyl-chloromethane reacts similarly but the reaction is much slower). Moreover, the acetate is formed when dry ammonia is passed into a solution of triphenyl-bromomethane to which a small amount of acetic acid has been added. Two products are possible in this case; the bromide may react with the ammonium acetate to give the acetate, or it may react with the excess ammonia to give the amine.

$$R_3C\text{—}Br + CH_3COONH_4 \longrightarrow R_3C\text{—}O\text{—}COCH_3 + NH_4Br \qquad (1)$$

$$R_3C\text{—}Br + 2NH_3 \longrightarrow R_3C\text{—}NH_2 + NH_4Br \qquad (2)$$

The first reaction proceeds with sufficient rapidity so that with an excess of acetic acid present, practically no amine is formed.

---

[1] Gomberg and Davis, *Ber.*, **36**, 3924 (1903).

Consequently, the triaryl carbinols can be used as the starting products in the preparation of the acetates. The carbinol is treated in benzene with acetyl bromide to obtain the triarylmethyl bromide, a small amount of acetic acid is added, and then the solution is saturated with dry ammonia. The excess of acetyl bromide reacts with ammonia to give aceto-amide, most of which separates from the solution with the ammonium salts since aceto-amide is but slightly soluble in cold benzene. The precipitate is filtered off, the benzene evaporated, and the residue heated for a short time on the steam-bath under reduced pressure to effect the removal of the remaining small amount of aceto-amide by sublimation. The product is then dissolved in petroleum ether or in ether, from which the acetate is usually obtained pure by a single crystallization. Several triarylmethyl acetates have been prepared in this manner with yields of more than 90%. Two of the corresponding triarylmethyl amines have also been prepared and described.

Triphenylmethyl Acetate.—1. Two g. of triphenyl-bromomethane and 4 g. of dry, finely divided ammonium acetate in benzene were shaken for ten hours. The ammonium salts were then filtered off, the benzene was evaporated, and the residue dissolved in petroleum ether from which the acetate crystallized; yield, 1.80 g., or 96%.

Anal. Subs., 0.5115: 16.32 cc. of 0.1 N NaOH (for hydrolysis). Calcd. for $C_{21}H_{18}O_2$: 16.92 cc.

2. A solution of 2 g. of bromide and 4 g. of anhydrous acetic acid in benzene was saturated with dry ammonia; the ammonium salts were filtered off, and the acetate was obtained as described above; yield, 1.75 g., or 94%.

Anal. Subs., 0.5105: 16.35 cc. of 0.1 N NaOH. Calcd.: 16.89 cc.

3. Five g. of triphenyl carbinol in benzene was treated with 4 g. of acetyl bromide, 2.5 g. of acetic acid was added, and after a few minutes the solution was saturated with dry ammonia and allowed to stand for several hours. The precipitated aceto-amide and ammonium salts were then filtered off, the benzene was evaporated and the residue heated on the steam-bath under reduced pressure to remove the remainder of the aceto-amide. The product was crystallized from petroleum ether; yield, 5.45 g., or 94%.

Anal. Subs., 0.5052: 16.42 cc. of 0.1 N NaOH. Calcd.: 16.71 cc.

α-Naphthyl-diphenyl-methyl Acetate.—Five g. of α-naphthyl-diphenyl carbinol in benzene was treated with 4 g. of acetyl bromide, 2.5 g. of acetic acid was added and after a few minutes the solution was saturated with dry ammonia. The acetate was obtained by the procedure described above except that ether instead of petroleum ether was used for crystallization; yield, 5.25 g., or 92%. It crystallizes from ether in colorless, elongated plates; m. p., 137–138°. It is readily soluble in benzene and in ethyl acetate, fairly soluble in ether, and slightly soluble in petroleum ether.

Anal. Calcd. for $C_{25}H_{20}O_2$: C, 85.20; H, 5.72. Found: C, 85.20; H, 5.70. Subs., 0.5878: 16.05 cc. of 0.1 N NaOH. Calcd.: 16.69 cc.

Di-α-naphthyl-phenyl-methyl Acetate.—Five g. of di-α-naphthyl-phenyl carbinol (containing 1.5 moles of benzene of crystallization) was dissolved in benzene and treated with 4 g. of acetyl bromide; 2.5 g. of acetic acid was added and after a few minutes, the solution was saturated with dry ammonia. Following the procedure outlined above, the acetate was obtained from ether in short, colorless needles; yield, 3.90 g., or 93%. The crystals turn brown at about 190° and melt with decomposition above 200°. The compound is readily soluble in benzene, slightly soluble in ethyl acetate, and very slightly soluble in ether and in petroleum ether.

Anal. Calcd. for $C_{29}H_{22}O_2$: C, 86.53; H, 5.51. Found: C, 86.27; H, 5.57. Subs., 0.5031: 11.93 cc. of 0.1 *N* NaOH. Calcd.: 12.50 cc.

α-Naphthyl-diphenyl-aminomethane.—Five g. of α-naphthyl-diphenyl-bromomethane was dissolved in benzene and the solution saturated with dry ammonia. The precipitated ammonium bromide was filtered off, the benzene evaporated, and the residue dissolved in ether from which the amine was obtained in large, colorless crystals; m. p., 168–169°; yield, 3.95 g., or 95%. The compound is readily soluble in benzene, slightly soluble in ether and very slightly soluble in alcohol and in petroleum ether.

Anal. Calcd. for $C_{23}H_{19}N$: N, 4.53. Found (Kjeldahl): 4.50.

Di-α-naphthyl-phenyl-aminomethane.[2]—Two and one-half g. of di-α-naphthyl-phenyl-bromomethane was dissolved in benzene and the solution saturated with dry ammonia. Following the above procedure, the amine was obtained from ether in small, colorless crystals; m. p., 164–165°; yield, 1.75 g., or 82%. The compound is readily soluble in benzene, somewhat soluble in ether and slightly soluble in petroleum ether and in alcohol.

Anal. Calcd. for $C_{27}H_{21}N$: N, 3.90. Found (Kjeldahl): 3.84, 3.89.

Summary

A convenient method for the preparation of triarylmethyl acetates has been described.

α-Napthyl-diphenyl-methyl acetate, di-α-napthyl-phenylmethyl acetate, and the corresponding triarylmethyl amines have been prepared and described.

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL RESEARCH, PARKE, DAVIS AND COMPANY, NO. 31]

TETRA-ALKYL-SUCCINIMIDES AND THEIR PHARMACOLOGICAL ACTION

BY ARTHUR W. DOX

RECEIVED MARCH 5, 1925 PUBLISHED MAY 5, 1925

On account of certain analogies in structure between the dialkyl-barbituric acids and other well-known hypnotics, on the one hand, and the tetra-alkyl-succinimides on the other hand, it was desired to prepare representatives of the latter for the purpose of determining their physiological action. It is commonly supposed that two alkyl groups, particularly ethyls, attached to the same carbon atom tend to impart hypnotic properties to the molecule. Numerous illustrations might be cited, including the simple ketones, the sulfonal series, the dialkyl derivatives of acetylurea I, hydantoin II and barbituric acid III, and the recently described dialkyl-

---

[2] The properties of this compound and also the method of preparation have been incorrectly described in a previous article, THIS JOURNAL, 44, 192 (1922).