[JOINT CONTRIBUTION FROM THE WM. H. CHANDLER CHEMISTRY LABORATORY, LEHIGH UNIVERSITY, AND THE RESEARCH AND DEVELOPMENT DIVISION, SMITH, KLINE AND FRENCH LABORATORIES]

Decomposition of Quaternary Ammonium Salts[1]

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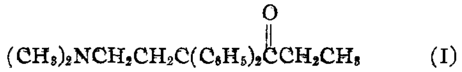
Pyrolytic decomposition of the methiodide of 6-dimethylamino-4,4-diphenyl-3-heptanone gave 3,3-diphenyl-2-ethylidene-5-methyltetrahydrofuran, which was characterized by ozonization to give 2,2-diphenyl-4-pentanolactone and acetaldehyde. The same ethylidenetetrahydrofuran was prepared from 4,4-diphenyl-6-heptene-3-one by addition of hydrogen bromide, followed by removal of hydrogen bromide *in vacuo*. The ethylidenetetrahydrofuran formed a monobromo derivative. Pyrolytic decomposition of both the methiodide and corresponding hydroxide of 6-dimethylamino-4,4-diphenyl-3-hexanone gave 3,3-diphenyl-2-ethylidenetetrahydrofuran. The ethylidenetetrahydrofurans formed adducts with ketonic reagents. 6-Chloro-4,4-diphenyl-3-hexanone was formed from the ethylidenetetrahydrofuran and hydrochloric acid; it readily split off hydrogen chloride to revert to the ethylidenetetrahydrofuran structure.

The decomposition of quaternary ammonium salts has been studied extensively by Hughes and Ingold.[3] They found that two types of reactions took place, usually simultaneously. The predominant one was determined by the characteristics of the salts themselves. These reactions were (1) the removal of an alkyl halide to give the tertiary amine and (2) the cleavage of hydrogen halide salt of the tertiary amine to give the olefin.

Other decomposition reactions which have been reported for quaternary ammonium salts are the carbon alkylation of active methylene compounds such as malonic ester[4] and the various rearrangements such as those reported by Stevens[5] and Hauser.[6] It had also been mentioned[7] that refluxing the quaternary ammonium iodide of methadon in 25% sodium hydroxide causes cleavage of the propionyl group. During chemical studies on methadon (6-dimethylamino-4,4-diphenyl-3-heptanone) we found that the decomposition of the quaternary hydroxide gave the same result, but the pyrolysis of the methiodide was found to give a solid neutral material "A," melting at 79–80°.

A study of the simpler compounds of this type, for example, 6-dimethylamino-4,4-diphenyl-3-hexanone (I), revealed that the decomposition of the quaternary salt of this hexanone gave a solid derivative "B" which melted at 104.5–105.5°, and resembled very closely the product "A." In this case the pyrolysis of the quaternary hydroxide of the hexanone also gave "B."



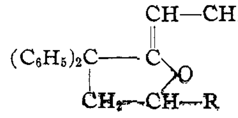
$$(CH_3)_2NCH_2CH_2C(C_6H_5)_2\overset{\overset{\displaystyle O}{\|}}{C}CH_2CH_3 \qquad (I)$$

Both A and B reacted rapidly with bromine to give monobromo derivatives. The bromine atoms in the monobromo derivatives are very unreactive, as shown by their recovery after refluxing in morpholine for 72 hours. Compounds A and B reacted with ketone reagents such as hydroxylamine and 2,4-dinitrophenylhydrazine to give derivatives which analyzed for addition products, without the loss of a molecule of water. No carbonyl band was found in the ultraviolet spectra of compounds A and B.

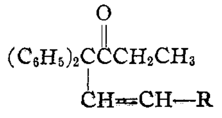
Treatment of A and B with concentrated hydrochloric acid in ethanol gave compounds which contained chlorine. The material obtained from B with hydrochloric acid (VI) could be purified by crystallization from petroleum ether but the corresponding compound from A was not obtained in a pure state. The ultraviolet spectrum of VI indicates the presence of a carbonyl group.

It was believed that an internal alkylation of the gramine type[4] had taken place, but a study of diphenylcyclopentanone[8] and some derivatives proved that the product could not be of this type.

The production of benzophenone from the oxidation of these compounds eliminated the possibility of rearrangement of the phenyl groups. The two remaining possibilities were the tetrahydrofuran derivatives II and the unsaturated ketones III.

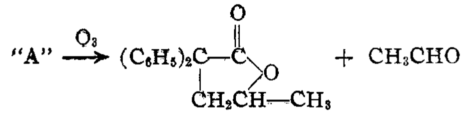


IIa, R = CH_3
IIb, R = H



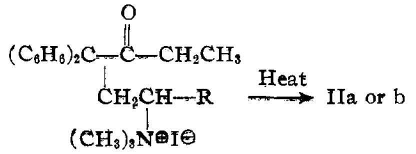
III

Ozonization of compound A gave the lactone IV[9] and acetaldehyde which would be expected from ozonization of a compound of structure IIa.



IV

It was also found that IIa could be obtained from 4,4-diphenyl-6-heptene-3-one by treatment with gaseous hydrogen bromide, followed by distillation which removed hydrogen bromide. These reactions can be indicated as



R = H, CH_3

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(1) Presented before the Division of Organic Chemistry of the American Chemical Society at Atlantic City, N. J., Sept. 18, 1952.

(2) Abstracted in part from the thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) E. D. Hughes and C. K. Ingold, *Trans. Faraday Soc.*, **37**, 657 (1941).

(4) H. R. Snyder and C. R. Smith, THIS JOURNAL, **66**, 350 (1944).

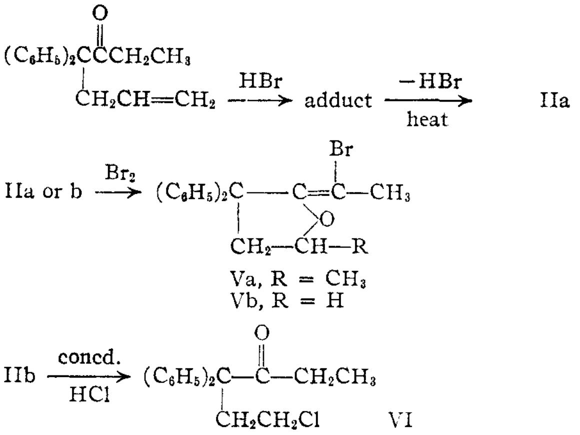
(5) T. S. Stevens, E. M. Creighton, A. B. Gordon and M. MacNicol, *J. Chem. Soc.*, 3195 (1928).

(6) C. R. Hauser and S. W. Kantor, THIS JOURNAL, **73**, 1437 (1951).

(7) E. L. May and E. J. Mosettig, *J. Org. Chem.*, **13**, 663 (1948).

(8) N. R. Easton and S. J. Nelson, THIS JOURNAL, **75**, 640 (1953).

(9) N. R. Easton, J. H. Gardner and J. R. Stevens, *ibid.*, **69**, 2941 (1947).



The ready reversibility of the chloroketone VI back to the ethylidenetetrahydrofuran structure IIb is indicative that the adduct obtained from 4,4-diphenyl-6-heptene-3-one and hydrogen bromide was formed in accordance with Markownikoff's rule.

The formation of the chloroketone VI from IIb can explain the formation of the ketonic derivatives from IIb without the usual loss of water. These derivatives may be considered to be the ketonic derivatives of 4,4-diphenyl-6-hydroxy-3-heptanone but further study of these compounds is in progress.

The preparation and inertness of the bromo derivatives (Va and b) from the ethylidenetetrahydrofurans (IIa and b) is consistent with the results of bromination of a-methylenecoumaran reported by Adams and Rindfusz.[10]

Although Wilson[11] has prepared a compound to which he ascribed formula IIa, another communication[12] has shown that this product was actually 3,3-diphenyl-2-ethyl-5-methyltetrahydrofuran.

Experimental

2-Ethylidene-3,3-diphenyltetrahydrofuran (IIb). a. Pyrolysis of 6-Dimethylamino-4,4-diphenyl-3-hexanone Methiodide.—In a 10-ml. Claisen flask, fitted with a side arm test-tube as a receiver, was placed 3.7 g. of the methiodide of 6-dimethylamino-4,4-diphenyl-3-hexanone. The system was evacuated to about 15 mm. pressure and the flask was heated gently with a free flame. The methiodide first melted and then a clear liquid, that rapidly solidified, distilled as decomposition took place. The product was taken up in ether and the ether solution was washed with dilute hydrochloric acid. The ether layer was then dried and concentrated to dryness. The residue weighed 2 g. On one recrystallization from ethanol it melted at 101–104°. An analytical sample IIb melting at 104.5–105.5° was obtained after two more recrystallizations from alcohol.

Anal. Calcd. for $C_{18}H_{18}O$: C, 86.36; H, 7.24. Found: C, 86.43; H, 7.25.

b. Pyrolysis of the Quaternary Hydroxide.—An aqueous alcoholic solution of 6-dimethylamino-4,4-diphenyl-3-hexanone methiodide was shaken vigorously with excess of silver oxide until a test with silver nitrate showed the liquid to be free of iodide ion. The suspension was filtered, the precipitate washed and the combined filtrate and washings concentrated, with the final evaporation taking place in a 10-ml. distilling flask, the system evacuated, and the residue heated slowly with a micro burner. The hydroxide decomposed with much foaming, and a slightly yellow oil, which crystallized upon standing, distilled. The product was recrystallized twice from alcohol. It melted at 104.5–106.0°, and its melting point was not depressed by the addition of the compound obtained by the pyrolysis of the methiodide.

Oxidation of 2-Ethylidene-3,3-diphenyltetrahydrofuran.—A mixture of 0.9 g. of IIb in acetic acid was oxidized with chromic anhydride on a steam-bath. Benzophenone was isolated in the usual manner. Its semicarbazone, m.p. 161–164°, was prepared. An authentic sample of benzophenone semicarbazone did not depress the melting point.

2-Ethylidene-3,3-diphenyl-5-methyltetrahydrofuran (IIa). a. Pyrolysis of Methadon Methiodide.—This was carried out in the same manner as the first pyrolysis above. The solid (IIa, 3,3-diphenyl-2-ethylidene-5-methyltetrahydrofuran) was recrystallized from ethyl alcohol and melted at 79–80°.

Anal. Calcd. for $C_{19}H_{20}O$: C, 86.32; H, 7.63. Found: C, 86.40; H, 7.99.

b. **From 4,4-Diphenyl-6-heptene-3-one.**—Diethylcadmium was prepared as follows. The Grignard reagent was prepared from 19.5 g. of magnesium, 88 g. of ethyl bromide and 250 ml. of ether. To this Grignard solution was added 100 ml. of ether and 73.0 g. of cadmium chloride over a 45-minute period. Then a solution of 48.7 g. of 2,2-diphenyl-4-pentenoyl chloride[13] in 80 ml. of benzene was added over a 5-minute period. The mixture was stirred at reflux for three hours. The mixture was decomposed with water and hydrochloric acid, and worked up in the usual manner. No acidic material was recovered from the reaction. Distillation gave 40.2 g. of ketone; b.p. 162–172° (4–5 mm.) (85%).

Anal. Calcd. for $C_{19}H_{20}O$: C, 86.32; H, 7.63. Found: C, 86.17; H, 7.87.

3,3-Diphenyl-2-ethylidene-5-methyltetrahydrofuran.—Excess bromine and 0.2 g. of iron filings were mixed in a benzene–ether mixture and heated to dryness on a hot plate. To this catalyst was added 25.8 g. of 4,4-diphenyl-6-heptene-3-one and 100 ml. each of anhydrous ether and chloroform (calcium chloride dried). Dry gaseous hydrogen bromide was introduced into this mixture for one hour at 0°. After standing for two hours at room temperature, the mixture was extracted thrice with water and dried over calcium chloride. Evacuation on the steam-bath left 34 g. of residue (theoretical wt. 33.6 g.). Upon vacuum distillation gaseous hydrogen bromide was evolved at 150° and 3 mm. pressure. After gas evolution ceased, an oil was distilled; b.p. 160–163° (13–14 mm.), 21 g. On standing, this oil crystallized, m.p. 63–68°. Recrystallization from petroleum ether and then from alcohol–water gave 10 g., m.p. 78–79°.

Anal. Calcd. for $C_{19}H_{20}O$: C, 86.32; H, 7.63. Found: C, 86.38; H, 7.48.

The product when prepared in this manner tended to autoxidize, with formation of aldehyde-like odors. The ultraviolet spectrum of this material was identical with that of the same compound prepared from methadon (above). Recrystallization of the bromo derivative from acetic acid and water gave white crystals, m.p. 184–185°. A mixed melting point with the bromo derivative prepared above (m.p. 189–190°) was found to be 186–187°.

Bromination of the Ethylidene Tetrahydrofurans.—The ethylidene tetrahydrofuran was dissolved in carbon tetrachloride and the solution was cooled in an ice-bath. An equivalent of bromine in carbon tetrachloride was added slowly. The bromine color disappeared immediately and the evolution of hydrogen bromide was noticeable. The mixture was concentrated at reduced pressure and the residue was recrystallized from ethanol.

The compound (Vb) melted at 175–177°.

Anal. Calcd. for $C_{18}H_{17}OBr$: Br, 24.28. Found: Br, 24.60.

The compound (Va) melted at 189–190°.

Anal. Calcd. for $C_{19}H_{19}OBr$: C, 66.48; H, 5.58; Br, 23.28. Found: C, 66.50; H, 5.52; Br, 23.30.

Reaction of 2-Ethylidene-3,3-diphenyltetrahydrofuran with Hydrochloric Acid.—A sample of 2-ethylidene-3,3-diphenyltetrahydrofuran was boiled for 10 minutes in a mixture of concentrated hydrochloric acid and ethanol. During this time the solid turned to an oil which crystallized on cooling and scratching, m.p. 72–74°. On several recrystallizations from petroleum ether it melted at 76.5–77.0°.

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(10) R. Adams and R. E. Rindfusz, THIS JOURNAL, 41, 648 (1919).

(11) W. Wilson, *J. Chem. Soc.*, 1993 (1948).

(12) N. R. Easton, C. A. Lukach, V. B. Fish and P. N. Craig, THIS JOURNAL, forthcoming publication.

(13) P. N. Craig and I. H. Witt, *ibid.*, 72, 4925 (1950).

Anal. Calcd. for $C_{18}H_{19}OCl$: C, 75.38; H, 6.68; Cl, 12.36. Found: C, 75.70; H, 6.83; Cl, 12.70.

A broad absorption band at 288 mμ indicates the presence of a carbonyl group (log E 2.67, 95% ethanol).

When methanol was used as the recrystallizing medium only the starting material was isolated.

The product obtained from the treatment of 2-ethylidene-3,3-diphenyl-5-methyl-tetrahydrofuran with concentrated hydrochloric acid and ethanol was not obtained in a pure state. It apparently reverted to the starting material on attempted purification.

Reaction of Hydroxylamine with IIa.—A mixture of 2 g. of the ethylidenetetrahydrofuran (IIa), 2 g. of hydroxylamine hydrochloride and 1 g. of pyridine in ethanol was refluxed for two hours and then allowed to stand overnight. A precipitate appeared which, after recrystallization from ethanol and then several times from methanol, melted at 190–192°.

Anal. Calcd. for $C_{19}H_{23}NO_2$: C, 76.76; H, 7.79; N, 4.71. Found: C, 76.43; H, 7.78; N, 4.65, 4.74.

Reaction of Hydroxylamine with IIb.—The reaction was run as above but since no crystals appeared, the mixture was diluted with water and an oil separated, which soon crystallized, m.p. 160–161° (from methanol).

Anal. Calcd. for $C_{18}H_{21}NO_2$: C, 76.30; H, 7.47; N, 4.84. Found: C, 76.60; H, 7.66; N, 4.94.

The Reaction of 2-Ethylidene-3,3-diphenyltetrahydrofuran with 2,4-Dinitrophenylhydrazine.—A solution of 0.5 g. of IIb and 0.275 g. of 2,4-dinitrophenylhydrazine in 30 ml. of ethanol was acidified with 3 drops of concentrated hydrochloric acid and refluxed 1.5 hours. The resulting solution was concentrated to 20 ml., and 8 ml. of water was added. An oil separated which was redissolved and crystallized on cooling slowly, m.p. 163–165°.

Anal. Calcd. for $C_{24}H_{23}O_5N_4$: N, 12.52. Found: N, 12.45, 12.43.

Ozonization of 3,3-Diphenyl-5-methyl-2-ethylidenetetrahydrofuran.—A chloroform solution of the ethylidenetetrahydrofuran (IIa) was treated with ozone and the ozonide was decomposed on standing overnight with water. The lactone[13] was isolated and identified by melting point and mixed melting points. Acetaldehyde was identified as the 2,4-dinitrophenylhydrazone (m.p. and mixed m.p. with authentic sample).

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BETHLEHEM, PA.

[CONTRIBUTION FROM THE LEWIS FLIGHT PROPULSION LABORATORY OF THE NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS]

Synthesis and Properties of Some Alkylsilanes

BY STANLEY TANNENBAUM, SAMUEL KAYE AND GEORGE F. LEWENZ

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Twelve alkylsilanes have been synthesized and the following physical properties were measured: boiling point, freezing point, index of refraction, molecular weight and density. Vinylsilane and isobutylsilane are reported for the first time. Vapor pressures were measured using a static system, and the heats of vaporization were calculated from the data. By the use of a special sample filling technique, it was possible to measure the heats of combustion in an oxygen bomb calorimeter and then to calculate the heats of formation.

Introduction

As a part of a program at this Laboratory involving the investigation of organometallic compounds, a number of alkylsilanes have been prepared and their physical properties determined. These compounds are methyl-, dimethyl-, trimethyl-, tetramethyl-, ethyl-, diethyl-, triethyl-, tetraethyl-, butyl-, isobutyl-, vinyl- and dimethyldipropylsilane. Isobutylsilane and vinylsilane are reported here for the first time.

Several procedures for the synthesis of alkylsilanes are available.[1–4] One of the most common methods is the Grignard reaction, which involves the interaction of a suitable alkylmagnesium halide with a halosilane in anhydrous ether. The reaction is illustrated by the equation for the preparation of trimethylsilane.[5] This method was used by the authors in the present work to prepare dimethyldipropylsilane and tetraethylsilane.

$$3CH_3MgBr + SiHCl_3 \xrightarrow[\text{ether}]{\text{ethyl}} Si(CH_3)_3H + 3MgBrCl$$

An excellent method for the preparation of a series of alkylsilanes was reported recently.[6] By reduction of the proper alkylchlorosilane with lithium aluminum hydride in anhydrous ethyl ether or dioxane, the alkylsilane can be obtained in high yield and free of side products. This type of reaction is illustrated by the following equation for the synthesis of ethylsilane

$$4Si(C_2H_5)Cl_3 + 3LiAlH_4 \xrightarrow{\text{dioxane}} 4Si(C_2H_5)H_3 + 3LiCl + 3AlCl_3$$

The reaction is rapid, and yields exceeding 80% are not uncommon. This method was chosen to prepare the following compounds: methyl-, dimethyl-, trimethyl-, ethyl-, diethyl-, triethyl-, vinyl-, butyl- and isobutylsilane. In addition, tetramethylsilane was purified from a commercially available product.

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(1) A. Ladenburg, *Ann.*, **164**, 302, 327 (1872).

(2) A. Stock and C. Somieski, *Ber.*, **52**, 695 (1919).

(3) F. C. Whitmore, E. W. Pietrusza and L. H. Sommer, THIS JOURNAL, **69**, 2108 (1947).

(4) E. G. Rochow, "The Chemistry of the Silicones," John Wiley and Sons, Inc., New York, N. Y., 1946, p. 32.

(5) A. G. Taylor and B. V. de G. Walden, THIS JOURNAL, **66**, 842 (1944).

(6) A. E. Finholt, A. C. Bond, Jr., K. E. Wilzbach and H. I. Schlesinger, *ibid.*, **69**, 2692 (1947).