the reaction with sulfur monochloride is one of addition and that at normal temperatures substitution accompanies this phenomenon. Lack of specificity is even more pronounced in this case. The thermal rise which was observed with approximately one-half of the oils whose behavior was studied is about the same as with the sulfur monochloride, but of greater significance is the fact that the rise per minute is appreciably greater. Palm oil is the only one which showed any suggestion of a similar behavior.

Conclusions

The thermal effect which is observed when selenium monochloride acts upon fatty oils is an additive one produced not only by substitution and addition but by the decomposition of the reagent itself. In view of this situation, the use of selenium monochloride under conditions which simulate in a measure those of sulfuric acid[5] is impractical as a test which has any diagnostic value for the fatty oils.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE ACTION OF SILVER ON DIPHENYL-TERTIARY-BUTYLETHYNYLBROMOMETHANE

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It was recently[1] shown that hexa-*tert.*-butylethynylethane reacted with liquid sodium-potassium alloy and with liquid sodium amalgams to give the corresponding alkali metal derivative of tri-*tert.*-butylethynylmethyl, thus indicating that aliphatic acetylenic groups possess the properties necessary to cause weakening of the central bond in a substituted ethane. These results would lead to the prediction that the replacement of two phenyls in hexaphenylethane by acetylenic radicals would not greatly decrease the dissociation. However, Moureu, Dufraisse and Houghton[2] have shown that the action of metals on diphenylphenylethynylchloromethane gives rise to a hydrocarbon which is much more stable than would be expected of *sym.*-tetraphenyldiphenylethynylethane. To gain further knowledge of the effect of acetylenic groups on the stability of hexa-substituted ethanes, a study of the closely related tetraphenyldi-*tert.*-butylethynylethane has been undertaken.

Diphenyl-*tert.*-butylethynylcarbinol was easily prepared from *tert.*-butylethynylmagnesium bromide and benzophenone. The bromide was prepared by the action of phosphorus tribromide on the carbinol. When an ether solution of this bromide was shaken with molecular silver in an

[1] Salzberg with Marvel, THIS JOURNAL, **50**, 1737 (1928).

[2] Moureu, Dufraisse and Houghton, *Bull. soc. chim.*, [4] **41**, 56 (1927).

atmosphere of nitrogen, a greenish-yellow solution with a very slight red fluorescence was obtained. The fluorescence disappeared when a stream of oxygen was run into the flask over the surface of the solution and then reappeared when the supply of oxygen was cut off. This indicated that the solution contained a free radical which was being oxidized. However, when an attempt was made to determine quantitatively the amount of oxygen absorbed it was found that only a very small amount (a few tenths of a cc.) was taken up by the solution. Furthermore, evaporation of the ether left a pure, stable, colorless hydrocarbon and not a peroxide.

This hydrocarbon had the composition of $C_{38}H_{38}$, corresponding to the expected ethane. However, there is some question as to its exact structure. It melts higher (155°) than hexa-*tert.*-butylethynylethane (131°) and this is unexpected since the bromide melts lower than tri-*tert.*-butylethynylbromomethane. The ethane was not cleaved at the ethane linkage by either 40% sodium amalgam or sodium–potassium alloy, as would be expected. It does react with them to give colored solutions of the metal derivative. Carbon dioxide decolorizes this solution but no appreciable amount of water-insoluble acid could be recovered from the reaction mixture. Furthermore, this hydrocarbon was stable toward heat.

In view of the ease with which hexa-*tert.*-butylethynylethane rearranged with heat to give a higher melting hydrocarbon, it was thought that rearrangement might have occurred during the formation of the hydrocarbon $C_{38}H_{38}$ obtained in this work. In order to test this theory, the reaction between the bromide and silver was carried out in the presence of oxygen, which should prevent the rearrangement by the formation of a peroxide. When this reaction was run, oxygen was rapidly absorbed and considerable heat was evolved. When the temperature was not controlled, two or three times the theoretical amount of oxygen was absorbed. By keeping the temperature at 0° the absorption of oxygen was only about one and one-half times the theoretical amount. However, all attempts to isolate a peroxide were unsuccessful. An oily material was obtained that had the odor of benzophenone.

The absorption of oxygen in this experiment is due to some reactive intermediate, presumably diphenyl-*tert.*-butylethynylmethyl. When tri-*tert.*-butylethynylbromomethane was treated with silver in the presence of oxygen, the absorption of oxygen was negligible. This shows that the percentage of free radical normally present in a reaction mixture of this type is not enough to cause oxygen absorption.

The most logical explanation of these observations seems to be that silver reacting with diphenyl-*tert.*-butylethynylbromomethane produces a free radical diphenyl-*tert.*-butylethynylmethyl which in the presence of oxygen is oxidized to products which are of lower molecular weight. In the absence of oxygen the free radical undergoes some rearrangement to produce a stable hydrocarbon $C_{38}H_{38}$. The structure of this hydrocarbon is now under investigation.

Experimental Part

Diphenyl-*tert.*-butylethynylcarbinol.—The Grignard reagent was prepared from 38 g. of *tert.*-butylacetylene by adding it from a dropping funnel to 115 cc. of a 4.116 *N* ether solution of ethylmagnesium bromide over a period of ten hours. The heat of the reaction caused the ether to reflux and a very efficient condenser filled with water at 0–5° was needed to avoid loss of the acetylene. When this reaction was finished a saturated solution of 85 g. of benzophenone in dry ether was added during one hour. The reaction mixture was then stirred for six hours, allowed to stand overnight and finally refluxed for about an hour. The reaction mixture was then decomposed by pouring it onto 500 g. of cracked ice and adding 25 g. of ammonium chloride and just enough dilute hydrochloric acid to dissolve any precipitate of basic magnesium salts. The ether layer was separated, dried over sodium sulfate, filtered and heated on a steam-bath to remove the solvent. The residue was dissolved in an equal volume of petroleum ether (b. p. 40–60°) and the solution was cooled to −15°. The carbinol separated as white crystals; m. p. 63–66.5°. This grade of product was used for preparing the bromide. Recrystallization gave a very pure product which melted at 66.5–67.5°.

Anal. Subs., 0.2370: CO_2, 0.7502; H_2O, 0.1625. Calcd. for $C_{19}H_{20}O$: C, 86.36; H, 7.58. Found: C, 86.32; H, 7.67.

In the first run considerable difficulty was experienced in obtaining a crystalline compound. The crude product was distilled under reduced pressure and the main portion boiled at 132–135° at 0.4–0.5 mm. The supercooled liquid had the following constants: n_D^{25}, 1.5550; sp. gr. $\frac{25}{25}$ = 1.0124. This material crystallized after standing for a few days at −15°.

Diphenyl-*tert.*-butylethynylbromomethane.—Three g. of the carbinol was dissolved in 25 cc. of petroleum ether and the solution cooled to 0°. Then 1 g. of phosphorus tribromide was added and the solution was stirred for one-half hour. To the mixture was added 100 cc. of 10% sodium bicarbonate solution and stirring was continued for ten minutes. The petroleum ether solution was separated, dried over sodium sulfate, filtered and evaporated under reduced pressure at room temperature. The residue was dissolved in 5 cc. of dry ether, 5 cc. of absolute alcohol was added and then the solution was evaporated under reduced pressure until crystals began to form. The mixture was then allowed to stand at 0° overnight in order that all of the bromide might crystallize. The bromide was collected on a filter and dried in a vacuum desiccator. The yield of crude product (m. p. 56.5–59.5°) was 3 g. (81% of the theoretical amount). Recrystallization from alcohol and ether gave a product melting at 58.5–60.5° (corr.).

Anal. (Stepanow). Subs., 0.2626, 0.2112: 17.62, 14.21 cc. of 0.0450 *N* $AgNO_3$. Calcd. for $C_{19}H_{19}Br$: Br, 24.43. Found: Br, 24.12, 24.22.

The Reaction between Diphenyl-*tert.*-Butylethynylbromethane and Silver

(a) **In Air or Nitrogen.**—A solution of 1 g. of the bromide in 15 cc. of dry ether was shaken in a mechanical shaker with 1 g. of molecular silver in a 30-cc. round-bottomed flask for about ten hours. A greenish-yellow solution with a slight red fluorescence resulted. The fluorescence disappeared when a stream of oxygen was passed over the surface of the solution but reappeared after the solution had stood in the air for a few minutes. This could be repeated three or four times before the color failed to reappear. The ether solution was concentrated until crystals began to appear. The mixture was then cooled to 0° until crystallization was complete. These crystals

(m. p. 151.5–154.5, corr.) were collected on a filter. Recrystallization from alcohol and ether gave a product which melted at 153.5–155° (corr.).

Anal. Subs., 0.1786: CO_2, 0.6011; H_2O, 0.1265. Calcd. for $C_{38}H_{38}$: C, 92.31; H, 7.69. Found: C, 91.78; H, 7.92. *Mol. wt.* Subs., 0.1527; benzene, 13.465; Δt, 0.134°. Constant for benzene, 5.12. Calcd. for $C_{38}H_{38}$: mol. wt., 494. Found: 434.

One run was made to determine the absorption of oxygen. One g. of the bromide in 5 cc. of toluene was shaken with 1 g. of molecular silver for fourteen hours in a sealed tube. Then the tube was broken in an oxygen chamber connected with a eudiometer. There was no absorption of oxygen after twenty hours. The mixture was then filtered and worked up as before. After two crystallizations 0.45 g. (39% of the theoretical amount) of the same hydrocarbon was isolated. Analysis of the silver–silver bromide residue showed that the bromine had been removed to the extent of over 90% of the theoretical amount.

Similarly, when the hydrocarbon was prepared in an atmosphere of carbon dioxide and then transferred to an oxygen atmosphere, there was no absorption. Fresh molecular silver was added to this reaction mixture and shaking continued without effect.

(b) **In Oxygen.**—A solution of 2 g. of the bromide in 10 cc. of toluene was shaken with 2 g. of molecular silver in a 30-cc. round-bottomed flask filled with oxygen and connected to a eudiometer filled with oxygen. When shaking was started, oxygen was rapidly absorbed and the temperature of the reaction mixture rose to 40–50°. On attempting to isolate the reaction products only about 0.1 g. of the hydrocarbon was obtained. One similar run made in ether solution and maintained at about 25° by means of a water-bath gave some white crystals melting at 96–102°. An attempt to purify these yielded an oil with a strong odor of benzophenone.

Several runs were made in xylene solutions in a tube surrounded by water to maintain the temperature at about 25–30°. In every case the absorption of oxygen was 2 to 3 times the theoretical amount. In one run using 0.3 g. of the bromide, the absorption of oxygen seemed to stop after the theoretical amount (10.3 cc.) for the formation of a peroxide had been taken up. However, on further shaking the absorption was renewed and finally about three times the theoretical amount of oxygen (34.9 cc.) was used.

In another run using 0.3 g. of the bromide the oxygen absorption was measured while the reaction mixture was held at about 0° by surrounding the reaction tube with ice water. After thirty-eight minutes, 14.8 cc. (144% of the theoretical amount for the formation of a peroxide) of oxygen was absorbed.

Reaction of the Hydrocarbon $C_{38}H_{38}$ with Sodium Amalgam.—Two cc. of 1% sodium amalgam and 0.25 g. of the hydrocarbon in 10 cc. of absolute ether were shaken in an atmosphere of nitrogen. No color was developed. The 1% amalgam was then replaced by 40% amalgam and shaking was continued. The solution turned red in less than a minute. After shaking overnight, the mixture was treated with dry carbon dioxide for an hour. The excess alloy was frozen and the reaction mixture was separated and decomposed with water and hydrochloric acid. The ether layer was extracted with 10% potassium hydroxide and the alkaline solution was filtered and then acidified with hydrochloric acid. No water-insoluble acid was obtained.

In a second run, 0.36 g. of the hydrocarbon in ether was shaken with 3.5 cc. of the 40% sodium amalgam in an atmosphere of nitrogen. A deep red color developed in seven minutes and after nine hours the color was almost black. Dry carbon dioxide was then passed into the mixture until the color had disappeared. On working up this mixture as described above, a few yellow crystals melting at 168–170° resulted. Not enough material was obtained for identification.

Reaction of the Hydrocarbon $C_{38}H_{38}$ with Liquid Sodium–Potassium Alloy.—A solution of 0.38 g. of the hydrocarbon in ether was shaken for three hours with 4 cc. of the liquid sodium–potassium alloy in an atmosphere of nitrogen. The solution turned red in one minute. Dry carbon dioxide was led into the mixture until the red color had disappeared, and then the ether solution was poured off and any suspended particles of alkali metal were decomposed with moist carbon dioxide. The ether solution was then extracted with water and the aqueous extract acidified with dilute hydrochloric acid. Only a slight turbidity resulted. Evaporation of the ether layer with dilute hydrochloric acid left only potassium and sodium chlorides.

Attempts to Rearrange the Hydrocarbon $C_{38}H_{38}$.—A solution of 0.44 g. of the hydrocarbon in 5 cc. of absolute alcohol was heated for one hour in a sealed tube at 100°. The solution was cooled to 15° and the original hydrocarbon (m. p. 150–151°) was isolated. The recovered hydrocarbon weighed 0.36 g.

Summary

1. Molecular silver removes the halogen from diphenyl-*tert.*-butylethynylbromomethane, and a hydrocarbon $C_{38}H_{38}$ is obtained when the reaction is carried out in air or nitrogen. In an atmosphere of oxygen this reaction does not produce a hydrocarbon but oxygen is absorbed very rapidly by the reaction mixture.

2. The hydrocarbon, $C_{38}H_{38}$, reacts with liquid sodium–potassium alloy and with 40% sodium amalgam to produce colored alkali metal derivatives but apparently the molecule is not cleaved as would be expected if it has the structure of tetraphenyldi-*tert.*-butylethynylethane.

3. To explain these observations the suggestion is made that tetraphenyldi-*tert.*-butylethynylethane is formed by the action of silver on diphenyl-*tert.*-butylethynylbromomethane but it rapidly dissociates and rearranges to some other more stable structure. If oxygen is present in large amounts the free radicals produced by the dissociation of tetraphenyldi-*tert.*-butylethynylethane are oxidized before this rearrangement occurs.

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NEW BOOKS

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