Anal. Subs., 0.0931: CO_2, 0.2708; H_2O, 0.0805. Calcd. for $C_{20}H_{28}O_2$: C, 79.94; H, 9.40. Found: C, 79.32; H, 9.67.

Summary

1. Hexa-*tert.*-butylethynylethane has been prepared and has been shown to be undissociated at room temperature and to undergo rearrangement at elevated temperatures.
2. Cleavage by alkali metals has indicated that the stability of the central ethane linkage is intermediate between that of the corresponding linkages in dibenzyl and hexaphenylethane.

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[CONTRIBUTION FROM THE LABORATORY OF THE J. B. WILLIAMS COMPANY]

REARRANGEMENTS OF THE TRIPLE BOND

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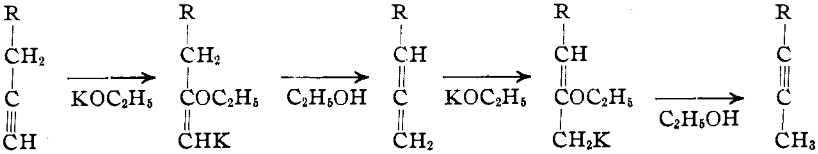
There are two types of the higher homologs of acetylene, the so-called true or monosubstituted acetylenes, RC≡CH (I), and the *iso*-acetylenes RC≡CR″ (II). That the one type may be transformed into the other was first observed by Favorsky,[1] who effected the rearrangement of type I into type II by the action of alcoholic potash and the reverse rearrangement with metallic sodium. His explanation of the former rearrangement postulated the presence of alcohol in the reaction mixture as essential. He stated that solid alkalies were unable to effect it. His scheme is represented as follows



$$RCH_2C{\equiv}CH \xrightarrow{KOC_2H_5} RCH_2C(OC_2H_5){=}CHK \xrightarrow{C_2H_5OH} RCH{=}C{=}CH_2 \xrightarrow{KOC_2H_5} RCH{=}C(OC_2H_5)CH_2K \xrightarrow{C_2H_5OH} RC{\equiv}CCH_3$$

He also found that there was a minimum temperature, characteristic for each acetylene, below which, if rearrangement proceeds at all, it must be extremely slow.

Wislicenus and Schmidt,[2] were unable to confirm Favorsky's statement that ethylacetylene is completely rearranged by alcoholic potash. These workers found some unaltered material in their reaction product.

Bourguel[3] states that sodamide acting on dihalides leads only to the formation of monosubstituted acetylenes, type I. This result is not in accord with the experience of the writer.[4] Some of type II was in-

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[1] Favorsky, *J. prakt. Chem.*, [2] **37**, 382, 417 (1888).

[2] Wislicenus and Schmidt, *Ann.*, **313**, 220 (1900).

[3] Bourguel, *Ann. Chemie* [10] **3**, 191, 325 (1925).

[4] Guest, THIS JOURNAL, **47**, 862 (1925).

variably produced by this method. Apparently no worker in this field has questioned the finality of Favorsky's work upon these rearrangements until the work of Hill and Tyson[5] on the vapor phase dehalogenation of dichloroheptane appeared. These authors found that instead of the expected type I heptine they obtained as the major product *iso*heptine, confirming some previous unpublished results of the present writer. They raised the question whether the heptine, undoubtedly the primary product of the dehalogenation, does not undergo a thermal rearrangement.

To determine whether the rearrangement from type I to type II could be brought about in the complete absence of alcohol, the writer conducted experiments under conditions identical with those described by Hill and Tyson.[5] Thus, by passing a hydrocarbon mixture of predetermined heptine content over soda lime, and observing the increase of *iso*heptine, it was found that rearrangement proceeded to the extent of 70%. Further, when pumice replaced soda lime, some rearrangement took place but not as smoothly or to as great extent as in the previous case. The probable reason for Favorsky's negative result with dry alkalies is that his reaction temperatures were too low.

The rearrangement from *iso*-form II to true form I is brought about, according to Favorsky,[1] by the action of sodium at temperatures slightly above 100° and also by sodamide at 160°.[3] This reagent Bourguel found causes a rearrangement of the triple bond to the end of the chain, for example, $RC{\equiv}CC_2H_5 \longrightarrow R(CH)_2C{\equiv}CH$, but not quantitatively. The length of time and temperature required vary with each acetylene. The *iso*-form obtained by the writer by vapor phase rearrangement was changed back to true heptine by sodamide to the extent of 65% of theoretical.

The proportion of each form was determined by the method of Behal,[6] recently improved by Hill and Tyson,[5] which depends upon the insolubility of the silver derivative of the type I acetylene in alcohol with liberation of the equivalent amount of nitric acid.

The evidence presented seems to indicate that the rearrangement from one form to another, in the absence of alcohol, is to be explained on the same basis as the corresponding olefinic rearrangement, $RCH{=}CH_2 \rightleftarrows R'CH{=}CHR''$, with the exception that in the case of the acetylene of type I an inert sodium derivative can be formed, which fact facilitates the rearrangement of type II to type I.

Incidentally, a general method for the synthesis of the higher homologs of acetylene was developed, which may be represented as follows

$$RMgBr + CH_2{=}CHCH_2Br \longrightarrow RCH_2CH{=}CH_2 \xrightarrow{Br}$$
$$RCH_2CHBrCH_2Br \xrightarrow{KOH} RCH_2C{\equiv}CH$$

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[5] Hill and Tyson, THIS JOURNAL, **50**, 172 (1928).

[6] Behal, *Ann. chim. phys.*, [6] **15**, 424 (1888).

The novel feature of this method is the use of finely powdered potassium hydroxide suspended in mineral oil as dehalogenation reagent.

Experimental Part

Preparation of Heptine.—A three-necked flask was fitted with a mechanical stirrer, a dropping funnel and a distillation column leading to a condenser. In it were placed 100 g. of finely powdered potash and 200 cc. of mineral oil. The temperature was raised to 250° (oil-bath) and 50 g. of dibromoheptane added slowly, the agitation being continued until no more oil distilled over; weight of distillate, 15 g., which is 81% of the theoretical. This distillate was found on analysis to contain 74% of heptine. This method has been found to give equally good results in the preparation of other acetylenes, for example, pentine.

Rearrangement of Heptine, $CH_3(CH_2)_4C{\equiv}CH$, to *Iso*heptines over Soda Lime.—Fourteen g. of a mixture of *iso*heptine and heptine, containing 90% of the latter, was slowly dropped into an iron tube filled with 280 g. of soda lime (50% NaOH). The tube was heated to 380°. (This tube was loaned by Professor A. J. Hill of Yale University and has been fully described by him.[5] The writer desires to express his thanks to Professor Hill.) The distillate was returned to the tube for a second treatment before final fractionation. There was obtained 11 g. of material, boiling over 100–110°. This fraction was analyzed by the method previously described and 16.5% of heptine was found. At a temperature of 250° there was practically no rearrangement.

Thermal Rearrangement of Heptine without a Catalyst.—On passing heptine (90% pure) through the tube, filled with large pieces of pumice and heated to 350°, there was a copious evolution of white fumes. The product was washed with water and distilled. It commenced to come over at a lower temperature. The heptine–*iso*heptine fraction was subjected to a carbon and hydrogen determination to verify its essential purity. This fraction showed a heptine content of 68%.

Rearrangement of *Iso*heptines to Heptine.—The mixture obtained from the rearrangement over soda lime, which contained upwards of 80% of *iso*heptine, was heated for twelve hours at 160° with finely divided sodamide suspended in 35 cc. of mineral oil, with mechanical agitation. After washing and distillation, the oil was analyzed. Heptine was present to the extent of 64%.

Summary

1. It has been found that true acetylenes $RC{\equiv}CH$ are changed into *iso*-acetylenes $R'C{\equiv}CR''$, in the absence of alcohol, by vapor phase thermal rearrangement. Further work upon the mechanism of rearrangement is in progress.

2. A general method for the preparation of acetylenes is given.

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