Dimethylbutadiene and $(SCN)_2$

The 2,3-dimethylbutadiene was prepared by the catalytic dehydration of anhydrous pinacone, according to the method of Kyriakides[10] employing hydrobromic acid. After purification and fractionation, it boiled at 67–60°

Twenty cc. (15 g.) of dimethylbutadiene dissolved in 75 cc. of glacial acetic acid was added to 500 cc. of glacial acetic acid containing 72 g. of dissolved potassium thiocyanate, and into the cooled mixture at 6° a solution of 18.6 cc. of bromine in 110 cc. of glacial acetic acid was allowed to drop slowly with stirring. After standing for twelve hours in the ice chest, the precipitate was filtered off and washed with water to remove acetic acid and inorganic salts. It was dried by washing with alcohol and ether, then boiled with 100 cc. of benzene and filtered hot through a hot water funnel. The yellow, insoluble $(SCN)x$ remains behind on the filter. The filtrate upon cooling crystallized in yellowish needles which were bone-blacked in boiling benzene and allowed to recrystallize. For analysis the compound was redissolved in boiling ethyl acetate and upon cooling crystallized in well formed, colorless, odorless, rhombohedrons; yield, 5 g. of pure product; m. p. 130° (corr.).

It is very difficultly soluble in boiling alcohol, ether or acetone, but dissolves in hot benzene, chloroform and ethyl acetate. It was dried in a high vacuum at 75° for analysis.

Anal. Subs., 0.1290 required 13.3 cc. of 0.1 N H_2SO_4 (Kjeldahl); 0.1342 gave 0.3159 g. of $BaSO_4$ (Carius). Calcd. for $C_8H_{10}S_2N_2$: S, 32.31; N, 14.14. Found: S, 32.27; N, 14.43.

Summary

Isoprene and dimethylbutadiene each add one molecule of thiocyanogen to form well defined, crystalline addition products which may be used to characterize these hydrocarbons.

AKRON, OHIO

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

HEXA-TERTIARY-BUTYLETHYNYLETHANE

BY PAUL L. SALZBERG WITH C. S. MARVEL

RECEIVED MARCH 1, 1928 PUBLISHED JUNE 5, 1928

The observed cases of dissociation of hexa-substituted ethanes have been limited to compounds containing at least two aryl groups attached to each of the carbon atoms which tend to separate and become trivalent. Consequently it has seemed logical to attribute the weak character of the ethane linkage to some properties of the neighboring aromatic nuclei, such as size (steric hindrance), weight and degree of unsaturation.

It has been suggested several times that the substitution of unsaturated aliphatic radicals for the hydrogen atoms of ethane might also weaken the central carbon–carbon bond. An indication of the similarity between the unsaturation of an acetylenic linkage and of a benzene nucleus has

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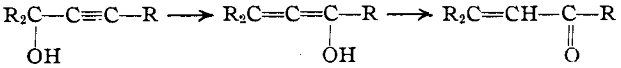
[10] Kyriakides, THIS JOURNAL, **36**, 991 (1914).

been obtained by Hess and Weltzien,[1] who has shown that phenylethynyldiphenylcarbinol, diphenylethynylphenylcarbinol and triphenylethynylcarbinol exhibit the halochromic properties which are characteristic of triphenylcarbinol. However, more recently Moureu, Dufraisse and Houghton[2] have prepared diphenylethynyltetraphenylethane and found that it does not absorb oxygen on heating but instead rearranges to an isomeric hydrocarbon. In this Laboratory, Gray and Marvel[3] have pointed out that the unsaturation present in three triple bonds might be comparable to that in two phenyl radicals, since in both cases there are twelve more electrons shared between carbons than would be the case in the corresponding saturated compounds. The molecular weight of the *tert.*-butylethynyl radical (81) is comparable to that of the phenyl radical (77) and there should be less possibility of steric hindrance with this compact acetylenic radical than with any other arrangement of six carbons with the required amount of unsaturation. Accordingly an attempt was made to prepare hexa-*tert.*-butylethynylethane. No definite results were obtained in that work.

In the present investigation crystalline hexa-*tert.*-butylethynylethane has been prepared from tri-*tert.*-butylethynylcarbinol as the starting material. This carbinol was prepared by addition of ethyl chlorocarbonate to *tert.*-butylethynylmagnesium bromide which was found to give better yields than sodium *tert.*-butylacetylide. The carbinol exhibited several of the characteristic halochromic properties of triphenylcarbinol. An ether solution became yellow on the addition of perchloric acid, dark red on the addition of concentrated sulfuric acid and formed a crystalline addition compound with stannic chloride. An attempt was made to dissolve the carbinol in a concentrated hydrochloric acid solution of zinc chloride in order to try the reduction to the ethane by means of vanadous chloride,[4] but this was unsuccessful.

The above tests carried out in the presence of strong mineral acids are complicated by the tendency of acetylenic carbinols to undergo a characteristic rearrangement to give α,β-unsaturated ketones, which may themselves exhibit halochromic properties. This rearrangement has been studied by Meyer and Schuster[5] for several phenylethynylcarbinols and they have shown that the reaction involves the migration of the hydroxyl group to the beta carbon atom and subsequent ketonization of the enol thus formed.



$$\underset{\displaystyle OH}{R_2\overset{}{C}}\text{—}C\equiv C\text{—}R \longrightarrow R_2C\text{=}C\text{=}\underset{\displaystyle OH}{C}\text{—}R \longrightarrow R_2C\text{=}CH\text{—}\underset{\displaystyle \overset{\|}{O}}{C}\text{—}R$$

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[1] Hess and Weltzien, *Ber.*, **54**, 2511 (1921).

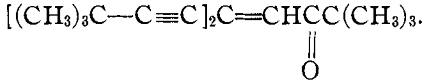
[2] Moureu, Dufraisse and Houghton, *Bull. soc. chim.*, [4] **41**, 56 (1927).

[3] Gray and Marvel, THIS JOURNAL, **47**, 2796 (1925).

[4] Conant and Sloan, *ibid.*, **45**, 2466 (1923); **47**, 572 (1925).

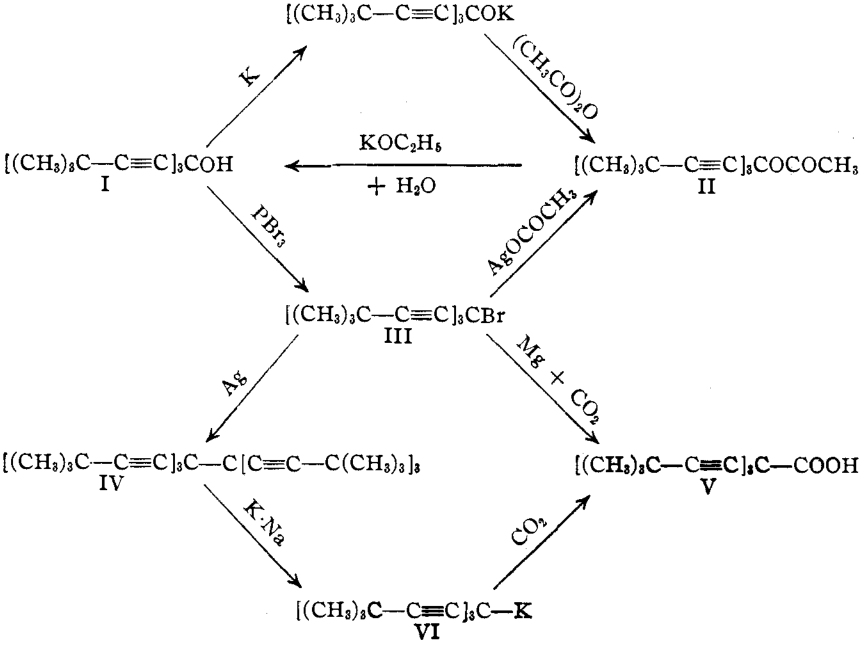
[5] Meyer and Schuster, *Ber.*, **55**, 819 (1922).

When tri-*tert.*-butylethynylcarbinol was treated with concentrated sulfuric acid under the conditions described for the rearrangement of phenylethynyldiphenylcarbinol, there was obtained a yellow product, isomeric with the original carbinol, which has been assigned the structure



$[(CH_3)_3C{-}C{\equiv}C]_2C{=}CH\underset{\underset{\displaystyle O}{\|}}{C}C(CH_3)_3.$

The conversion of the carbinol into tri-*tert.*-butylethynylbromomethane was attempted by the use of phosphorus tribromide according to the procedure described by Gray and Marvel[3] for the corresponding chloride, and also by the use of acetyl bromide. Both procedures gave two isomeric bromides which were separated by differences in their solubility. Qualitative tests with alcoholic silver nitrate indicated that the low melting bromide was the more reactive, and this suggested that it was the desired tri-*tert.*-butylethynylmethyl bromide. Attempts to convert either compound into the original carbinol by means of silver oxide were unsuccessful, probably due to their sensitivity toward oxidation by this reagent. It was possible, however, to convert the low melting bromide into an acetate by the action of silver acetate in boiling benzene. Tri-*tert.*-butylethynylmethyl acetate (II) was then prepared by the action of acetyl chloride or acetic anhydride on the sodium or potassium derivative of tri-*tert.*-butylethynylcarbinol (I), and its structure was proved by hydrolysis to the original carbinol by means of potassium ethylate,



according to the method described by Moureu, Dufraisse and Houghton.[6] This ester was found to be identical with that prepared from the low melting bromide, thus establishing the structure of this latter compound as tri-*tert.*-butylethynylbromomethane (III).

The bromide (III) was found to react with molecular silver to give hexa-*tert.*-butylethynylethane (IV). Solutions of the ethane showed no tendency to absorb oxygen at room temperature. The tests of dissociation at higher temperatures were found to be of no value because of a tendency of the compound to rearrange on heating to give an isomeric hydrocarbon.

Recently, Conant and Garvey[7] have developed a semi-quantitative method for determining the strength of the carbon–carbon linkage in substituted ethanes which is based on the differential cleavage by alloys of alkali metals to give metallic alkyls. The reaction of these alloys on hexa-*tert.*-butylethynylethane was tested in ether solution in accordance with their directions. As shown in Table I, cleavage of the ethane linkage to give the highly colored metallic alkyl (VI) was found to take place in every case.

TABLE I

ACTION OF ALLOYS OF ALKALI METALS ON AN ETHER SOLUTION OF HEXA-*tert.*-BUTYLETHYNYLETHANE

Alloy	First coloration	Appearance of red color	Total time shaken	Yield of crude acid
K·Na	Instantaneous	2 minutes	16 hours	70–90%
40% Na(Hg)X	3 minutes	4 hours	9 hours	Not accurately determined
1% Na(Hg)X	4 hours	Several days	9 days	About 10%

The metallic alkyl when treated with dry carbon dioxide and decomposed with water and hydrochloric acid yielded tri-*tert.*-butylethynylacetic acid (V). The structure of this acid was established by proving its identity with a sample of the acid prepared from tri-*tert.*-butylethynylbromomethane by the action of magnesium and carbon dioxide. From a comparison of these results with those reported by Conant and Garvey,[7] it can be concluded that the stability of the ethane carbon linkage in hexa-*tert.*-butylethynylethane is intermediate between that of dibenzyl and hexaphenylethane.

As yet the exact structures of the higher melting isomers of the bromide and of the ethane obtained by heating the solutions of the corresponding lower melting isomers (Formulas III and IV) have not been determined. This phase of the problem is now under investigation.

Experimental Part

Tri-*tert.*-butylethynylcarbinol.—Forty g. of *tert.*-butylacetylene was added from a dropping funnel to 135 cc. of a 3.673 *N* ether solution of ethylmagnesium bromide during

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[6] Moureu, Dufraisse and Houghton, *Bull. soc. chim.*, [4] **41**, 55 (1927).

[7] Conant and Garvey, THIS JOURNAL, **49**, 2080, 2599 (1927).

two hours. The heat of the reaction was sufficient to cause the ether and acetylene to reflux and this necessitated the use of a very efficient condenser cooled with water at 5°. The mixture usually solidified, presumably due to the precipitation of the *tert.*-butylethynylmagnesium bromide. Half of the theoretical amount of ethyl chlorocarbonate was then carefully added and the mixture was stirred overnight. Then the remainder of the ethyl chlorocarbonate was added during three or four hours. The mixture was decomposed by pouring it into cracked ice and adding the theoretical amount of dilute hydrochloric acid. The ether layer was dried over sodium sulfate and heated on a steam-bath to remove the solvent. The residue was distilled under reduced pressure and the fraction which boiled at 131–140° at 12 mm., or 122–124° at 4 mm., was collected and recrystallized from hexane or petroleum ether. The yield was 18–23 g. (40–50% of the theoretical amount); m. p. 100–102.2° (corr.). The vacuum distillation was omitted in several of the runs and purification carried out entirely by crystallization. Practically the same yield and purity of product were obtained.

Double Salt from the Carbinol and Stannic Chloride.—An excess of freshly distilled stannic chloride was added to 0.5 g. of tri-*tert.*-butylethynylcarbinol in benzene. A brown precipitate appeared. This was collected on a suction filter and washed with anhydrous ether. The color was thus removed and a white crystalline product remained.

Anal. Subs., 0.1407, 0.1185: 10.71, 9.1 cc. of 0.0993 N $AgNO_3$. Calcd. for $C_{19}H_{28}O{\cdot}SnCl_4$: Cl, 26.66. Found: Cl, 26.79, 27.02.

Rearrangement of the Carbinol with Sulfuric Acid.—Two g. of tri-*tert.*-butylethynylcarbinol was dissolved in 10 cc. of glacial acetic acid and 1 cc. of concd. sulfuric acid was added with cooling. A precipitate formed and the mixture was poured onto 20 g. of cracked ice. The organic material was collected in petroleum ether and this solution was evaporated to 15 cc. and cooled. The yellow product which separated was recrystallized three times from petroleum ether. It then melted at 109.5–110.5 (corr.) and gave no reaction when treated with metallic sodium in the cold.

Anal. Subs., 0.1366: CO_2, 0.4167; H_2O, 0.1248. Calcd. for $C_{19}H_{28}O$: C, 83.75; H, 10.36. Found: C, 83.20; H, 10.22.

Tri-*tert.*-butylethynylbromomethane.—Three g. of the carbinol was dissolved in 25 cc. of petroleum ether and stirred for one-half hour with 1 g. of phosphorus tribromide at 0°. To the mixture was added 100 cc. of 10% sodium bicarbonate solution and stirring was continued for ten minutes. The petroleum ether layer was then separated, dried over sodium sulfate and evaporated to dryness under reduced pressure at room temperature. The residue was dissolved in the minimum quantity of absolute ether and 5 cc. of absolute alcohol was added. This solution was evaporated under diminished pressure until crystals began to form and then cooled at 0° overnight. The bromide was collected on a filter and dried in a vacuum desiccator. The yield was 2 g. (54% of the theoretical amount); m. p. 66.5–68.5 (corr.). This product was sufficiently pure for most purposes, but the sample used for analysis was recrystallized several times from alcohol and ether and then melted at 69–70° (corr.).

Anal. Subs., 0.1597: CO_2, 0.3967; H_2O, 0.1158. Calcd. for $C_{19}H_{27}Br$: C, 68.04; H, 8.12. Found: C, 67.74; H, 8.11.

Anal. (Parr bomb). Subs., 0.3475: 10.27 cc. of 0.0993 N $AgNO_3$. Calcd. for $C_{19}H_{27}Br$: Br, 23.85. Found: Br, 23.45.

Mol. wt. (Rast method).[8] Subs., 0.0112, camphor, 0.1040: ΔT (depression), 13.3 (average of two observations); constant for camphor, 40. Calcd. for $C_{19}H_{27}Br$: mol. wt., 335. Found: 324.

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[8] Rast, *Ber.*, **55**, 1051, 3727 (1922).

High Melting Bromide from Carbinol.—The alcoholic mother liquor from the crystallization of tri-*tert.*-butylethynylbromomethane was allowed to evaporate at room temperature and the red, viscous mass which remained was dissolved in hot acetone, filtered and allowed to cool. The product which crystallized out was further purified by recrystallizations from acetone; m. p. 177–178° (corr.).

Anal. (Parr bomb). Subs., 0.2992, 0.3743: 8.67, 10.79 cc. of 0.1045 N $AgNO_3$. Calcd. for $C_{19}H_{27}Br$: Br, 23.85. Found: 24.17, 24.07.

This same compound was obtained by dissolving the lower melting bromide in absolute alcohol and heating for about an hour at 100° in a sealed tube.

Tri-*tert.*-butylethynylmethyl Acetate. (A) From Tri-*tert.*-butylethynylcarbinol.—Two g. of the carbinol was added to a suspension of 1 g. of powdered potassium in petroleum ether (b. p. 60–70°) and stirred for five to ten minutes. The supernatant liquid was decanted and treated with 2 cc. of acetic anhydride with stirring. The mixture was decomposed with water, neutralized with sodium bicarbonate solution and the upper layer dried with sodium sulfate, evaporated to 5 cc. and cooled. The ester crystallized. The yield was 1.2 g., m. p. 143–144° (corr.). Two recrystallizations from acetone raised the m. p. to 144.5–145.5° (corr.).

Anal. Subs., 0.1760: CO_2, 0.5186; H_2O, 0.1574. Calcd. for $C_{21}H_{30}O_2$: C, 80.21; H, 9.96. Found: C, 80.35; H, 10.01.

(B) From Tri-*tert.*-butylethynylbromomethane.—One g. of dry, pulverized silver acetate and 0.8 g. of the bromide, m. p. 70–71° (corr.), were refluxed in benzene for twenty-four hours. The solvent was evaporated under reduced pressure and the residue crystallized from petroleum ether, giving 0.1 g. of product melting at 142–143° (corr.). A mixture of this product with the ester obtained from the carbinol melted at 143.5–144.5° (corr.).

Hydrolysis of Tri-*tert.*-butylethynylmethyl Acetate.—Attempts to hydrolyze the ester with alcoholic solutions of potassium hydroxide or barium hydroxide were unsuccessful. The method of hydrolysis described by Moureu[8] was followed. One g. of the ester was shaken mechanically for twelve hours with 10 cc. of a saturated solution of potassium ethylate in alcohol. The resulting solution was decomposed with dilute sulfuric acid and the carbinol crystallized from petroleum ether. It melted at 101° and showed no depression of the melting point when mixed with known tri-*tert.*-butylethynylcarbinol.

Hexa-*tert.*-butylethynylethane.—Two g. of tri-*tert.*-butylethynylbromomethane was shaken mechanically with 2 g. of molecular silver[9] in 10 cc. of absolute ether for twenty-four hours. The ether was evaporated under reduced pressure almost to dryness and 5 cc. of absolute alcohol was added. The evaporation was continued until crystallization began and then the mixture was cooled. The yield was 0.7 g. (46% of the theoretical amount); m. p. 130–131° (corr.).

Benzene was also used as the reaction solvent but this solvent had to be completely removed or difficulty was found in the subsequent crystallization. The condensation was carried out both in the presence of nitrogen and in the presence of air, but no difference in the yield or nature of the product could be detected. Zinc dust was found to have no action on the bromide.

Anal. Subs., 0.1596: CO_2, 0.5214; H_2O, 0.1554. Calcd. for $C_{38}H_{54}$: C, 89.34; H, 10.66. Found: C, 89.09; H, 10.94.

Mol. wt. (Cryoscopic in benzene). Subs., 0.0981, 0.2401; benzene, 12.9452: ΔT (depression), 0.079, 0.181°. Constant for benzene: 5.12. Calcd. for $C_{38}H_{54}$: Mol. wt., 510. Found: 491, 525.

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[9] Vanino, "Preparativen Chemie," F. Enke, Stuttgart, **1913**, Vol. I, p. 417.

Mol. wt. (Rast method). Subs., 0.0114; camphor, 0.1174. ΔT (depression), 8.0°; constant for camphor, 40. Found: Mol. wt., 485.

In the first run of this condensation, the reaction mixture, after twenty-two hours' shaking, was tested for oxygen absorption. The oxygen was introduced from a gas buret and the mixture agitated for two hours. There was no decrease in the volume of oxygen and the unchanged ethane was isolated in a 32% yield.

The Rearranged Hydrocarbon.—A solution of 0.1 g. of the ethane in 1 cc. of xylene was heated in an atmosphere of nitrogen in order to test for the appearance of color indicating thermal dissociation. The solution turned slightly yellow at 120°, and bright yellow at 140°. The color was not discharged on cooling. Evaporation of the solvent left a residue which after crystallization from alcohol melted at 172–174° (corr.). The same compound was obtained by heating the ethane in alcohol. One-tenth g. of the ethane and 3–5 cc. of absolute alcohol were heated for one hour in a sealed tube immersed in boiling water. The contents were poured into a small beaker and cooled below 0°. The yield of rearranged hydrocarbon was 40–60% of the theoretical amount, m. p. 172–174° (corr.). Recrystallization raised the m. p. to 174–175° (corr.).

Anal. Subs., 0.1221: CO_2, 0.3975; H_2O, 0.1169. Calcd. for $C_{38}H_{54}$: C, 89.34; H, 10.66. Found: C, 88.78; H, 10.71.

Mol. wt. (Cryoscopic in benzene). Subs., 0.0822; benzene, 12.8369; ΔT (depression), 0.065°; constant for benzene, 5.12. Calcd. for $C_{38}H_{54}$; mol. wt., 510. Found: 504.

Cleavage of Hexa-*tert.*-butylethynylethane with Metals.—The tests for cleavage were carried out in a 50-cc., round-bottomed flask. Absolute ether distilled over ethylmagnesium bromide was used as a solvent, and the air was replaced by dry, oxygen-free nitrogen. The proportions used were those suggested by Conant and Garvey,[7] 0.1 g. ethane, 1 cc. of liquid alloy and 10 cc. of solvent. The flask containing this reaction mixture was shaken mechanically at the rate of 320 oscillations per minute. The results with different alloys have been recorded in Table I.

Tri-*tert.*-butylethynylacetic Acid (A) from Hexa-*tert.*-butylethynylethane.—Five cc. of potassium–sodium (10/4) alloy and 0.57 g. of the ethane were shaken in ether for sixteen hours. Dry carbon dioxide was passed into the mixture for three hours, and the mixture decomposed carefully with moist carbon dioxide, moist ether and finally dilute hydrochloric acid. The ether layer was evaporated with a solution of 1 g. of potassium hydroxide in 10 cc. of water. The alkaline solution was filtered and the filtrate was acidified with hydrochloric acid. The acid thus precipitated was yellow to red in color and weighed 0.39 g. (70% yield). It was reprecipitated twice from alkaline solution with hydrochloric acid and recrystallized once from dilute methyl alcohol using some decolorizing carbon (Norit). The product thus obtained was still yellow in color but treatment with Norit in petroleum ether completely removed the color and gave a product melting at 202–205° (corr.).

(B) From Tri-*tert.*-butylethynylbromomethane.—In a 25 cc., three-necked, round-bottomed flask, were placed 1.52 g. of the bromide, 0.26 g. of magnesium, 0.09 g. of iodine and 10 cc. of dry ether. Stirring was begun and a slow stream of dry carbon dioxide was passed over the solution for seven hours. The mixture was decomposed with dilute hydrochloric acid and the organic acid was reprecipitated twice from the aqueous solution of its potassium salt. The product was recrystallized once from methyl alcohol and three times from petroleum ether (using Norit), after which it melted at 201–203° (corr.). A mixture of the acid from (A) and (B) melted at 201–204° (corr.).

Neutral Equivalent. Subs., 0.2463: 7.21 cc. of 0.1138 *N* NaOH. Calcd. for $C_{20}H_{28}O_2$: 300.2. Found: 300.5.

The acid was recovered and recrystallized from petroleum ether, m. p., 202–205° (corr.).

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.

URBANA, ILLINOIS

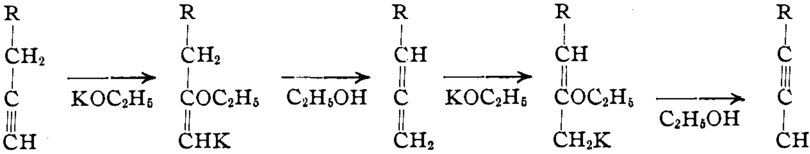
[CONTRIBUTION FROM THE LABORATORY OF THE J. B. WILLIAMS COMPANY]

REARRANGEMENTS OF THE TRIPLE BOND

BY HERBERT H. GUEST

RECEIVED MARCH 5, 1928 PUBLISHED JUNE 5, 1928

There are two types of the higher homologs of acetylene, the so-called true or monosubstituted acetylenes, $RC\equiv CH$ (I), and the *iso*-acetylenes $RC\equiv CR''$ (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



$$\begin{array}{ccccccccc}
\mathrm{R} & & \mathrm{R} & & \mathrm{R} & & \mathrm{R} & & \mathrm{R} \\
| & & | & & | & & | & & | \\
\mathrm{CH_2} & & \mathrm{CH_2} & & \mathrm{CH} & & \mathrm{CH} & & \mathrm{C} \\
| & \xrightarrow[\mathrm{KOC_2H_5}]{} & | & \xrightarrow[\mathrm{C_2H_5OH}]{} & \| & \xrightarrow[\mathrm{KOC_2H_5}]{} & \| & \xrightarrow[\mathrm{C_2H_5OH}]{} & ||| \\
\mathrm{C} & & \mathrm{COC_2H_5} & & \mathrm{C} & & \mathrm{COC_2H_5} & & \mathrm{C} \\
||| & & \| & & \| & & | & & | \\
\mathrm{CH} & & \mathrm{CHK} & & \mathrm{CH_2} & & \mathrm{CH_2K} & & \mathrm{CH_3}
\end{array}$$

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).