# METHOD FOR THE CONDENSATION OF DIACETYLENE WITH CARBONYL COMPOUNDS

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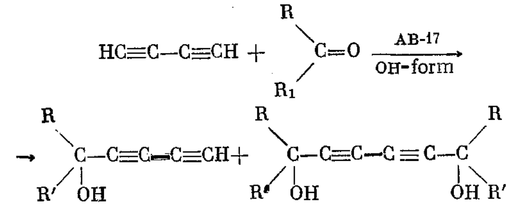
Among the numerous alkaline agents which induce condensation of acetylene with carbonyl compounds, the OH-form of Amberlite IRA-400 anion-exchange resin is mentioned in a British patent [1]. The reaction of acetylene with acetone, methyl ethyl ketone, and cyclohexanone in the presence of this anion-exchange resin (anionite) proceeds at elevated temperatures, and the yields of final products are low.

The development of pyrolytic methods for the production of acetylene entails a search for routes for the use of the side products formed during the process, primarily diacetylene. One of the promising methods for tieing up diacetylene is its condensation with carbonyl compounds. Special attention should be directed to condensation in liquid media.

This paper is devoted to an investigation of the possibility of the use of the OH-form of anion-exchange resins for the condensation of carbonyl compounds with diacetylene. The OH-form of AB-17 ion-exchange resin containing 2 mg-eq/g of active groups was used as the ion-exchange resin. The reactions proceed via the general scheme



$R=R'=CH_3$ (I)
$R=CH_3$; $R'=C_2H_5$ (II)
$R=CH_3$; $R'=n\text{-}C_4H_9$ (III)
$R=R'=C_2H_5$ (IV)
$R-R'=-(CH_2)_4$ (V)
$R=CH_3$; $R'=C_6H_5$ (VI)

$R=R'=CH_3$ (VII)
$R-R'=(CH_2)_5$ (VIII)
$R=CH_3$; $R'=C_2H_5$ (IX)
$R=R'=C_2H_5$ (X)

Several syntheses can be carried out on the same portion of the ion-exchange resin, and the activity of the resin, which gradually decreases, can be practically restored by treatment with 4% alkali.

The condensation of acetone with diacetylene in the presence of AB-17 anion-exchange resin proceeds both in aqueous and anhydrous media at various temperatures. The yields and purities of the carbinol (I) and glycol (VII) obtained depend on the conditions used to carry out the reaction and the amount of anionite used in the reaction. Thus, at 18° with 10 g of anionite, 25.3% of a liquid fraction was isolated along with 32.0% (based on diacetylene) of glycol (VII); this liquid fraction is a mixture of carbinol and diacetone alcohol in a ratio of 36 : 64%. The diacetone alcohol is formed as a result of simultaneous aldol condensation. However, when the reaction is carried out in aqueous media [acetone–water (1 : 1)] at 40-50° with an increased amount of anionite (80 g), the yield of glycol (VII) reaches 50.0% and that of carbinol 11.9%, but the purity of the carbinol is 96% (gas–liquid chromatographic analysis), and its constants agree with those presented in the literature. On repeated reaction on the same sample of resins the yield of glycol is 41.4%

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while that of carbinol (I) together with diacetone alcohol is 25.9% (the percentage of carbinol (I) in the mixture is 95.5%). The highest yield of glycol (VII) (82.7%) was obtained when the reaction was carried out in acetone (without dilution with water) at 18° with 75 g (150 mg-eq) of AB-17 anionite. An increase in the yield of the final product on increasing the amount of anionite was also observed when diacetylene was subjected to reaction with methyl ethyl ketone. Thus, when the amount of anionite was increased from 10 to 75 g, the yield of carbinol (II) increased from 32.8 to 41.0%, and carbinol (II) was the only reaction product.

Cyclohexanone also quite readily reacts with diacetylene to form 79.0% of glycol (VIII). Acetophenone reacts with diacetylene in the presence of AB-17 anionite with considerably greater difficulty, and the yield of carbinol (VI) amounts to only 14.7%.

The use of organic solvents in this reaction gives poorer results. In tetrahydrofuran the condensation of methyl ethyl ketone with diacetylene leads to carbinol (II) in a total yield of 10.9%.

Judging from gas–liquid chromatographic and thin-layer chromatographic data, IR and NMR spectra, and elemental analysis, carbinols (II), (III), and (IV) are pure substances, free of traces of the products of the aldol condensation. Vinylacetylene and acetylene undergo practically no reaction with carbonyl compounds in the presence of AB-17 anionite.

## EXPERIMENTAL METHOD

Condensation of Diacetylene with Acetone. Diacetylene (6 g) was passed for 2 h through a mixture of 40 g of acetone and 10 g of AB-17 anionite, the mixture was stirred for 2 h, and the resin was filtered and washed with ether. The ether extract was combined with the filtrate and dried with $K_2CO_3$. The solvents were removed, and the mixture was distilled to give 3.3 g of a fraction with bp 40° (1 mm); $n_D^{22.7}$ 1.4564. The fraction was a mixture of carbinol (I) and diacetone alcohol in a ratio of 36 : 64%. In addition, 5.1 g (32.0%) of glycol (VII) with mp 136-137° (from benzene) was obtained. A sample of this glycol did not depress the melting point of the glycol obtained by oxidative dimerization of dimethylethynylcarbinol. According to [2], the glycol melts at 133°.

The condensation of diacetylene with methyl ethyl ketone, methyl n-butyl ketone, and cyclopentanone was carried out similarly. The condensation of diacetylene with diethyl ketone, cyclohexanone, and acetophenone was carried out by shaking in a long-necked hydrogenation flask or in a

TABLE 1. Experimental Conditions and Results with Respect to the Condensation of Diacetylene with Carbonyl Compounds

| Expt. No. | Carbonyl compound | Amount, g |  |  | Reaction temp., °C | Time, h | Carbinol yield, % † | bp, °C (mm Hg) | $n_D$ (t, °C) | Glycol yield, % † | mp |
|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  | ketone | diacetylene | AB-17 |  |  |  |  |  |  |  |
| 1 * | Acetone | 40 | 6 | 10 | 18 | 3 | 25,3 (I) | 40 (1) | 1,4564 (22,7) | 32,0 (VII) | 136—137 |
| 2 * | Acetone—water (1:1) | 60 | 17 | 8 | 40—50 | 4 | 20,1 | 35—34 (1) | 1,4901 (20) | 14,2 | 136—137 |
| 3 * | The same | 60 | 16 | 80 | 40—50 | 4 | 11,9 | 41 (1) | 1,4906 (20) | 50,0 | 136—137 |
| 4 * | " | 56 | 7,5 | 65 | 40—50 | 4 | 25,9 | 34—35 (1) | 1,4908 (20) | 41,5 | 136—137 |
| 5 | Acetone | 80 | 7,2 | 75 | 18 | 4 | — | — | — | 82,7 | 136—137 |
| 6 | Methyl ethyl ketone | 60 | 6,9 | 10 | 18 | 5 | 32,8 (II) | 64 (3,5) | 1,4730 (23) | 2,6 (IX) | 93 |
| 7 | " " " | 80 | 12,3 | 75 | 18 | 5 | 41,0 | 65 (4) | 1,4737 (21) | — | — |
| 8 | Methyl butyl ketone | 60 | 7,8 | 15 | 18 | 15 | 22,3 (III) | 67 (1) | 1,4838 (22) | — | — |
| 9 | Diethyl ketone | 9,5 | 2 | 3 | 18 | 48 | 27,3 (IV) | 69 (4,5) | 1,4970 (22) | 11,2 (X) | 117—120 |
| 10 | Cyclopentanone | 18 | 2 | 3 | 18 | 64 | 28,6 (V) | 79—80 (1) | 1,5200 (22) | — | — |
| 11 | Acetophenone | 23 | 2 | 3 | 18 | 64 | 14,7 (VI) | 55—56 (1) | 1,5352 (22) | — | — |
| 12 | Cyclohexanone | 6,2 | 1 | 3 | 50 | 24 | — | — | — | 79 (VIII) | 181 |

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*In experiments 1-4 the overall yield of carbinol I and diacetone alcohol are given. The percentage ratio of I and diacetone alcohol according to gas–liquid chromatography is 36:64 in experiment 1, 92:8 in experiment 2, 96:4 in experiment 3, and 95.5:4.5 in experiment 4.

† For I, bp 45-47°C (1.5 mm and $n_D^{20}$ 1.4935 [3]. For II: found %: C 79.87; H 8.26. $C_8H_{10}O$. Calc. %: C 78.65; H 8.25. For III: found %: C 80.02 H 9.36. $C_{10}H_{14}O$. Calc. %: C 79.95; H 9.39. For IV, bp 44-45°C (0.3 mm) and $n_D^{20}$ 1.4964 [4]. For V, bp 87°C (4 mm) and $n_D^{20}$ 1.5260 [5]. For VIII, mp 173-174°C [6]. For IX, mp 89-90°C [7]. For X, mp 113-114°C [8].

sealed ampul. The compounds were isolated in the same way as described above. The results of the experiments are presented in Table 1.

## CONCLUSIONS

A new method is proposed for the condensation of diacetylene with carbonyl compounds.

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