SYNTHESIS OF DIVINYL-α-DIKETONES AND DIALKOXYETHYL VINYL KETONES

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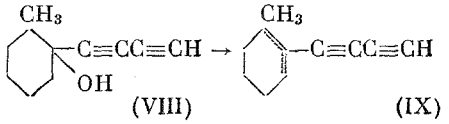
We synthesized new and interesting compounds, possessing great synthetic potentialities, from diacetylene derivatives. Under the influence of mercury salts, diacetylene glycols (I), which we produced earlier [1, 2], are isomerized to divinyl diketones (III), like ethynyl vinyl ketones [3], while alkoxyvinylacetylene alcohols (II) are isomerized to divinyl ketones (IV); under the reaction conditions, the latter add alcohol, being converted to (V)

$$(R)_2C(OH)C{\equiv}CC{\equiv}CC(OH)(R)_2 \rightarrow (R)_2C=CHCOCOCH=C(R)_2$$
$$\text{(I)} \qquad\qquad\qquad\qquad \text{(III)}$$
$$(R)_2C(OH)C{\equiv}CCH=CHOR \rightarrow (R)_2C=CHCOCH=CHOR \rightarrow (R)_2C=CHCOCH_2CH(OR)_2$$
$$\text{(II)} \qquad\qquad \text{(IV)} \qquad\qquad \text{(V)}$$

On the other hand, tertiary diacetylenic alcohols of the type of (VI) and (VIII), when heated with H_2SO_4, are readily dehydrated to vinyldiacetylenic hydrocarbons (VII) and (IX).

$$(CH_3)_2C(OH)C{\equiv}CC{\equiv}CH \rightarrow CH_2=C(CH_3)C{\equiv}CC{\equiv}CH$$
$$\text{(VI)} \qquad\qquad\qquad\qquad \text{(VII)}$$



(VIII) (IX)

The structures of the compounds obtained were confirmed by their IR and UV spectra. We mixed 5 g of (I; R = CH_3) in 15 ml of benzene and 5 ml of methanol with 0.5 of $HgSO_4$ at 65° for 9 h, left the mixture overnight, treated in the usual way, and obtained 2.2 g (44%) of (III), b.p. 83-84° (2 mm); n_D^{20} 1.5257. Found: C 72.16; H 8.70%. $C_{10}H_{14}O_2$. Calculated: C 72.25; H 8.48%. To a mixture of 0.14 g of HgO, 0.15 ml of BF_3 etherate, a and 5 ml of methanol at 25°, we added 4.4 g of (II); R = CH_3) and mixed for 0.5 h; we isolated 2 g (37%) of (V), b.p. 84-85° (7 mm); n_D^{20} 1.4555. Found: C 62.86; H 9.36%. $C_9H_{16}O_3$. Calculated: C 62.80; H 9.30%. A mixture of 10.8 g (VI) and 11 ml of 50% H_2SO_4 was mixed at 45° for 80 min. We isolated 2.7 g (30%) of (VII) in the usual way, b.p. 32-33° (35 mm); $n^{21}D$ 1.5192. Found: C 92.99; H 6.84%. C_7H_6. Calculated: C 93.28; H 6.72%. Analogously, in the reaction of 19.5 g of (VIII) (produced according to the procedure of [1]; m.p. 62-63°) with 20 ml of 50% H_2SO_4 (2 h and 25°), we isolated 4.8 g (28%) of (IX), b.p. 52° (0.03 mm); n_D^{24} 1.5460. IR spectrum: 3300, 2195, 2050, 1627 cm^{-1}.

LITERATURE CITED

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