# SYNTHESIS OF ortho-SUBSTITUTED ETHYNYLBENZENES

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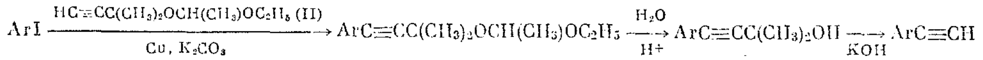
Groups, located ortho to the halogen, exert the greatest effect on the reactivity of aromatic iodo derivatives in the acetylenic condensation [1, 2]. In the present paper we employed some o-substituted iodobenzenes (Ia–f), and also the α- and β-iodonaphthalenes (Ig, h), in this reaction. As the acetylenic component we used the acetalized 2-methyl-3-butyn-2-ol (II). The obtained aralkyl alcohols (III) were converted to the to the arylacetylenes (IV) by the scheme:



$$\underset{(I)}{ArI} \xrightarrow[Cu,\ K_2CO_3]{HC\equiv CC(CH_3)_2OCH(CH_3)OC_2H_5\ (II)} \underset{(V)}{ArC\equiv CC(CH_3)_2OCH(CH_3)OC_2H_5} \xrightarrow[H^+]{H_2O} \underset{(III)}{ArC\equiv CC(CH_3)_2OH} \xrightarrow[KOH]{} \underset{(IV)}{ArC\equiv CH}$$

$Ar = o\text{-}C_6H_4R$, where $R = CH_3$ (a), $OCH_3$ (b), Cl (c), CN (d), $CH{=}CHCOOCH_3$ (e), $C\equiv CC(CH_3)_2OCH(CH_3)OC_2H_5$ (f), α-naphthyl (g), β-naphthyl (h)

The activity of the (I) iodides was estimated approximately by comparing their condensation rates (Table 1). The electron-acceptor substituents exert a slight but clearly expressed activating effect on the halogen. In their reactivity the aryl halides, containing donor substituents, are close or somewhat higher than that of iodobenzene [2]. In the synthetic aspect it is important that such heavy and bulky substituents as the o-carbomethoxyvinyl or the acetalized 3-hydroxy-3-methylbutynyl group, do not hinder the reaction. Due to this it proves possible to synthesize, for example, the methyl ester of o-ethynylcinnamic acid (IVe) (52.5% yield when based on starting iodide), the preparation of which by other methods is very complicated. The yields of the (III) alcohols from the (I) aryl iodides were 77–92%. The ethynylarenes (IV) were obtained in 52.5–85% yield by distilling the (III) alcohols in the presence of KOH.

## EXPERIMENTAL METHOD

The iodides (I) were synthesized by the diazotization of aromatic amines and replacing the diazo group by iodine. Compound (Ie), previously described as a liquid [3], has mp 40–41°. NMR spectrum (in $CCl_4$, HMDS used as standard, δ given in ppm): 3.71 ($CH_3$); 6.19 and 7.76 (doublets, J 16 Hz, trans-CH=CH); 6.94 and 7.25 (triplets); 7.48 and 7.80 (doublets) (benzene ring).

Condensation of Aryl Iodides (I). The condensation of 0.02 mole of (I) with 0.06 mole of (II) in 50 ml of pyridine, in the presence of 0.6 g of Cu and 5.2 g of $K_2CO_3$, was run as described in [1]. The reaction time was determined by GLC. At the end of reaction the reaction mass was diluted with ether, the Cu and insoluble salt were separated, and the filtrate was washed with aqueous ammonia and then filtered through a bed of basic $Al_2O_3$. The product was purified by chromatographing. In those cases where it was difficult to completely remove the secondarily formed dehydrodimer of the starting (II) by this method, an analytical sample was prepared by the acetalization [1] of the pure (III), which was obtained in the next step. The yields and constants of the (V) compounds are given in Table 1.

Compound (If) was synthesized in a similar manner from equimolar amounts of o-iodobenzene and (II), yield 48.7%, $n_D^{20}$ 1.5520. Found: C 50.19; H 5.47; I 35.19%. $C_{15}H_{19}O_2I$. Calculated: C 50.29; H 5.35; I 35.43%. Infrared spectrum in $CCl_4$ (ν, $cm^{-1}$): 1053; 1083; 1125; 1165 (C–O–C–O–C); 2235 (C≡C). The corresponding alcohol, namely 1-(o-iodophenyl)-3-methyl-1-butyn-3-ol has $n_D^{20}$ 1.6050. Found: C 45.61; H 4.02; I 43.54%. $C_{11}H_{11}OI$. Calculated: C 45.56; H 3.82; I 43.76%. Infrared spectrum in $CCl_4$ (ν, $cm^{-1}$): 3610 (OH); 2235 (C≡C).

1-Aryl-3-methyl-1-butyn-3-ols (III). The (V) compounds were hydrolyzed in acid aqueous–dioxane solution at 20° [1]. The results are given in Table 2.

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## TABLE 1. Condensation of Aryl Iodides (I) with Acetal (II)

| Condensation product | Yield, % | Reaction time, h | $n_D^{20}$ | Found, % |  | Empirical formula | Calculated, % |  | Infrared spectrum in $CCl_4$ ($\nu$, $cm^{-1}$) |  |
|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  | C | H |  | C | H | C ≡ C | C—O—C—O—C |
| (Va) | 94,5 | 50—52 | 1,5052 | 78,00 | 9,06 | $C_{16}H_{22}O_2$ | 78,01 | 9,00 | 2230 | 1060, 1081, 1122, 1165 |
| (Vb) | 94,0 | 50—54 | 1,5290 * | — † | — | $C_{16}H_{22}O_3$ | — | — | 2225 | 1052, 1085, 1120, 1165 |
| (Vc) | 91,0 | 30 | 1,5172 ‡ | 67,40 | 7,21 | $C_{15}H_{19}ClO_2$ | 67,53 | 7,18 | 2235 | 1065, 1085, 1130, 1165 |
| (Vd) | 98,0 | 25—30 | 1,5154 | — ** | — | $C_{16}H_{19}NO_2$ | — | — | 2235 c (C≡N) | 1060, 1085, 1130, 1160 |
| (Ve) | 90,6 | 37—40 | 1,5393 | 72,25 | 7,76 | $C_{19}H_{22}O_4$ | 72,12 | 7,63 | — †† | 1050, 1080, 1125, 1165 |
| (Vf) | 75,5 | 38 | 1,5057 [1] | — | — | $C_{24}H_{31}O_4$ | — | — | — | — |
| (Vg) | 91,3 | 30 | 1,5632 | — † | — | $C_{19}H_{22}O_2$ | — | — | 2230 | 1065, 1085, 1125, 1165 |
| (Vh) | 95,0 | 51 | 1,5707 | 81,03 | 7,83 | $C_{19}H_{22}O_2$ | 80,81 | 7,85 | 2230 | 1055, 1085, 1130, 1170 |

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*Bp 115-118° (1 mm).

†Chromatographically pure; a satisfactory analysis could not be obtained.

‡Bp 107-180° (1 mm); Found: Cl 13.52%; Calculated: Cl 13.29%.

†† $\nu_{C \equiv C}$ weak; 985 $cm^{-1}$ (trans-CH ≡ CH); 1720 $cm^{-1}$ (C = O).

## TABLE 2. Hydrolysis of (V) Acetals

| Acetylenic alcohol | Yield, % | $n_D^{20}$ | Found, % |  | Empirical formula | Calculated, % |  | Infrared spectrum in $CCl_4$ ($\nu$, $cm^{-1}$) |  |
|---|---|---|---|---|---|---|---|---|---|
|  |  |  | C | H |  | C | H | C≡C | OH |
| (IIIa) | 92,2 | 1,5457 | 82,35 | 8,26 | $C_{12}H_{14}O$ | 82,72 | 8,09 | 2225 | 3605 |
| (IIIb) | 92,0 | 1,5592 | —* | — | $C_{12}H_{14}O_2$ | — | — | 2235 | 3610 |
| (IIIc) | 87,3 | 1,5600 | 67,57† | 5,86 | $C_{11}H_{11}ClO$ | 67,86 | 5,70 | 2225 | 3615 |
| (IIId) | 93,8 | 1,5565 | ‡ | — | $C_{11}H_{11}NO$ | — | — | 2235 s (C≡N) | 3610 |
| (IIIe) | 85,3 | Mp 84—85° | 73,72 | 6,67 | $C_{15}H_{16}O_3$ | 73,75 | 6,60 | 2240 ** | 3613 |
| (IIIf) | 98,8 | 1,6198 | 85,62 | 6,87 | $C_{15}H_{14}O$ | 85,68 | 6,71 | 2225 | 3610 |
| (IIIg) | 91,0 | Mp 86,5—87° | 85,68 | 6,55 | $C_{15}H_{14}O$ | 85,68 | 6,71 | 2225 | 3610 |

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*Chromatographically pure; NMR spectrum in $CCl_4$ (δ, ppm); 1.51 ($CH_3$); 3.76 ($CH_3O$); 3.22 (OH); 6.6-7.3 (multiplet; benzene ring); a satisfactory analysis could not be obtained.

†Found: Cl 18.42%; Calculated: Cl 18.22%.

‡Found: N 7.41%; Calculated: N 7.56%.

**$\nu_{C = O}$ 1720 $cm^{-1}$. NMR spectrum in $CCl_4$ (δ, ppm): 1.59 ($CH_3$); 3.70 ($CH_3O$); 6.35 and 8.04 (doublets, J 16 Hz; trans-CH = CH); 7.0-7.4 (multiplet; benzene ring).

Methyl Ester of o-Ethynylcinnamic Acid (IVe). A mixture of 2.5 g of (IIIe) and 60 mg of KOH powder was distilled at a residual pressure of 1 mm, and the product was chromatographed on $Al_2O_3$ (II activity). The yield of (IVe) was 1.3 g (68.2%), mp 61.5-62° (from petroleum ether). Found: C 77.37; H 5.56%. $C_{12}H_{10}\cdot O_2$. Calculated: C 77.40; H 5.41%. NMR spectrum (in $CCl_4$; $\delta$, ppm): 3.35 (H−C≡C); 3.71 ($CH_3$); 6.38 and 7.99 (doublets, J 16 Hz, trans-CH=CH); 7.10-7.60 (multiplet; benzene ring). Infrared spectrum in $CCl_4$ ($\nu$, $cm^{-1}$): 3315 (H−C≡C); 2210 (C≡C); 1720 (C=O); 985 (trans-CH=CH). In like manner were obtained: (IVa), yield 65.3%; (IVb) 67.1%, mp 23.5-24° (previously described as a liquid [4]); (IVc) 52.5%; (IVg) 80.3%; (IVh) 84.7%. The constants and the IR and NMR spectra of the synthesized (IV) compounds agreed with those given in the literature.

## CONCLUSIONS

1. The condensation of o-substituted iodobenzenes, and $\alpha$- and $\beta$-iodonaphthalene, with ethyl 2-methyl-3-butyn-2-yl acetacetal, followed by hydrolysis and subsequent alkaline cleavage of the obtained alcohols, gave the corresponding ethynylarenes.

2. Aryl iodides, containing electron-acceptor groups in the o-position of the benzene ring, are more reactive in the acetylenic condensation than the unsubstituted iodobenzene.

## LITERATURE CITED

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