NEW TRANSFORMATIONS OF AROMATIC ACETYLENES

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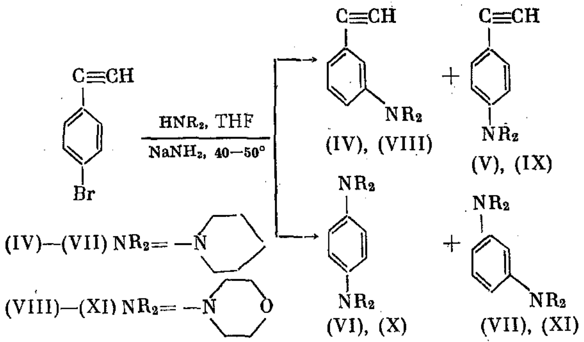
An unusual reaction, which leads to the formation of diaminobenzenes, was observed by us when p-bromophenylacetylene (I) was reacted with piperidine (II) and morpholine (III) in the presence of sodium amide in THF. Besides the expected kinetic replacement of bromine by the amino group, the C–C bond between the benzene ring and the ethynyl moiety is cleaved and the latter is also replaced by the amino group



From 30 g of (I) and 30 g of (II) at 40°C for 20 h was obtained 60% of a mixture of (IV) and (V) [bp 85-110° (10^{-2} mm). Found: C 84.24; H 8.46; N 7.66%. $C_{13}H_{15}N$. Calculated: C 84.28; H 8.16; N 7.56%], and 26% of a mixture of (VI) and (VII) [bp 110-116° (10^{-2} mm). Found: C 78.65; H 10.00; N 11.52%. $C_{16}H_{24}N_2$. Calculated: C 78.62; H 9.90; N 11.47%]. In a similar manner, from 30 g of (I) and 30 g of (III) was obtained 60% of a mixture of (VIII) and (IX) [bp 100-125° (10^{-2} mm). Found: C 76.86; H 8.36; N 6.80%. $C_{13}H_{17}NO$. Calculated: C 76.80; H 8.43; N 6.89%], and 24% of a mixture of (X) and (XI) [bp 137-143° (10^{-2} mm). Found: N 11.40. $C_{14}H_{20}N_2O_2$. Calculated: N 11.28%]. The structure of all of the obtained compounds was confirmed by the IR and NMR spectral data. The analogous mixtures of (VI)-(VII) and (X)-(XI) were obtained by counter synthesis from p-dibromobenzene and (II) or (III). In the case of phenylacetylene and p-piperidinophenylacetylene the cleavage of the C–C bond fails to occur under the same conditions.

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