4498 *Macromolecules* **1997,** *30,* 4498−4498

Notes

Styrene Dianions: Two-Electron Transfer

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Received January 2, 1997
Revised Manuscript Received May 6, 1997

The reduction of styrene by potassium anions yielding styrene dianions was reported recently by Jedlinski and his co-workers.[1] It is a somewhat unexpected reaction. The reduction proceeds presumably in two steps

$$K^-,(K^+,\text{crown complex}) + PhCH{=}CH_2 \rightarrow PhCH{=}CH_2^{\bullet -} + K^0,(K^+,\text{crown complex}) \qquad (1)$$

followed by electron transfer to the resulting styrene radical anion from K^0 (or from e^-,K^+, produced by its self-ionization, a spontaneous process converting K atom into solvating K^+ and a solvating electron). Thus

$$K^0 + PhCH{=}CH_2^{\bullet -} \rightarrow K^+,PhCH^-CH_2^- \qquad (2)$$

Electron transfer to the negative radical anion seems to be hindered, although solvation of the incipient K^+ cation by the solvent (THF) may facilitate the process.[2] Strong evidence for the formation of styrene dianion is provided by the detection of ethylbenzene as the main product of protonation caused by the subsequent addition of MeOH to the reduced solution.[1] Nevertheless, additional evidence might still be desired.

The experiments reported in ref 1 were therefore repeated, but MeOD, instead of MeOH, was used to quench (at ambient temperature) the reduction products. Tetrahydrofuran (THF), used as the solvent, is a sufficiently strong acid to allow rapid protonation of dianions at ambient temperature.[3] Indeed, mass spectroscopic examination of the hydrocarbons resulting from MeOD addition to the reduced and partially protonated styrene ($PhCH^-CH_3$) revealed the formation of $PhCHD^\bullet CH_3$ (∼50%), as well as $CH_3CH(Ph)^\bullet CH_2CHD^\bullet Ph$ (∼30%) and $Ph^\bullet CHD^\bullet CH_2CH_2CHD^\bullet Ph$ (∼20%). Apparently, THF and the unreduced styrene, present originally in excess, compete for the styrene dianions. The protonation by the former agent yields $PhCH^-CH_3$ carbanions and $PhCHDCH_3$ on subsequent deuteriation, whereas $PhCH^-CH_2CH_2CH^-Ph$ dianions result from the reaction with styrene. The latter yields $PhCHDCH_2CH_2CHDPh$ on deuteriation (later, an alternative mode of its formation is discussed). Some of the $PhCH^-CH_3$ carbanions have a chance to react with the still unconsumed styrene. These yield $CH_3CH(Ph)CH_2CHDPh$ on deuteriation.

THF does not protonate benzylic carbanions at ambient temperature, but it does protonate the nonconjugated strongly basic primary carbanions. Their negative charge density is high, e.g. 0.663 on the β carbon of styrene dianion, much larger than that on the benzylic α carbon, (0.207 only).[4]

Finally, it should be remarked that the transfer of the second electron (reaction 2) has to follow the first one (reaction 1) within less than $\cong 10^{-8}$ s (a typical duration time for an encounter complex in liquids). Otherwise, the styrene radical anion and K^0 would diffuse out of the encounter cage, and then K^0 may reduce another styrene molecule, an event leading to the formation of dimeric dianions and eventually to 1,4-diphenylbutane upon methanol addition. The reported 1,4-diphenylbutane might result from such a process, but its relatively low yield indicates the low probability of that course.

Significantly, the K^- initiating complex, an initiator transferring two electrons, produces in THF solution at ambient temperature mainly polymers growing from one end only (in contrast to naphthalenide yielding polymers growing from both ends). The rapid protonation of the terminal nonconjugated primary carbanion of the initially formed dianion accounts for this result.

The protonation by THF becomes imperceptible at lower temperatures (about −70° C), and then polymers growing from both ends, possessing the $-CH(Ph)CH_2CH_2CH(Ph)-$ group in their middle, would be formed. The role of THF in this initiation process, not mentioned in the previous reports,[1] but clearly demonstrated by the present results, deserves, therefore, stressing.

References and Notes

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MA970005P

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S0024-9297(97)00005-3 CCC: $14.00