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Solvolytic Stereoselective Debromination of *vic*-Dibromides with HMPA[1]

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A simple and efficient procedure for the debromination of *vic*-dibromides has been reported with hexamethylphosphoric triamide at 155–160 °C under a nitrogen atmosphere without the aid of any reagent.

The debromination of *vic*-dibromides to the corresponding alkenes is an important transformation in organic synthesis. Debrominations have been carried out with diverse reducing agents.[2] Recent reports on debrominations include reactions with sodium dithionite,[3] selenium,[4] tellurides,[5] copper, and copper(II) perchlorate,[6] samarium,[7] indium,[8] and iron.[9] Both stereospecific and stereoselective eliminations have been reported under different conditions. The role of a solvent in these reactions has not been thoroughly examined. Methanol has been reported to bring about the methanolysis of *meso*-stilbene dibromide.[10] While working on elimination reactions, we observed that debrominations could be achieved by *N*,*N*-dimethylformamide without the aid of any reagents.[11] In view of the importance of debromination in organic synthesis, reports on debromination with newer and expensive reagents keep pouring in.

Results and Discussion

We now report on the quantitative debromination of *vic*-dibromides to the corresponding olefins with dry hexamethylphosphoric triamide (HMPA) at 155–160 °C under a nitrogen atmosphere without the aid of any reagent (Eq. 1). HMPA acts not only as a solvent, but also as a reagent, since no debrominations have been observed in *o*-dichlorobenzene and xylene under similar reaction conditions. Debrominations have been carried out on a variety of *vic*-dibromides. The eliminations are complete in 15–60 min under the aforesaid conditions, and the olefins are obtained in high yields by a simple work up. Small amounts of α-bromochalcones were also obtained in the reactions of chalcone dibromides. The results are listed in Table 1. The reactions are much slower at 100 °C as *meso*-stilbene dibromide and *dl*-stilbene dibromide underwent complete debromination in 4 h and 7 h (15 min at 155–160 °C), respectively. No debrominations were observed at room temperature as starting materials were recovered unchanged after 24 h. Debrominations are stereoselective as both *meso*- and *dl*-stilbene dibromides yielded (*E*)-stilbene predominantly (Eq. 2). The possibility for the isomerization of (*Z*)-stilbene to (*E*)-stilbene under these conditions has been ruled out by (i) an independent reaction of (*Z*)-stilbene with HMPA, when (*Z*)-stilbene was recovered unchanged quantitatively, and (ii) a reaction of (*Z*)-stilbene with bromine at 100 °C. The reaction mixture showed the distinct formation of *dl*-stilbene dibromide, the debromination of which was the aim of this paper. Therefore, the possibility of an E2 elimination or elimination by an S_N2 attack from the N/O end of HMPA, followed by E2 elimination, is unlikely because both of these pathways would lead to a stereospecific elimination, contrary to our observations. Also, the anti-alignment, favored by orbital symmetry rules[12] in *meso*- and *dl*-stilbene dibromides, is opposed in the latter case conformationally by a free-energy diffrence of 4.4 kcal mol^{-1}.[13] Stereoselective elimination via free radicals by electron transfer from HMPA or pyrolysis has been ruled out by a reaction of *meso*-stilbene dibromide with HMPA in the presence of cumene (10 molar excess), which yielded stilbenes (*E*- and *Z*-) exclusively.

$$\mathrm{ArCHBrCHBrR} \xrightarrow[\Delta,\ 155\text{-}160\ ^\circ\mathrm{C}]{\mathrm{HMPA,\ N_2}} \mathrm{ArCH{=}CHR} \qquad (1)$$

R = Aryl, Acyl

$$meso\text{-}\ \&\ dl\text{-}\ \mathrm{PhCHBrCHBrPh} \xrightarrow[\Delta,\ 155\text{-}160\ ^\circ\mathrm{C}]{\mathrm{HMPA,\ N_2}} (E)\text{-}\mathrm{PhCH{=}CHPh} \qquad (2)$$

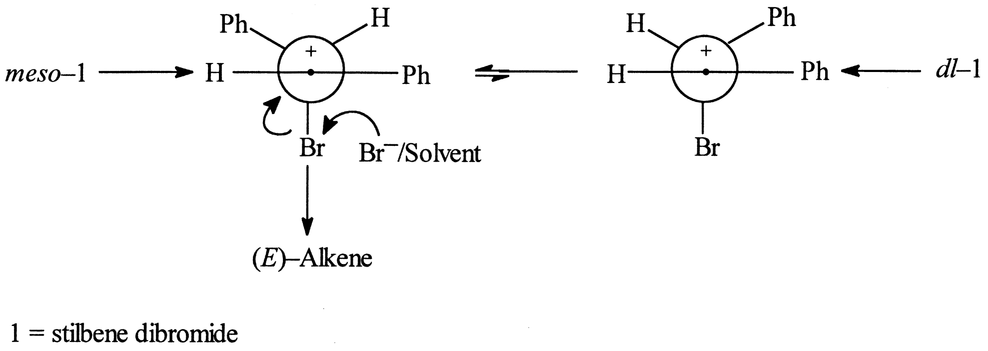
These debrominations are proposed to proceed by the E1 pathway by initial ionization to a stable onium species, i.e. a bromide/carbonium ion pair or isolated carbocation, which collapses to (*E*)-alkenes. HMPA has been reported to promote even the ionization of hydrocarbons.[14] The carbocation, formed initially from *dl*-stilbene dibromide, undergoes rapid C–C bond rotation owing to a conformational instability, to a more stable onium species (Scheme 1).[10,11,15]

Rate retardation by sodium bromide is not applicable to all *vic*-dibromides, which could be due to the reduced ability of HMPA to stabilize the carbocation or due to the participation of sodium bromide, itself, in debromination.[16] The observed order of reactivity, Br > Cl, in our reactions, since only 10% and 27% of dechlorination was observed in the reaction of *meso*-stilbene dichloride with HMPA after 60 and 120 min, respectively, is in agreement with the order of reactivity of E1 reactions, I > Br > Cl > F.[17] The formation of an intermediate onium species is further corroborated by the formation of α-bromochalcone derivatives in the reactions of chalcone dibromides (Scheme 2). The absence of any elimination in the reaction of diphenylacetylene dibromide is due to its inability to form a stable onium species. The formation of a mixture of

Table 1. Reactions of *vic*-Dibromide with Dry HMPA under N_2 Atmosphere at 155–160 °C

Run	Substrate (*vic*-dibromide)	Reaction time/min	Isolated yield/% (olefin)
1	*meso*-Stilbene dibromide	15	93 (97)[a)]
2	*dl*-Stilbene dibromide	15	83 (96.4)[b)]
3	*meso-p,p′*-Dichlorostilbene dibromide	30	99
4	*meso-o,p′*-Dinitrostilbene dibromide	30	99
5	*meso-p,p′*-Dinitrostilbene dibromide	60	98
6	*meso-p,p′*-Dimethylstilbene dibromide	60	96
7	*meso-p*-Chloro-*p′*-nitrostilbene dibromide	30	98
8	*p*-Nitrostilbene dibromide	15	94
9	*p*-Chlorostilbene dibromide	60	82
10	*9,9′*-Dibromobifluorenyl	120	87
11	Cinnamic acid dibromide	60	78
12	Methyl cinnamate dibromide	20	59[c)]
13	Chalcone dibromide	30	80[d)]
14	*p*-Nitrochalcone dibromide	30	68[e)]
15	*p*-Bromochalcone dibromide	30	62[e)]
16	*p*-Chlorochalcone dibromide	60	65[e)]
17	*p′*-Chlorochalcone dibromide	30	67[e)]
18	*p′*-Methylchalcone dibromide	30	70[e)]
19	Diphenylacetylene dibromide	240	—[f)]

a) Yield in brackets is HPLC yield. HPLC also showed the presence of 3.0% of (*Z*)-stilbene.
b) Yield in brackets is HPLC yield. HPLC also showed the presence of 3.6% of (*Z*)-stilbene.
c) Other unidentified products were also obtained.
d) 6% of α-bromochalcone was also isolated.
e) Products believed to be corresponding α-bromochalcones were also obtained in 7–15% yield.
f) The starting material was recovered unchanged.



Scheme 1.

Scheme 2.

products in the reactions of aliphatic *vic*-dibromides could be due to a rapid rearrangement of carbocations and other competing elimination reactions.

Experimental

vic-Dibromides were prepared by the addition of bromine to the corresponding olefins. Hexamethylphosphoric triamide (Aldrich) was dried by allowing it to stand over calcium oxide for 24 h, followed by filtration and distillation under a vacuum. The melting points were determined on a Tropical Labequip apparatus, and are uncorrected. IR and NMR spectra were recorded on a Perkin–Elmer FT-IR and Hitachi FT-NMR 60 MHz, respectively. HPLC analyses were carried out on a Shimadzu LC-4A using SIL (Zorbax 150×4.6 mm) column and hexane as the eluent.

General Procedure. In a dried, N_2-filled round-bottomed flask mounted over a magnetic stirrer and fitted with a reflux condenser, was placed a mixture of *vic*-dibromide (1 g) and dry HMPA (4 mL). The system was de-aerated by flushing with N_2 for 15 min. The contents of the flask were heated in an oil bath maintained at 155–160 ˚C. The progress of the reaction was monitored by TLC (eluent: petroleum ether/benzene). After the starting material disappeared, the flask was cooled to room temperature and the mixture was poured into ice cold water (25 mL), at which time a solid was obtained. The solid was filtered at the pump, dried, and analyzed by mp, mixed mp, and spectra. The reactions of *meso*- and *dl*-stilbene dibromides were repeated. The reaction mixture was extracted with diethyl ether (2×15 mL) and subjected to an HPLC analyses. The crude-product mixture from reactions 13–18 was extracted with diethyl ether (2×15 mL) and concentrated on a rotary evaporator. The concentrate was chromatographed on a silica-gel column (100–200 mesh) using petroleum ether/benzene as the eluent. The products were isolated and identified.

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