The Addition of Bromine to 1,2-Diphenylethene

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The addition of bromine to a double bond, such as the double bond in cyclohexene, has been shown conclusively to be an anti addition *(1).* Another frequently used textbook example of anti addition to a double bond is the addition of bromine to *cis*-2-butene to yield the enantiomeric mixture, while the addition of bromine to *trans*-2-butene yields the meso product *(2).* In the undergraduate laboratory, the most often used example is the stereospecific addition of bromine to (*E*)- and (*Z*)-1,2-diphenylethene (*trans*-, *cis*-stilbene, respectively) to yield *meso*-1,2-dibromo-1,2-diphenylethane and *d,l*-1,2-dibromo-1,2-diphenylethane, respectively.

However, the stereochemical outcome becomes more complex when a variety of solvents and brominating reagents are used. Below, we outline how we "discovered" the complexity, present a table of data showing our experimental results, and suggest how the bromination of 1,2-diphenylethene, using a variety of solvents and brominating agents, can be used in both introductory and advanced organic chemistry courses. The reactions can be used to illustrate the effects of changing solvents and reagents, as well as to reveal interesting aspects of organic reaction mechanisms.

Background

For a number of years, we used the addition of bromine in dichloromethane to (*E*)-1,2-diphenylethene also dissolved in dichloromethane to demonstrate anti addition. Anti addition yields the meso adduct, melting point 240 °C *(3),* as compared to a melting point of 112 °C *(3)* for the racemic mixture, which would result from syn addition. Our students performed this experiment many times, obtaining high yields (70% yield range) of the pure meso adduct, which precipitates from the reaction mixture and is collected by suction filtration.

We considered having some of the students use (*Z*)-1,2-diphenylethene for comparison, but the higher cost of the cis isomer discouraged us. Finally, we decided to spend the money and have a few students in each section carry out the reaction with (*Z*)-1,2-diphenylethene. To their surprise and ours, they also obtained the meso product in decent yield (40% yield range), rather than the d,l product, which would result from anti addition.

Interestingly, if the bromination is carried out in glacial acetic acid using pyridinium bromide perbromide (PBPB), (*Z*)-1,2-diphenylethene yields the predicted racemic product *d,l*-1,2-dibromo-1,2-diphenylethane [see, for example, the laboratory texts by Fieser and Williamson *(4),* by Mayo, Pike, and Butcher *(5),* and by Mayo, Pike, and Trumper *(5)*]. The addition of bromine (produced by in situ generation of bromine using hydrobromic acid and potassium bromate in acetic acid) to (*E*)-1,2-diphenylethene to yield *meso*-1,2-dibromo-1,2-diphenylethane is described as one of the "Puzzles for the Organic Laboratory" by McGowens and Silversmith *(6).*

Experiment

We carried out the experiments as described in the laboratory manuals mentioned above to confirm the reported results and also carried out permutations of some of the procedures; that is, bromine in glacial acetic acid (2.25 M) and PBPB in dichloromethane, in which the PBPB is reasonably soluble. The amount of (*Z*)-1,2-diphenylethene used was 400 ± 3 mg (2.22 mmole). The results of the experiments are given in Table 1.

Hazards

Solutions of bromine and PBPB should be handled with care, with all steps in the reaction process carried out in fume hoods. Students must wear gloves that will provide adequate protection from the bromine solutions. Glacial acetic acid can also burn the skin. In the case of skin contact with a bromine- or PBPB-containing solution, immediately apply a dilute aqueous solution of 2% ammonia and then wash with copious quantities of water. The aqueous ammonia solution can also be used to remove any traces of bromine or PBPB from the glassware used for the preparation.

Table 1. Conditions and Yields for Bromination of (*Z*)-1,2-Diphenylethene

Brominating Agent	Solvent	*meso*-DBDPE[b]			*d,l*-DBDPE[b]		
		Mass/ mg	Amount/ mmole	Yield (%)	Mass/ mg	Amount/ mmole	Yield (%)
PBPB[a]	HOAc (glacial)	72	0.21	9.6	595	1.74	79.5
Bromine	HOAc (glacial)	152	0.45	20.1	503	1.48	65.8
PBPB[a]	CH_2Cl_2	69	0.20	9.2	627	1.84	83.4
Bromine	CH_2Cl_2	364	1.07	48.9	371	1.09	44.8

[a]Pyridinium bromide perbromide ($C_5H_6N^+Br_3^-$). [b]1,2-Dibromo-1,2-diphenylethane.

Results

None of the products from the set of experiments were recrystallized, which would have improved the melting points, particularly of *d,l*-1,2-dibromo-1,2-diphenylethane (*d,l*-DBDPE). However, the melting points were reasonable (d,l: 100–110 °C with previous softening; meso: 240–250 °C with previous softening especially if contaminated with some of the d,l) and indicated clearly the identity of the major product. Note that bromine in glacial acetic acid gives an acceptable yield of *d,l*-DBDPE, that PBPB in dichloromethane gives a slightly better yield of *d,l*-DBDPE than does PBPB in glacial acetic acid, and that even bromine in dichloromethane yields about 45% of *d,l*-DBDPE. The reason our students never isolated any of the *d,l* form in their experiment [(*Z*)-1,2-diphenylethene plus bromine in dichloromethane] is that they were instructed to simply filter the product. We recovered 49% of the d,l product by evaporating completely the dichloromethane. The relative amounts of the meso and d,l products can be determined more accurately by gas chromatographic analysis *(7).*

Discussion

These observations lead to some interesting questions: Why should PBPB in either glacial acetic acid or dichloromethane produce a majority of the d,l product from (*Z*)-1,2-diphenylethene while bromine in dichloromethane produces about a 50:50 mixture of the d,l and the meso? How does glacial acetic acid affect the reaction since its use with either brominating agent with (*Z*)-1,2-diphenylethene yields primarily the d,l product?

As a partial answer to these questions, a perusal of organic chemistry texts (and especially exercises) reveals that if groups are present that can stabilize a positive charge (for example, phenyl groups), mixtures of addition products are formed. The phenyl groups stabilize a carbocation leading to loss of stereospecificity; as a consequence, the reaction no longer proceeds via the cyclic bromonium ion. For a more detailed explanation, textbooks by Lowry and Richardson *(8)* or by Carey and Sundberg *(9)* can be consulted.

The most complete answers can be found by searching the original literature. As might be expected, the addition of bromine to 1,2-diphenylethenes has been well studied. One key article is by Buckles, et al. *(10).* They found that the reaction was 90–100% stereospecific in relatively nonpolar solvents. As solvents of higher dielectric constant were used, the addition became less stereospecific giving more of the meso product from (*Z*)-1,2-diphenylethene. However, when a bromide or tribromide salt was present, the stereospecificity was restored. Similar results were also observed by Heublein *(11).* He argued that a bromonium ion was the intermediate in the nonpolar solvents, and a classical carbonium ion intermediate in the polar aprotic solvents. More recent studies of the addition of bromine to 1,2-diphenylethene and ring-substituted 1,2-diphenylethenes have been carried out by Bellucci and co-workers (*12* and references cited therein). Explanations of solvent interaction with the carbonium or bromonium intermediates appear reasonable. However, another significant factor affecting stereochemical outcome, arises from the solvent interactions with the counter-anion (*13* and reference cited therein). Thus, the reaction results in acetic acid, a polar protic solvent, and dichloromethane, a polar aprotic solvent, can be explained based on solvent effects. Interestingly, the explanation for the reaction results using PBPB in either solvent will need to include consideration of hydrogen bonding involving the pyridinium ion.

For the introductory organic chemistry course, the students could do the four permutations to demonstrate the varied results that can be obtained by the use of different brominating agents in different solvents. The above theoretical questions could be posed in an advanced organic chemistry course after the students have performed the four permutations shown in Table 1. The students could be challenged to discover possible explanations in the original literature or to formulate hypotheses based on their understanding of solvent effects in organic reactions.

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