Pergamon

Tetrahedron Letters 40 (1999) 7267–7270

TETRAHEDRON
LETTERS

Aminium salt induced cyclodimerization of stilbenes in 1,1,1,3,3,3-hexafluoropropan-2-ol

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Received 20 May 1999; accepted 27 July 1999

Abstract

The aminium salt induced reactions of stilbenes (**1a–d**), affording a mixture of indane (**2a–c**) and/or tetrahydronaphthalene derivatives (**3a,c,d**), were found to occur with remarkably higher efficiency in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP) than, if at all, in dichloromethane (DCM) solutions. This solvent effect seems consistent with an electron-transfer mechanism via radical cations $\mathbf{1}^{+\cdot}$ that chemical evidence indicates to be favoured over an alternative electrophilic mechanism involving carbocations $\mathbf{1}\mathrm{H}^{+}$. © 1999 Elsevier Science Ltd. All rights reserved.

1,1,1,3,3,3-Hexafluoropropan-2-ol (HFP) is a solvent of high ionizing power, low nucleophilicity and high hydrogen bonding donor strength, which has been profitably employed in radical cation (as well as carbocation) chemistry. The prevailing feature that has been exploited so far in spectroscopic and mechanistic investigations is its remarkable stabilizing influence upon radical cations. In most cases it is well understood that such a stabilization is at least partly due to the very low reactivity of nucleophiles forming tightly solvated hydrogen bonded complexes with HFP.[1]

Continuing our interest for reactions induced by triarylaminium salts as hole transfer catalysts on electron-rich substrates,[2] we decided to investigate the possibly favourable influence of HFP, compared with the commonly employed dichloromethane (DCM),[2,3] in enhancing the oxidative power of these one-electron oxidants.

The substrates used in reactions carried out in HFP and in DCM solutions with catalytic amounts of tris-(2,4-dibromophenyl)aminum hexachloroantimonate (**A**) [E^{red}=1.66 V vs SCE] and tris-(4-bromophenyl)aminum hexachloroantimonate (**B**) [E^{red}=1.16 V vs SCE], are represented by *cis*-stilbene (**1a**) [E^{ox}=1.70 V vs SCE], *trans*-stilbene (**1b**) [E^{ox}=1.59 V vs SCE], *trans*-4,4′-dimethylstilbene (**1c**) [E^{ox}=1.45 V vs SCE], *trans*-4,4′-dimethoxystilbene (**1d**) [E^{ox}=1.24 V vs SCE], and *trans*-4,4′-dichlorostilbene (**1e**) [E^{ox}=1.85 V vs SCE]. In the cases in which a transformation was observed, these compounds were found to undergo cyclodimerization affording indane (**2a,c**) and/or tetrahydronaphthalene derivatives (**3a,c,d**), as indicated in Scheme 1. It is worth noting that there are no precedents

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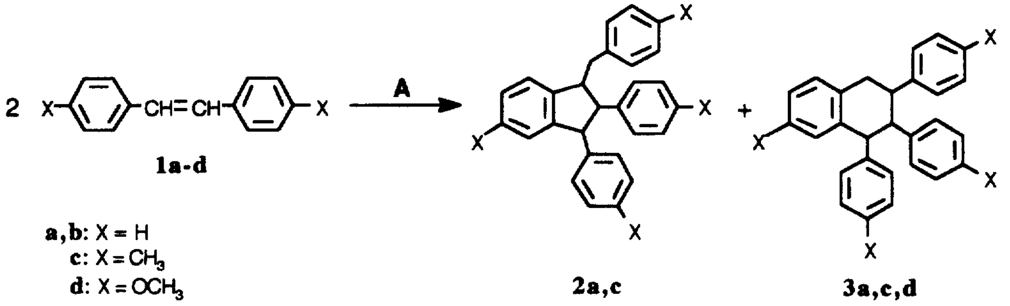
PII: S0040-4039(99)01447-1

for a similar process occurring on reaction of stilbenes with other oxidant/solvent combinations, or photochemical methodologies.[4]



Scheme 1.

Typical experimental conditions were as follows: a catalytic amount of aminium salt **A**, or **B** (0.1 mmol, 10 mol%) was rapidly added to solutions of **1a–e** (1 mmol) in the appropriate solvent (10 ml), with stirring at room temperature. Aliquots of the reaction mixtures were analyzed by GC/MS spectrometry and the results are reported in Table 1. The reaction products **2a,c** and **3a,c,d**, isolated by silica gel column chromatography, were fully characterized by physical and spectral data.[5]

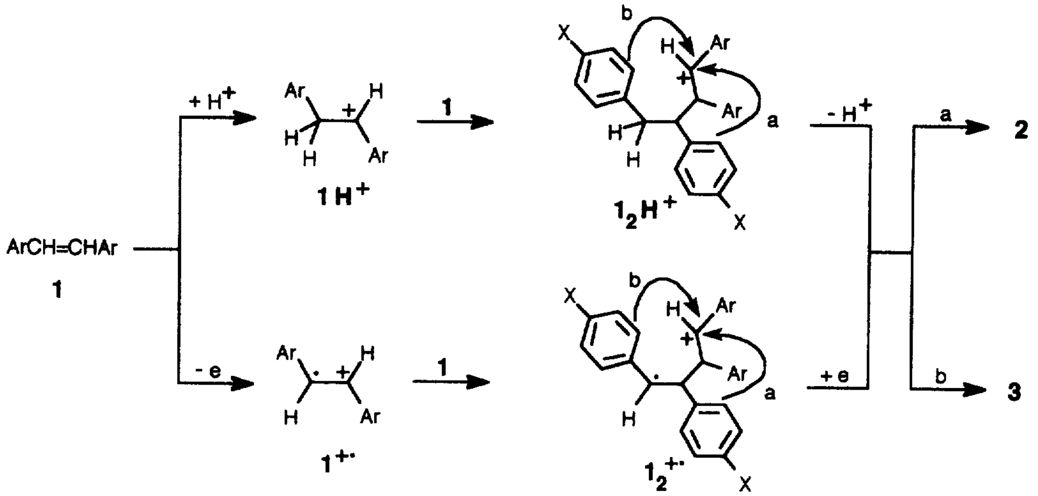
The data in Table 1 show a higher efficiency of reactions carried out in HFP (runs 1, 4, 7, 10) in comparison to those performed in DCM (runs 2, 5, 8, 11). According to the above-mentioned peculiar properties of HFP, it is likely that this solvent might exert a favourable influence on the preliminary activation step, when radical cations $1^{+\cdot}$ and/or carbocations $1H^+$ would be generated by the aminium salt acting as a one-electron acceptor and as a source of acidic conditions, respectively.[2,3,6] It is important

Table 1
Reaction products from stilbenes and aminium salts in HFP and DCM solutions

run	stilbene	aminium salt[a]	solvent	reactn time (h)	conv[b] (%)	product[b] distribution (%)
1	**1a**	**A**	**HFP**	2.5	100	**2a** (40) : **3a** (60)
2	**1a**	**A**	**DCM**	24	<1	
3	**1a**	**B**	**HFP**	24		**1b**[c]
4	**1b**	**A**	**HFP**	6	100	**2a** (30) : **3a** (70)
5	**1b**	**A**	**DCM**	24	<1	
6	**1b**	**B**	**HFP**	24	0	
7	**1c**	**A**	**HFP**	0.5	100	**2c** (15) : **3c** (85)
8	**1c**	**A**	**DCM**	24	10	**2c** (15) : **3c** (85)
9	**1c**	**B**	**HFP**	24	5	**2c** (15) : **3c** (85)
10	**1d**	**A**	**HFP**	0.15	100	**3d** (100)
11	**1d**	**A**	**DCM**	24	10	**3d** (100)
12	**1d**	**B**	**HFP**	0.15	90	**3d** (100)
13	**1e**	**A**	**HFP**	24	0	
14	**1e**	**A**	**DCM**	24	0	

[a] 10 mol % of **A** or **B** were used. [b] Gas chromatographic conversions and yields were determined by using an internal standard; the yields, based on substrate consumption, were occasionally confirmed by product isolation, resulting in all cases > 98%. [c] Isomerization of **1a** into **1b** was observed.

to note that both these species are equally compatible with the product nature, each one providing access to a distinct reaction pathway as indicated in Scheme 2. By addition to a new substrate molecule, in fact, radical cations $1^{+\cdot}$ and carbocation $1H^+$ would give the corresponding dimers $1_2^{+\cdot}$ and 1_2H^+, whose cyclization by internal electrophilic attack on γ-aryl (path *a*) or δ-aryl (path *b*) nucleus affords indane derivatives **2** and/or tetrahydronaphthalene derivatives **3**, respectively. Product formation should be ultimately accompanied by proton release in the case of carbocation-mediated transformation, or by one-electron capture in the case of radical cation, thus accounting for the catalytic character of the whole process.



Scheme 2.

Since radical cation formation would be favoured by increasing oxidative power of the aminium salt, the observed higher performance of **A** (runs 1,4,7,10) compared to **B** (runs 3,6,8,12) in promoting cyclodimerization supports an ET mechanism but does not rule out the alternative mechanism altogether. As a matter of fact, we found similar relative reactivity of the two aminium salts in analogous reactions that were proved to proceed via carbocation formation.[2a,b] Also, the relative reactivities of the various substrates, e.g., the high reactivity of **1d** (run 10) and the unreactivity of **1e** (run 13), are evidently accountable within both the mechanisms on the basis of the reported oxidation potentials or of the predictable basicity order of stilbenes.

However, conventional criteria to discriminate between ET and electrophilic mechanism were applied by carrying out reactions in the following conditions: (a) in the presence of equimolar amounts (vs aminium salt **A**) of a hindered and non-nucleophilic base, such as 2,6-di-*tert*-butylpyridine (DBP); (b) by adding to HFP and DCM solutions of stilbenes equimolar amounts of trifluoroacetic acid (TAA) to produce strongly acidic conditions. In the latter conditions cyclodimerization was found to occur, but less efficiently, only in the case of the more basic **1d**, which gave **3d** with 90% and 10% conversion after 24 h in HFP and DCM, respectively. This suggests that stilbene basicity would be inherently too weak for believing the carbocation mediated mechanism could be significantly involved in aminium induced cyclodimerization. On the other hand, consistently with an ET mechanism, DBP-modified reactions of **1a–d** solutions in HFP were apparently slower and less efficient than the unmodified ones, but in no case was cyclodimerization prevented. Further, that **A** and **B** are capable of stimulating radical cation reactivity on stilbenes is reinforced by the results of a mechanistic study on aminium salt-catalyzed cyclopropanation of these substrates.[7a,b]

In conclusion, we have found that HFP has a strong favourable effect on the aminium salt-induced cyclodimerization of stilbenes. In view of a most likely radical cation mechanism, we give a tentative interpretation of such a solvent effect in terms of enhanced oxidizing power of the aminium salt that might simply arise from tight hydrogen bonding solvation exerted by HFP on the reduced form of the triarylaminium/triarylamine redox couple. Further studies are warranted in order to define the scope and limitations of HFP as a suitable solvent for aminium salt induced chemistry.

Acknowledgements

This work was supported in part by Ministero della Ricerca Scientifica e Tecnologica, Rome — Progetto Cofinanziato 'Radicali Liberi e Radicali Ioni nei Processi Chimici e Biologici'.

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5. 1-Benzyl-2,3-diphenylindane (**2a**): m.p. 101–102°C (from ethanol 95%); *m/z* (rel. abund.): 360 (M^+, 10), 269 (M^+–[$PhCH_2$], 100), 191 (85), 91 (78); ^{1}H NMR ($CDCl_3$) δ 6.9–7.4 (m, 19H), 4.28 (d, 1H, J=9.7 Hz), 3.8 (partially resolved ddd, 1H), 3.11 (t, 1H, J=9.7 Hz), 3.07 (dd, 1H, J=14.3, 5.1 Hz), 2.95 (dd, 1H, J=14.3, 8.1 Hz) ppm; ^{13}C NMR ($CDCl_3$) δ 39.51 (C-10), 51.84 (C-7), 59.37 (C-9), 63.38 (C-8), 123.88, 124.97, 125.94, 126.39, 126.42, 126.94, 127.06, 128.07, 128.16, 128.26, 128.49, 129.27, 139.97, 142.18, 143.38, 145.33, 145.67 ppm; IR (KBr) 3027, 2919, 2603, 1739, 1605, 1510, 1303, 1249, 1034, 739 cm^{-1}. Anal. calcd for $C_{28}H_{24}$: C, 93.29; H, 6.71. Found: C, 93.53; H, 6.88. Consistent spectroscopic data have been recorded for **2c**. 1,2,3-Triphenyl-1,2,3,4-tetrahydronaphthalene (**3a**): m.p. 108–109°C (from ethanol); *m/z* (rel. abund.): 360 (M^+, 15), 269 (M^+–[$PhCH_2$], 12), 180 (100), 165 (22), 91 (9); ^{1}H NMR ($CDCl_3$) δ 6.8–7.3 (m, 19H), 4.25 (d, 1H, J=10.5 Hz), 3.40 (td, 1H, J=11.8, 4.2 Hz), 3.30–3.20 (m, 2H), 3.07 (dd, 1H, J=16.3, 4.2 Hz) ppm; ^{13}C NMR ($CDCl_3$) δ 40.04, 46.62, 55.38, 56.18, 125.60, 125.88, 125.91, 126.09, 127.59, 127.92, 128.04, 128.24, 129.31, 130.05, 136.87, 142.56, 144.20, 145.40 ppm; IR (KBr) 3025, 2919, 1739, 1601, 1491, 749, 698 cm^{-1}. Anal. calcd for $C_{28}H_{24}$: C, 93.29; H, 6.71. Found: C, 93.46; H, 6.93. Consistent spectroscopic data have been recorded for **3c** and **3d**.
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