is overruled by the deactivation of two sulfo substituents.

A compilation of the observed and predicted[35] positional reactivity orders for the [10]annulenes **1** and **2** is given in Table V. On the basis of additivity of the effects of the [10]annulene group and the sulfo groups (see before) and the data of Table IV it follows that $k_{2,8\rightarrow4} = k_{2,4\rightarrow8} > k_{2,4\rightarrow7} > k_{2,7\rightarrow4}$. Accordingly the rate of conversion of the disulfonic acids will decrease in the order 2,4- > 2,8- > 2,7-disulfonic acid. The lower reactivity of the 2,7-isomer is actually apparent in the **2** series (cf. Table III, entries 9a,b and 10).

Experimental Section

Starting from 1,4,5,8-tetrahydronaphthalene,[38] the [10]-annulenes **1** and **2** were synthesized, following the sequences shown in Scheme I, as described extensively elsewhere.[39,40] The synthesis of **3** was reported before.[41]

The sulfonation in dioxane as solvent was effected by adding at ca. 20 °C 0.4 mmol of the [10]annulene in ($^2H_8$)dioxane (0.30 mL) to the (heterogeneous) solution of the desired amount of SO_3 in ($^2H_8$)dioxane (1.00 mL). The sulfonation in nitromethane was effected by adding to 0.4 mmol of the [10]annulene in ($^2H_3$)-nitromethane (0.40 mL) at ca. 20 °C a solution of the desired amount of SO_3 in ($^2H_3$)nitromethane (1.00 mL). The progress of the reaction was determined by recording ^1H NMR spectra at appropriate time intervals. In a number of cases, the reaction mixtures were quenched with ^2H_2O, the aprotic solvents removed by separation or—after neutralization—by freeze-drying and subsequent dissolution of the residual salts in ^2H_2O, and the ^1H NMR spectra of the resulting solutions of the sulfonic acids or sulfonates in ^2H_2O recorded. The ^1H NMR spectra were recorded with a Varian XL-12 CW and a Bruker WM-250 spectrometer with reference to $SiMe_4$ as virtual internal standard.

The sulfo product compositions of the various reaction mixtures were determined by multicomponent ^1H NMR analysis.[23] For the various mono- and disulfonic acids, the sulfonation isomer distribution ratios have been calculated from the compositions of the mono- and disulfonic acids and the di- and trisulfonic acid mixtures, respectively, by the method exemplified before for 1,2,3-trimethylnaphthalene-5-sulfonic acid,[42] assuming the very small amounts of the 2,4,7-trisulfonic acids of **2** present in the reaction mixture (cf. Table III, entry 8a) to result for 50% from the corresponding 2,4- and 2,7-disulfonic acids.

Acknowledgment. We thank Drs. S.M. van der Kerk and P. de Wit for valuable discussions and Mr. C. Kruk and Mmes N.E. Bruinzeel, H. van der Laan-Ctvrteckova, and C. A. M. Mittendorf-van Rijn for recording the NMR spectra.

Registry No. 1, 10474-24-5; 1-2-S, 79865-00-2; 1-2,4-S_2, 108743-77-7; 1-2,7-S_2, 108743-78-8; 1-2,8-S_2, 108743-79-9; 1-2,4,7-S_3, 108743-80-2; 1-2,7,12-S_3, 108743-81-3; **2**, 88635-77-2; **2**-2-S, 108743-82-4; **2**-3-S, 108743-83-5; **2**-2,4-S_2, 108743-84-6; **2**-2,7-S_2, 108743-85-7; **2**-2,8-S_2, 108743-86-8; **2**-2,4,7-S_3, 108743-87-9; **2**-2,4,8-S_3, 108743-88-0; **3**, 36628-80-5; **3**-2-S, 102234-10-6; **3**-2,7-S_2, 108743-89-1; **4a**, 108772-64-1; **4b**-2,7-S_2, 108743-90-4; **5a**-2-S, 108743-91-5.

Supplementary Material Available: ^1H and ^{13}C NMR spectral data of 1–3 and their sulfonation products in ($^2H_8$)dioxane, ($^2H_3$)nitromethane, and ^2H_2O as solvents (4 pages). Ordering information is given on any current masthead page. Syntheses of 1 and 2 starting from 1,4,5,8-tetrahydronaphthalene are given in ref 39.

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Retro-Ene Reactions of N-Substituted Derivatives of 4-Aza-2,2-dimethyl-1-phenyl-3-butenone and Related Compounds

Diego Armesto,*† William M. Horspool,‡ Rafael Pérez-Ossorio,† and Ana Ramos†

Departamento de Química Orgánica, Facultad de Química, Universidad Complutense, 28040 Madrid, Spain, and Department of Chemistry, The University, Dundee DD14HN, Scotland

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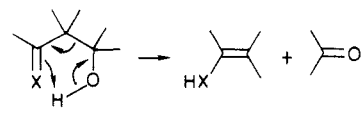
The retro-ene reactions of N-substituted derivatives of 4-aza-2,2-dimethyl-1-phenyl-3-butenone with methanol and benzylamine are described. The reactions with methanol yield methyl benzoate and N-substituted derivatives of 2-methylpropanimine. Reaction of *N*-benzyl-4-aza-2,2-dimethyl-1-phenyl-3-butenone with benzylamine yields *N*-benzyl-2-methyl-1-phenylpropanimine and *N,N'*-dibenzylformamidine.

Fragmentation reactions of the retro-ene type have been the subject of extensive studies and have been reviewed in recent times.[1,2] Many β,γ-unsaturated alcohols[3] and a few β,γ-unsaturated amines[4] undergo retro-ene fragmentations at high temperature according to the path shown in Scheme I. The thermal amine-catalyzed retro-aldol condensation also fits into this reaction system.[5] However, as a general rule, there are only a few examples where a CN double bond is utilized as the terminus for the hydrogen transfer,[6,7] and in most systems where the C=N is used it is part of a heteroaromatic system.

In a previous paper we reported the first example of retro-ene type fragmentation in acyclic iminoketones.[8]

Scheme I



Later, De Kimpe et al.[9] described a similar reaction in the fragmentation of α,α'-dichloro-β-iminocarbonyl com-

† Universidad Complutense.
‡ The University, Dundee.

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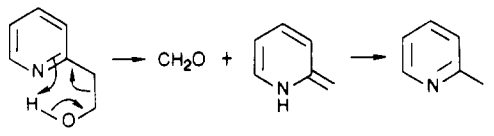
0022-3263/87/1952-3378$01.50/0

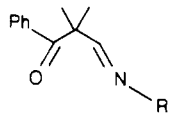
Scheme II



6

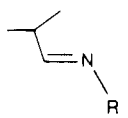
pounds. We wish to report now our observations on the nucleophile-induced fragmentation of imino ketones.

The synthesis of the imines **1a–c** has already been described by us.[10] Imine **1d** was synthesized by the same procedure and its spectroscopic and analytical data are completely in accord with the proposed structure.



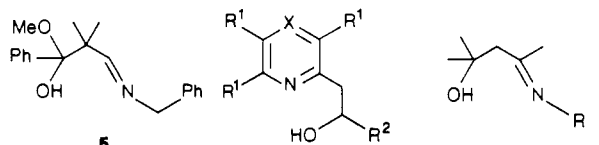
1a: R = $PhCH_2$
b: R = *i*-Pr
c: R = Ph
d: R = Ph_2CH

The dissolution of the imine **1a** in wet ether brought about the slow deposition of a precipitate. Analysis of this showed it to be benzylammonium benzoate. A more rapid reaction occurred when imino ketone **1a** was refluxed in methanol for 1 h. Thin-layer chromatography indicated that the reaction was quantitative. Workup afforded methyl benzoate and *N*-benzyl-2-methylpropanimine **2**, which was identified by comparison with an authentic sample. Similar behavior was observed for imino ketones **1b** and **1d**, which both yielded methyl benzoate and the corresponding propanimines **3** and **4**, both of which were identified by comparison with authentic samples. Imino ketone **1c** also reacted under those conditions, but only methyl benzoate was identified after workup of the reaction mixture.



2: R = $PhCH_2$
3: R = *i*-Pr
4: R = Ph_2CH

The normal behavior of alkylimino groups in the presence of water is hydrolysis resulting in the cleavage of the CN double bond.[11] In this instance such a path could not account for the formation of the observed products in either the water or methanol reactions. Thus, an alternative interpretation, that of attack on the carbonyl group, has to be considered. This attack most likely produces an hemiacetal **5**. The relationship between this intermediate



5

6: $R^1 = R^2 = H$; X = CH
7: $R^1 = Me$; $R^2 = Ph$; X = N

8

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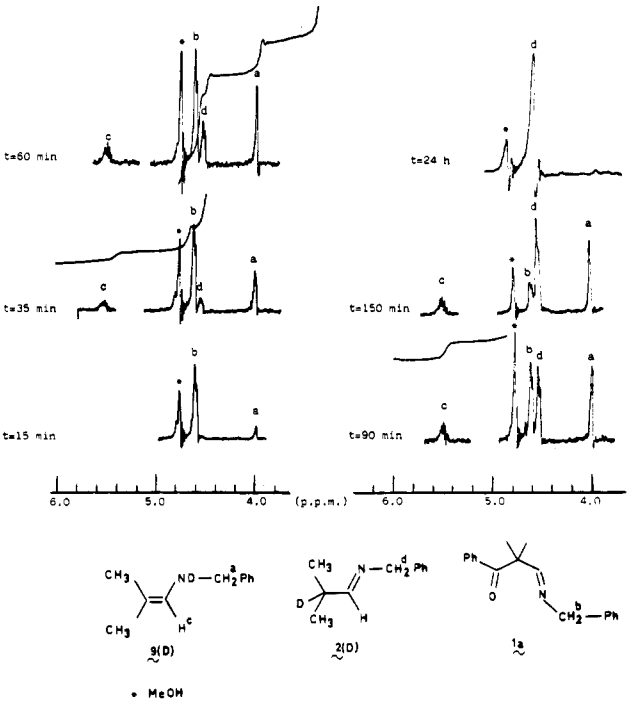
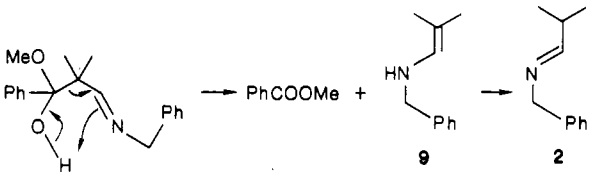


Figure 1. Time-dependent ^1H NMR spectra for the reaction of **1a** and CD_3OD.

Scheme III



5 9 2

and molecules **6**[12] and **7**,[6] which have previously been shown to undergo retro-ene reactions, is instantly obvious. These molecules undergo bond fission at elevated temperatures (150 °C) in the manner shown in Scheme II.

Similar behavior, although at much lower temperature, accounts for the amine-catalyzed retro-aldol condensation of diacetone alcohol—where the imino alcohol **8** is proposed as the key intermediate.[5] Thus, we propose that the fragmentation of imino hemiacetal **5** follows the path outlined in Scheme III analogous to Scheme II. This readily accounts for the formation of methyl benzoate and the imine **2**, provided that enamine **9** is formed as an intermediate. Enamines of this class are usually unstable and readily isomerize to imines like **2**.[13] The intermediacy of **9** is difficult to demonstrate under these reaction conditions. The course of the reaction of imine **1a** with CD_3OD was followed by ^1H NMR. Under these conditions only imine **2** was detected. The failure to observe enamine **9** in this experiment was considered to be due to the acidity of the CD_3OD, which rapidly brought about the isomerization of **9** into **2**. To prevent or slow down the isomerization a little Na_2CO_3 was added to the solution of imine **1a** in CD_3OD. The results of this are shown in Figure 1, which represents the δ 3–6 region of the spectrum (the signals in this region are better defined and provide more conclusive evidence of the reaction path than the signals previously reported in our earlier note[8]). After 35 min new signals appear at δ 4.0 and 5.5 and are attributable to the

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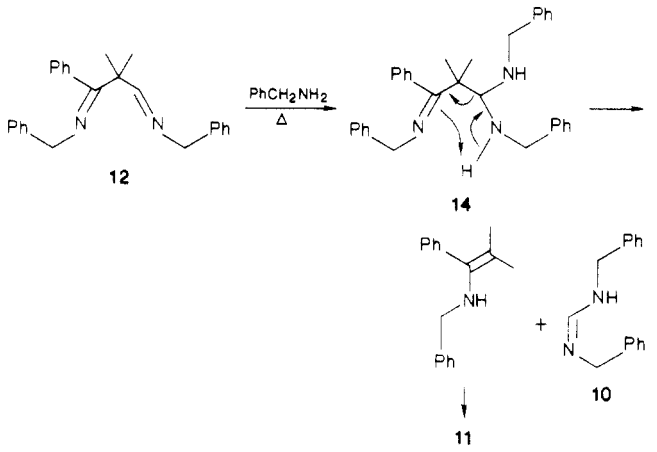
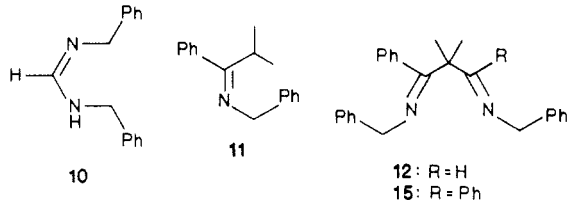
(13) Knorr, R.; Weiss, A.; Löw, P.; Räpple, E. *Chem. Ber.* **1980**, *113*, 2462.

Scheme IV

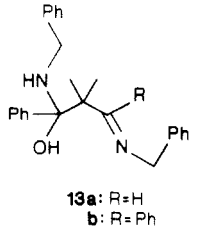


methylene and vinyl protons of **9** (deuteriated on N). After 60 min these signals are still present but a new signal at δ 4.5, the methylene of imine **2**, begins to grow in and continues to increase through 150 min. After 24 h only the methylene signal of **2** is left. Thus the proposal of Scheme III is substantiated. A similar reaction path can account for the formation of benzylammonium benzoate formed by reaction of imine **1a** in wet ether. In this case nucleophilic attack by water yields the keto hydrate, which would fragment to benzoic acid and enamine **9**. Reaction of these products followed by hydrolysis would yield benzylammonium benzoate.

The imino ketone **1a** also reacts with benzylamine at reflux. Workup of the mixture after 30 min afforded *N,N'*-dibenzylformamidine (**10**) and the imine **11**. Clearly the reaction follows a slightly different path from that outlined in Scheme III since the products from that mode of reaction would not include a formamidine.



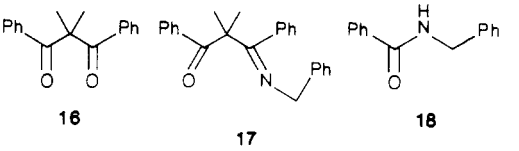
Interestingly the products **10** and **11** are also formed in the reaction of the diimine **12** with benzylamine. Thus, the first step in the reaction of imino ketone **1a** with benzylamine could be the formation of the diimine **12**. This reaction could proceed via the intermediate **13a**, but dehydration to yield **12** must be more favored than a retro-ene reaction.



The products **10** and **11** must arise, therefore, by addition of benzylamine to the diimine **12** as outlined in Scheme IV. The attack of the amine takes place at the less hindered and more reactive aldimine carbon affording intermediate **14**, the nitrogen analogue of **5**, which fragments by a retro-ene process yielding formamidine **10** and an enamine which isomerizes to yield imine **11**.

There is no literature precedent for retro-ene fragmentations of the type illustrated for **14**. The diimine **15** is unreactive under identical conditions. The difference in reactivity between diimine **12** and diimine **15** is presumably the result of the lower reactivity of arylimines to nucleophilic attack.

The reaction of the 1,3-diketone **16** with benzylamine is related to this problem. Under the usual conditions it was not possible to isolate the monoimine **17** since this apparently readily undergoes nucleophilic attack at the more reactive carbonyl carbon followed by retro-ene fragmentation to yield imine **11** and amide **18**. The difference in reactivity of **17** and **1a** does present some difficulties. It is likely that both **17** and **1a** react similarly with benzylamine to yield analogous intermediates **13b** and **13a**. Intermediate **13a** apparently dehydrates to **12**, which then follows the path outlined in Scheme IV. However, intermediate **13b** prefers to fragment by the retro-ene path to yield imine **11** and amide **18**. This difference in behavior could be related to the enhanced basicity of the imine nitrogen in **17** (or intermediate **13b**), due to the conjugation of the imino group with a phenyl ring. Pollack and Cooper[5] have shown a similar effect in their study on amine-catalyzed cleavage of diacetone alcohol.



The experiments described by us give evidence for the novel fragmentation path of 1,3-imino ketones on reaction with alcohols and amines. Our interpretation of these identifies the process as novel retro-ene reactions of a type previously unrecognized in such systems. The ease with which these reactions occur is contrasted with the much higher temperature processes described for imine systems where the imine is part of a heterocyclic ring.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 257 spectrophotometer; band positions are reported in wavenumbers (cm^{-1}). ^1H NMR spectra were obtained on a Varian T-60A spectrometer, and chemical shifts (δ) are expressed in parts per million downfield from internal Me_4Si. The mass spectra were determined with a Varian MAT-711 spectrometer. Elemental analyses were performed by the Consejo Superior de Investigaciones Científicas, Madrid.

Synthesis of Monoimines. Monoimines **1a–c** were prepared by the previously described method.[10]

***N*-(Diphenylmethyl)-4-aza-2,2-dimethyl-1-phenyl-3-butenone (1d).** This was prepared with the same experimental conditions described by us[10] for the synthesis of monoimines, on a 17-mmol scale, and yielded **1d** (4.2 g, 70%) as a white crystalline solid; mp 81–83 °C (from ethanol); ^1H NMR ($CDCl_3$) δ 1.5 (s, 6 H, $2CH_3$), 5.4 (s, 1 H, CH), 7.0–7.4 (m, 13 H, Ar), 7.5–7.8 (m, 2 H, Ar), 7.9 (s, 1 H, CH=N); IR (KBr) 1680, 1650 cm^{-1}; MS, *m/e* (relative intensity) 313 ($M^+ - 28$, 26), 168 (53), 167 (100), 165 (56), 152 (39), 121 (23), 105 (56), 77 (37); UV (EtOH) λ_{max} 245 nm (ϵ 12000), 284 (1200). Anal. Calcd for $C_{24}H_{23}NO$: C, 84.42; H, 6.79; N, 4.10. Found: C, 84.71; H, 7.07; N, 4.25.

Synthesis of Diimines. Diimine **15** was prepared by the previously described method.[14]

***N,N'*-Dibenzyl-1,5-diaza-3,3-dimethyl-2-phenyl-1,4-pentadiene (12).** This was prepared with the same experimental condition described by us[14] for the synthesis of diimines. From **1a** (1.5 g, 5.7 mmol), benzylamine (15 mL, 138 mmol) and titanium(IV) chloride (0.9 mL, 8 mmol) yielded 1 g (50%) of **12**: bp 190 °C (0.1 mmHg); ^1H NMR (CCl_4) δ 1.3 (s, 6 H, $2CH_3$), 4.2 (s, 2 H, CH_2), 4.5 (br s, 2 H, CH_2), 7.0–7.4 (m, 15 H, Ar), 7.8 (br s,

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1 H, CH=N); IR (film) 1660, 1635 cm^{-1}; MS, m/e (relative intensity) 354 (M^+, 0.2), 339 (2), 237 (31), 105 (23), 91 (100), 77 (18). The product was unstable and gave unreliable microanalytical data.

Reaction of 1a with Water. A solution of **1a** (1 g, 4.0 mmol) in ether saturated with water (100 mL) was set aside for 1 week. After this time a white crystalline product had deposited. This was removed by filtration, and the product (0.85 g, 94%) was identified as benzylammonium benzoate by comparison with an authentic sample.

Reaction of 1a with Methanol. A solution of **1a** (1 g, 4 mmol) in methanol (80 mL) was refluxed for 1 h. The solvent was removed and the residual oil was distilled under reduced pressure. [In all the experiments, with the exception of that for **1c**, NMR spectroscopy of the crude showed that the reaction had gone to 100% completion forming the fragmentation products exclusively.] The fraction collected at 25 °C (0.1 mmHg) was methyl benzoate, and the fraction at 35 °C (0.1 mmHg) was identified as *N*-benzyl-2-methylpropanimine (**2**). Proof of identity was obtained by comparison with an authentic sample prepared by the method of Tiollais.[15]

Reaction of 1b with Methanol. A solution of **1b** (1.7 g, 8 mmol) in methanol (0.5 mL) was refluxed for 8 h. Distillation of the crude yielded a fraction at 95 °C identified as *N*-isopropyl-2-methylpropanimine (**3**) by comparison with an authentic sample prepared by the method of Tiollais[15] and a fraction at 100 °C (80 mmHg) identified as methyl benzoate.

Reaction of 1c with Methanol. A solution of **1c** (1 g, 4 mmol) in methanol (80 mL) was refluxed for 8 h. The solvent was removed, and the residual oil was distilled under reduced pressure. The fraction at 25 °C (0.1 mmHg) was identified as methyl benzoate, and the ^1H NMR spectrum of the residue showed a complex pattern of signals.

Reaction of 1d with Methanol. A solution of **1d** (1 g, 3 mmol) in methanol (60 mL) was refluxed for 8 h. The solvent was removed, and the residual oil was distilled under reduced pressure. The fraction collected at 100 °C (80 mmHg) was methyl benzoate, and the residue was identified as *N*-(diphenylmethyl)-2-methylpropanimine (**4**) by comparison with a pure sample synthesized by the method of Tiollais.[15]

Reaction of 1a with Benzylamine. A mixture of **1a** (1 g, 4 mmol) and benzylamine (5 mL, 46 mmol) was refluxed for 30 min. The benzylamine was removed by distillation under reduced pressure, and the crude was washed with hexane. The residual oil crystallized from *n*-pentane yielding 0.35 g (41%) of *N,N'*-dibenzylformamidine (**10**), mp 75 °C (lit.[16] mp 75.5–77.5 °C). Evaporation of hexane from the organic layer yielded 0.61 g (68%) of *N*-benzyl-2-methyl-1-phenylpropanimine (**11**). Both **10** and **11** were identified by comparison with pure samples synthesized by the methods of Taylor et al.[16] and Pérez-Ossorio et al.,[17] respectively.

Reaction of 12 with Benzylamine. A mixture of **12** (0.44 g, 1.2 mmol) and benzylamine (3 mL, 28 mmol) was refluxed for 30 min. The crude was treated as described before, yielding 0.23 g (83%) of **10** and 0.26 g (88%) of **11**.

Reaction of 15 with Benzylamine. A mixture of **15** (175 mg, 0.4 mmol) and benzylamine (3 mL, 28 mmol) was refluxed for 30 min. After this time workup yielded the unchanged imine.

Reaction of 16 with Benzylamine. A mixture of **16** (1 g, 4 mmol) and benzylamine (5 mL, 46 mmol) was refluxed for 30 min. After removal of the benzylamine, the crude was washed with hexane. The residual solid was recrystallized from hexane/ethanol, giving 0.72 g (86%) of *N*-benzylbenzamide (**18**) as white needles, mp 105–106 °C (lit.[18] mp 105–106 °C). Evaporation of hexane from the organic layer yielded 0.68 g (72%) of **11**.

Acknowledgment. We thank the British Council, The Ministerio de Educación y Ciencia of Spain, and the Comisión Asesora de Investigación Científica y Técnica for financial support.

Registry No. **1a**, 86537-64-6; **1b**, 108344-34-9; **1c**, 108344-35-0; **1d**, 108365-39-5; **2**, 22483-21-2; **3**, 28916-24-7; **4**, 62740-71-0; **10**, 2304-00-9; **11**, 101583-56-6; **12**, 108344-36-1; **15**, 108344-37-2; **16**, 41169-42-0; **18**, 1485-70-7; benzylammonium benzoate, 34243-68-0; methyl benzoate, 93-58-3.

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(18) Blacher, C. *Chem. Ber.* **1895**, *28*, 434.

Electron Transfer on the Photodehalogenation of 2-(4-Chlorophenyl)benzoxazole Assisted by Amines

Suzanne Fery-Forgues, Dominique Lavabre, and Nicole Paillous*

Laboratoire des IMRCP, UA au CNRS no. 470, Université Paul Sabatier, 31062 Toulouse Cedex, France

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The photochemical reactivity of 2-(4-chlorophenyl)benzoxazole in the presence of a series of amines has been investigated. A fluorescence quenching study provides evidence for the formation of an exciplex between the singlet excited state of the benzoxazole derivative and the amine in its ground state. This exciplex gives rise to a charge-transfrer complex (CTC). The quenching fluorescence date can be fitted by a Weller–Marcus system, thus leading to large reorganization energies. The measurement of dehalogenation, which is drastically increased in the presence of amines, allowed us to estimate the reactivity of the CTC. In the case of tertiary amines, 1% of the CTC formed via the singlet state leads to the dehalogenation. For secondary amines a hydrogen transfer between the amine and the excited triplet state of the chloro compound is also postulated.

Electron transfers between the excited state of light-absorbing molecules and electron-rich or electron-poor substrates have been extensively investigated in the last 2 decades.[1] Only a few reports have focussed on the involvement of such a process during the dehalogenation reactions of aromatic compounds. Chlorides of the benzene,[2,3] naphthalene,[2,4] biphenyl[2,5] and anthracene[5]

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