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Single electron transfer vs Diels Alder reaction: A comparative study of the reaction of 1-(anthracen-9-yl)-*N*,*N*-dimethylmethanamine and (anthracen-9-ylmethyl)(methyl)sulfane with dibenzoylethylene

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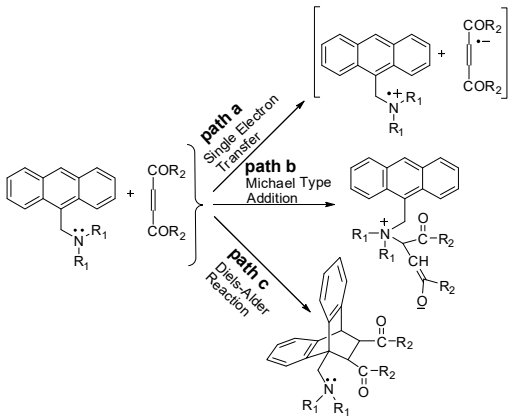
ABSTRACT



We have examined the reactions of 1-(anthracen-9-yl)-*N*,*N*-dimethylmethanamine and (anthracen-9-ylmethyl)(methyl)sulfane with dibenzoylethylene in different solvents. Single electron transfer mediated reactions predominated in the case of 1-(anthracen-9-yl)-*N*,*N*-dimethylmethanamine while the Diels-Alder pathway was important for (anthracen-9-ylmethyl)(methyl)sulfane.

Keywords: (anthracen-9-yl)methanamines, (anthracen-9-yl)methylsulfanes, dibenzoylethylene, cycloaddition, electron transfer reaction.

INTRODUCTION

Electron transfer reactions are ubiquitous in nature[1]. Thanks to the presence of lone pair electrons, amines and sulfanes are easy to oxidize[2] and hence are good single electron donors.[3-7] Both amines and sulfanes are active Michael donors as well.[8,9]

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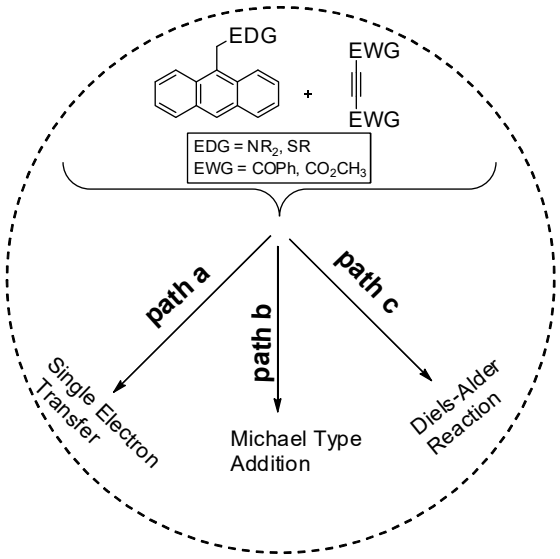
Competing one electron transfer, two electron transfer and Diels-Alder reaction possibilities exist for (anthracen-9-yl)methanamines[10] and (anthracen-9-yl)methylsulfanes.[11] We have successfully established dramatic solvent and concentration dependence of the reaction of (anthracen-9-yl)methanamines[12] and sulfanes[13] with suitable electron deficient acetylenes such as dimethyl acetylenedicarboxylate (DMAD) and dibenzoylacetylene (DBA). Reactions of (anthracen-9-yl)methanamines and (anthracen-9-yl)methylsulfanes with electron deficient acetylenes followed a similar pattern in different solvents at different concentrations.[12,13] Both amines and sulfanes gave products arising through single electron transfer, nucleophilic addition and cycloaddition. At concentrations <0.05 M, the cycloaddition pathway did not

operate for amines. But with sulfides, cycloaddition was predominant in all solvents at all concentrations.



Scheme 1. Competing reactions between anthracenemethanamines/anthracenemethylsulfanes with electron deficient acetylenes.

Both DMAD and DBA are highly reactive and hence less selective in their reactions. Moreover, extensive oligomerization of DBA and DMAD rendering product separation tedious was observed in their reactions with amines and sulfanes. We reasoned that selection of a dienophile of lower reactivity is more appropriate to unravel selectivity among the competing reaction pathways available for amine/sulfane reaction with dienophiles. Hence, we selected dibenzoylethylene (DBE) as the reactive dienophile for the present investigation. We observed that DBE exhibits differential reactivity towards amine and sulfanes: as single electron acceptor towards (anthracen-9-yl)methanamines and as a dienophile towards (anthracen-9-yl)methylsulfanes.

Results and Discussion

1-(Anthracen-9-yl)-*N*,*N*-dimethylmethanamine (**1**) and (anthracen-9-ylmethyl)(methyl)sulfane (**2**) were synthesised by modified procedures developed in our laboratory.[10,11] DBE (**3**) is commercially available (Chart 1).

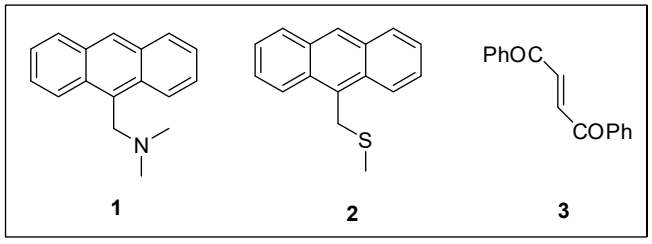


Chart 1. Starting materials for studying the diverse reactivity of anthracenemethanamines and anthracenemethylsulfanes with electron deficient alkene.

We examined the reaction of **1** and **2** with DBE (**3**) in different solvents at low concentration (0.05 M). As expected, reactions proceeded very slowly and even after 60 h, substantial quantities of starting materials remained unchanged (35-70%). In most cases, 9-methylanthracene (**4**), 9-anthraldehyde (**5**), lepidopterene (**6**), 1,2-bis(9-anthracenyl)ethane (**7**) and 9,10-anthraquinone (**8**) formed in variable amounts (Chart 2).

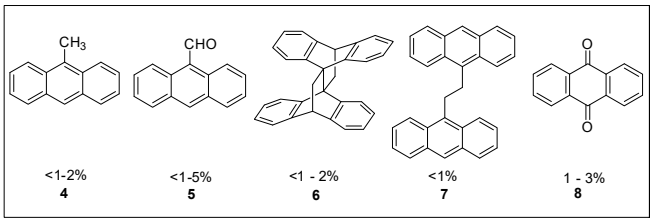


Chart 2. Products formed through one electron transfer and oxidation reactions.

Reactivity of dibenzoylethylene with (anthracen-9-yl)methanamines and (anthracene-9-ylmethyl)sulfanes in different solvents

Reactions in non-polar medium: xylene

A 0.050 M solution of 1-(anthracen-9-yl)-*N*,*N*-dimethylmethanamine (**1**) was refluxed with four equivalents of DBE (**3**) in xylene. Due to the lower reactivity of DBE, its reaction with **1** was very slow. After 60 h, in addition to unreacted starting materials (70%), 9-methylanthracene (**4**), 9-anthraldehyde (**5**), lepidopterene (**6**), 1,2-bis(9-anthracenyl)ethane (**7**), 9,10-anthraquinone (**8**), dibenzoylethane (**9**)[14] and 1,6-diphenyl-3,4-dibenzoyl-l,6-butanedione (**10**)[15] were obtained in low yields.

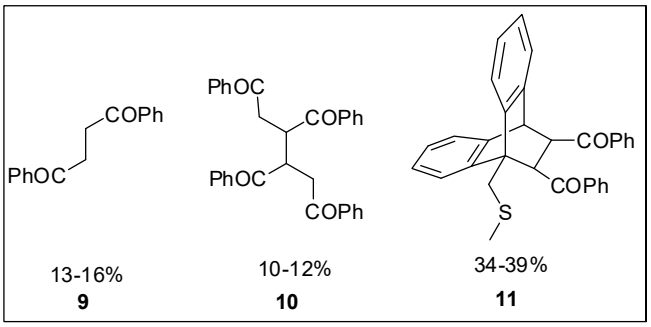


Chart 3. Diels-Alder adduct and radical mediated products formed from DBE.

In continuation, we examined the reaction of (anthracen-9-ylmethyl)(methyl)sulfane (**2**) with DBE (**3**) in refluxing xylene. Even after 60 h, substantial amount of **2** remain unchanged. Though products such as **4-8** were formed in trace amounts, DBE derived products such as **9** and **10** were not formed in detectable amounts. Anthraquinone (**8**) was generated in yields comparable with that obtained with **1**. The major product formed in this case was the Diels-Alder adduct **11** (Chart 3).

These results point towards different reactivity pattern for amines and sulfanes towards DBE.

Reactions in polar aprotic medium: dimethylformamide

To assess the role of solvent polarity in controlling selectivity in the reaction of dibenzoylethylene with (anthracen-9-yl)methanamines and anthracene-9-ylmethylsulfanes, we examined the reaction between **1**/**2** with DBE in polar aprotic medium: dimethylformamide (DMF) under reflux for 60 h. In the reaction between **1** and DBE, substantial quantities of **1** remained unchanged and products **4-10** were isolated in yields comparable with those obtained in xylene. On the other hand, in the reaction between **2** and DBE, cycloadduct **11** was obtained in major amounts along with unchanged **2** (48%) and **4-8** in trace amounts. It appears that even in polar aprotic solvents, the one electron transfer pathway predominates for (anthracen-9-yl)methanamines and the Diels-Alder pathway is more important for anthracenemethylsulfanes.

Reactions in polar protic medium: a) methanol

Compounds **1**, **2** and DBE (**3**) exhibited poor solubility in methanol and remained almost insoluble in other alcohols such as ethanol, propanols and butanols. In the reaction between **1** and **3** at low concentration in methanol, even after refluxing continuously for 150 h, unchanged starting material could be isolated in near quantitative amounts. Similar results were obtained with **2** and **3** in refluxing methanol. It appears that at low concentration and temperature below 65 °C, amine **1** and sulfane **2** remain unreactive towards DBE.

Reactions in polar protic medium: b) acetic acid

We refluxed a 0.050 M solution of 1-(anthracen-9-yl)-*N*,*N*-dimethylmethanamine (**1**) with four equivalents of DBE (**3**) in acetic acid. After, 60 h acetolysis product (anthracen-9-yl)methyl acetate (**12**)[16,17] and its Diels-Alder adduct **13** (Chart 4) along with electron transfer mediated products **4-7** and anthraquinone (**8**) were formed. Reaction of (anthracen-9-ylmethyl)(methyl)sulfane (**2**) with DBE (**3**) on the other hand gave cycloadduct **11** as the major product along with single electron transfer mediated products **4-7** and anthraquinone (**8**) in trace amounts. Acetolysis was not observed in this case, It appears that (anthracen-9-yl)methanamines in acetic acid follow single electron transfer and Michael type addition while anthracenemethylsulfanes follow usual cycloaddition pathway.

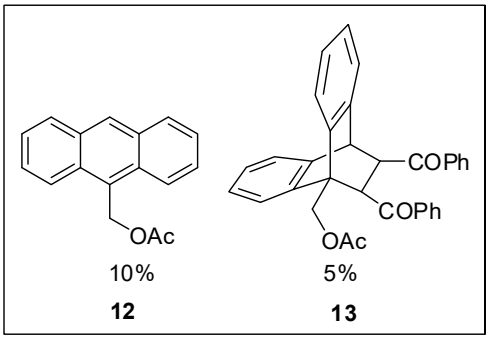


Chart 4. Acetolysis and Diels-Alder products formed by the reaction of **1** with **3**.

In our previous investigations on the reaction of anthracenmethanamines and sulfanes with reactive acetylenes such as DBA and DMAD, selectivity was not observed: both amines and sulfanes reacted in similar fashion under identical conditions.[12,13] We have now observed that DBE, thanks to its lower reactivity, exhibits selectivity in its reactions with anthracemnmethanamines and sulfanes. However, several common products are obtained in reactions of anthracenmethanamines and sulfanes with DBA, DMAD and DBE. Mechanisms for the formation of different products under different conditions are understood in terms of those proposed in our previous articles and are is included as supporting information.[12,13] Anthraquinone (**8**) is formed by the reaction with adventitious oxygen. We could isolate **8** in comparable quantities when 0.05 M solutions of **1** and **2** (in the absence of DBE) were refluxed for 60 h in solvents such as xylene, DMF and acetic acid.

CONCLUSION

Nucleophilic addition, single electron transfer and cycloaddition possibilities coexist in the reaction between anthracenemethanamines/sulfides and dibenzoylethylene. Both nature of substrate and solvent play important roles in deciding the major reaction pathway. With anthracenemethanamines, single electron transfer and nucleophilic addition possibilities are favoured, while for sulfanes, cycloaddition is favoured in all solvents. Thus it appears that anthracenemethanamines are better single and two electron donors in comparison with anthracenemethylsulfanes in their reaction with DBE.

EXPERIMENTAL

General methods

All reactions were carried out using oven dried glasswares. All experiments were done with distilled and dried solvents by using standard protocols. All starting materials were purchased from either *Sigma-Aldrich* or *Spectrochem* Chemicals and were used without further purification. Separation and purification of compounds were done by column chromatography using either silica gel (*Spectrochem Chemicals*, 60-120 mesh) or neutral alumina (*Spectrochem Chemicals*). The products were further purified by recrystallization from suitable solvent systems. Melting points are uncorrected and were determined on a *Neolab* melting point apparatus. Infra-red spectra were recorded using *Jasco 4100* and *ABB Bomem (MB Series)* FT-IR spectrometers. The ^{1}H and ^{13}C NMR spectra were recorded at 400 MHz on a *Bruker Avance III* FT-NMR spectrometer with tetramethylsilane (TMS) as internal standard. Chemical shifts (δ) are reported in parts per million (ppm) downfield of TMS. Elemental analysis was performed using *Elementar Systeme (Vario EL III)*. Molecular mass was determined by electron impact (EI) method using GC-MS (*Agilent GC-7890A*, *Mass-5975C*) and fast atom bombardment (FAB) using *JMS 600 JEOL* mass spectrometer. Here we are giving the spectral and analytical data only for novel compounds and the corresponding reference cited for known compounds. 1-(anthracen-9-yl)-*N*,*N*-

dimethylmethanamine (**1**), (anthracen-9-yl)methyl methyl sulfane (**2**) were synthesized using previously reported procedures and dibenzoylethylene (**3**) procured commercially was used as such.

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Solutions of **1** and **2** in solvents such as xylene, DMF and acetic acid (0.05 M) were refluxed for 60 h. Work up of the reaction mixture gave anthraquinone (<3%) along with unchanged starting materials (>95%).

General experimental procedure for the reactions of 1-(anthracen-9-yl)-*N*,*N*-dimethylmethanamine (1)/(anthracen-9-ylmethyl)(methyl)sulfane (2) with electron-deficient dienophile DBE (3)

To a solution (0.050 M) of 1-(anthracen-9-yl)-*N*,*N*-dimethylmethanamine (**1**, 700 mg, 3.0 mmol)/(anthracen-9-ylmethyl)(methyl)sulfane (**2**, 710 mg, 3.0 mmol) in corresponding solvent (60 mL), DBE (**3**, 4 equivalents) was added, and the mixture was refluxed for 60 h. Progress of the reaction was monitored by TLC. At the end of 60 h, the reaction mixture was cooled, and the solvent was removed under reduced pressure. The product mixture obtained was separated and purified by column chromatography on silica gel using hexane and dichloromethane.

CHARACTERIZATION DATA

Compound 11:- Off-white crystalline solid (34-39%); mp: 175-176 °C; IR ν_{max} (KBr): 3061, 3029, 2983, 2911, 2853, 1660, 1645, 1598, 1448, 1385, 1276, 1069, 690 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.88-6.92 (m, 18H), 4.89 (d, 1H, J = 6.0 Hz), 4.45 (d, 1H, J = 1.6 Hz), 3.84 (dd, 2H, J = 6.4 Hz and 2.0 Hz), 3.68 (d, 1H, J = 12.4 Hz), 2.03 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 201.7, 197.3, 142.4, 139.7, 136.3, 133.2, 133.1, 128.9, 128.4, 128.3, 126.4, 126.3, 126.0, 125.9, 124.8, 122.8, 122.6, 54.2, 48.8, 36.1, 18.0; MS: *m/z* 475 *(M+1)*; Anal. Calcd for $C_{32}H_{26}O_2S$: C: 80.98; H: 5.52; S: 6.76; Found: C: 80.91; H: 5.43; S: 6.69.

Compound 13: White solid (5%); mp: 209-211 °C; IR ν_{max} (KBr): 1736, 1670, 1594, 1245 cm^{-1}; ^1H NMR ($CDCl_3$): 7.00-7.38 (m, 18H), 5.17 (d, 1H, J = 11.6 Hz), 4.97 (d, 1H, J = 11.6 Hz), 4.84 (d, 1H, J = 6.0 Hz), 4.06 (dd, 1H, J = 6.0 and 2.0 Hz), 1.81 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 201.6, 197.9, 170.6, 142.8, 142.4, 139.9, 139.7, 138.1, 136.1, 133.3, 133.2, 128.9, 128.6, 128.5, 128.4, 126.6, 126.5, 126.4, 126.2, 125.0, 123.2, 123.1, 121.5, 62.9, 54.5, 49.1, 48.6, 46.7, 20.5; MS: *m/z* 486 (M^+), 105; Anal. Calcd for $C_{33}H_{26}O_4$: C: 81.47, H: 5.38; Found: C: 81.48, H: 5.38.

Supporting Information

Detailed mechanisms of the above reactions and ^1H and ^{13}C NMR data of novel compounds are included.

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