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Diels-Alder reaction of 9-anthracenemethanol and dimethylacetylene-dicarboxylate; potential route for the synthesis of regiospecific products of 9-substituted anthracene with unsymmetrical acetylenes

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Diels-Alder reaction of 9-anthracenemethanol with dimethylacetylene-dicarboxylate gives rise to the formation of a lactone derivative by condensation of the alcoholic function of the 9-substituent with the nearby carboxylate group in the Diels-Alder adduct. Opening of the lactone derivative with an alcohol yields the desired Diels-Alder adduct. If the alcohol used for opening the lactone is different from the alcohol part of the dicarboxylate, the reaction gives the regiospecific adduct in which the alkoxy group (used for opening the lactone) is *ortho* to the 9-substituent.

Keywords: 9-Anthracenemethanol, unsymmetrical dienophile, stereoselective, regiospecific, unsymmetrical acetylene dicarboxylates, regioisomer

Diels-Alder reaction of substituted anthracenes with olefinic dienophiles has been quite interesting. The reaction of 1- and 2-substituted anthracenes with olefinic dienophiles leads to the formation of stereoselective products[1,2] (*endo:exo* or *syn: anti*). In the case of the 2-substituted anthracenes, the electronic effects of the substituents have been found to be the dominant factors in deciding the stereoselectivity of the reaction[1]: -the electron donating substituents favouring the *endo* (*syn*) adduct as against the electron withdrawing substituents favouring the *exo*(*anti*) adduct. However, in the case of 1-substituted anthracenes, the steric factors appear to be the dominant factor in deciding the isomer ratio/ stereoselectivity[2], as the 1-substituent happens to be closure to the reaction centres: -bulky groups favouring the *exo* (*anti*) adduct.

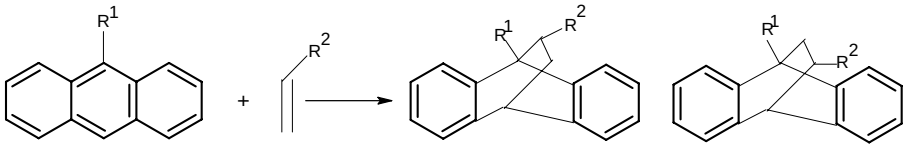
9-Substituted anthracenes, on the other hand, give rise to regioselective products with unsymmetrical olefinic dienophiles. For instance, the reaction of 9-substituted anthracene **1** with the unsymmetrical dienophile **2** would yield two regioisomers *ortho* **3a** and *meta* **3b (Scheme I)**.

In most of the cases reported[3,4], the *ortho* regioisomer has been found to be the major isomer except in a few cases where the *meta* regioisomer has been preferred. The regioselectivity has been attributed to be kinetic in origin[4]. In an interesting case[5], the reaction of 9-substituted anthracene with 2-acetamido acrylate has been found to be highly regioselective where the *meta/ortho* isomer ratio has been more than 99:1.

Diels-Alder reaction of 9-substituted anthracenes with symmetrical acetylenic dienophiles would give only one product. However, reaction of 9-anthracenemethanol with symmetrical acetylene dicarboxylates has been found to be quite unique. It paves the way for the synthesis of regiospecific products of the Diels-Alder reaction of 9-substituted anthracenes with unsymmetrical acetylene dicarboxylates starting with symmetrical ones as discussed below.

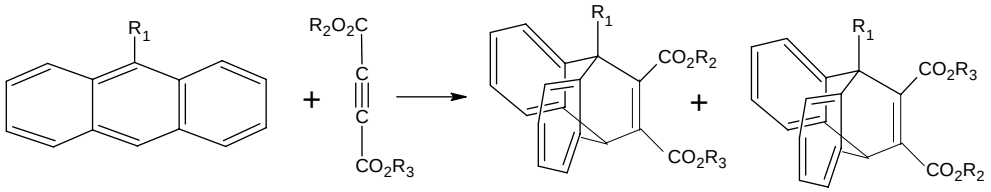
Results and Disscussion

Diels-Alder reaction of 9-substituted anthracenes with unsymmetrical disubstituted acetylenes would lead to the formation of two regioisomeric adducts as shown in the following reaction (**Scheme II**). It will be extremely difficult to get regiospecific products- either **6a** or **6b** only. In the first place, unsymmetrical disubstituted acetylenes themselves will be expensive and hard to get. In the second case, there is another problem of separating the isomeric mixture if one has to isolate **6a** or **6b**. However, it is found that such regiospecific products can be obtained by reaction of 9-anthracenemethanol with symmetrical acetylene dicarboxylates. The reaction proceeds through the



1 **2** **3a** **3b**

Scheme I



4 **5** **6a** **6b**

Scheme II

formation of a lactone intermediate **9**. For instance, on refluxing a mixture of 9-anthracenemethanol **7a** and dimethylacetylene dicarboxylate (DMAD) **8** in toluene for 24 hr, the lactone derivative **9a** is obtained by internal nucleophilic displacement of the corresponding dicarboxylate adduct[6]. Opening[7] of the lactone **9a** with methanol gives the desired product **10a** whereas opening of the lactone **9a** with ethyl alcohol will give regiospecific products of Diels-Alder reaction of 9-anthracenemethanol with ethyl methyl acetylene dicarboxylate, in which the ethoxycarbonyl group is adjacent (*ortho*) to the 9-substituent and carbomethoxy group *meta* to the 9-substituent **10c**.

If one desires the other isomer, *viz.* the carbomethoxy group adjacent (*ortho*) to the 9-substituent and carboethoxy group *meta* to the 9-substituent, it can be achieved by reaction of 9-anthracenemethanol with diethyl acetylene dicarboxylate, *via* the lactone analogous to **9** in which the carbomethoxy group is replaced by carboethoxy group. Opening of the said lactone analogous to **9** with methanol will give the desired product as shown (**Scheme III**).

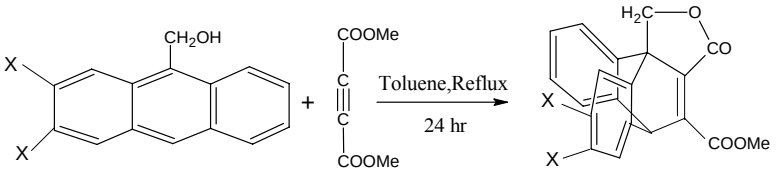
Thus, starting with symmetrical dicarboxylates, regiospecific products of the reaction of 9-substituted anthracenes with unsymmetrical acetylene dicarboxylates can be obtained.

Since the alcoholic function at the 9-position can be transformed to a variety of functional groups **(Scheme IV)**, the process paves the way for the synthesis of a wide variety of adducts of 9-substituted anthracene and unsymmetrical acetylene dicarboxylates, which otherwise, would have been difficult to achieve. The present reaction scheme is thus a novel and promising method for the synthesis of region-specific products starting with symmetrical acetylene dicarboxylates.

9-Anthracenemethanol **7a** was obtained by reduction of 9-anthracenealdehyde with sodium borohydride in tetrahydrofuran. 2,3-Dichloro-9-anthracenemethanol **7b** was obtained by reduction of 2,3-dichloro-9-anthracenealdehyde which had been synthesized from 2,3-dichloroanthracene. The details of the synthesis of the compounds mentioned in the above schemes are presented in the experimental section.

Experimental Section

The melting points were recorded on a Veego melting point apparatus and are uncorrected. IR spectra were recorded in KBr on a Shimadzu FT-IR-8400, at the Department of Chemistry; Manipur University and the absorbances are reported in cm^{-1}. ^1H NMR spectra were recorded in deuterated chloroform on a Brucker ACF 300 MHz spectrometer using TMS as internal standard. Chemical shifts (δ)



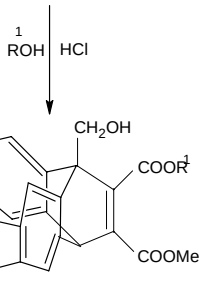
7

7a: 10 = H, **7b:**10 = Cl

8

9

9a: X = H, **9b:** X = Cl



10

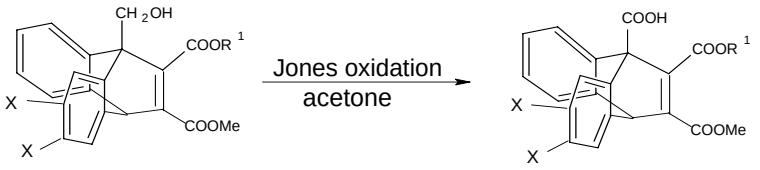
10a: X = H, R^1= CH_3

10b: X = Cl, R^1= CH_3

10c: X = H, R^1= C_2H_5

10d: X = Cl, R^1= C_2H_5

Scheme III



10

10a : X = H, R^1= CH_3

10b: X = Cl, R^1= CH_3

10c: X = H, R^1= C_2H_5

10d: X = Cl, R^1= C_2H_5

11

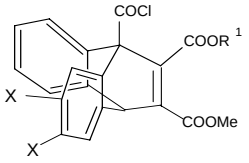
11a: X = H, R^1= CH_3

11b: X = Cl, R^1= CH_3

11c: X = H, R^1= C_2H_5

11d: X = Cl, R^1= C_2H_5

oxalyl chloride/ benzene



12

12a: X=H, R^1=CH_3

12b:X=Cl, R^1=CH_3

,

Scheme IV

are given in ppm (parts per million) relative to internal standard tetramethylsilane. The compounds were purified by column chromatography on silica gel using petroleum ether and ethyl acetate as solvent mixture, followed by crystallization from different solvents. The purity of the compounds was checked by TLC on silica gel plates using ethyl acetate and petroleum ether as eluent, UV radiation or iodine or $KMnO_4$ were used as visualizing agents.

Synthesis of 9-anthracenemethanol 7

9-Anthracenealdehyde (2 g, 9.7 mmole) in tetrahydrofuran (THF, 15 mL) was kept stirring at RT. To the mixture was then added a solution of $NaBH_4$ (0.35 g, 10.04 mmole) in 3 mL water and 1mL THF in about 3 minutes. After stirring for 1 hr, the reaction-mixture was poured into 50 mL ice water when 9-anthracenemethanol was precipitated as pale white crystals. Yield: 97%; m.p. 158-60°C (lit.[9] m.p. 162-64°C)

Diels-Alder reaction of 9-anthracenemethanol with dimethylacetylene dicarbo-xylate (DMAD): preparation of 9a

A mixture of 9-anthracenemethanol **7a** (1.7 g, 8.16 mmole) and dimethyl-acetylene dicarboxylate (DMAD) **8** (1.5 mL, 12.2 mmole) in 10 mL toluene was refluxed for 24 hr. After evaporating the solvent under reduced pressure the mixture was chromatographed on a column of silica gel using ethyl acetate and hexane (1:4 v/v) as the eluent. The product obtained **9a** was found to be a lactone derivative. Yield: 85%; m.p. 174-75°C. ^{1}H NMR ($CDCl_3$): δ 3.88 (3H, s, -$COOCH_3$), 5.55 (2H, s, -CH_2-O), 5.82 (1H, s, bridgehead), 7.08-7.11 (4H, m), 7.33-7.36 (2H, m), 7.47-7.50 (2H, m); IR (cm^{-1}): 1770 (lactone), 1718 (ester > C=O). Anal. Calcd. (for $C_{20}H_{14}O_4$) C, 75.46; H, 4.42. Found: C, 75.50; H, 4.40%.

Methanolysis of the lactone derivative: preparation of 10a

The lactone derivative **9a** (1.0 g, 3.1 mmole) in 12 mL methanol and 0.1 mL Conc. HCl was kept stirring at RT for 48 hr. The volume of methanol was reduced to about 5 mL and then 30 mL of ethyl acetate was added to the reaction-mixture and the solution was washed with water free from HCl and then with saturated brine. The ethyl acetate solution was dried over anhydrous $MgSO_4$ and filtered. On evaporation of the solvent the desired product was obtained contaminated with traces of the starting material. The product was recrystallized from ethyl acetate and hexane when the product **10a** was obtained in the pure form. Yield: 74%; m.p. 164-65°C. ^{1}H NMR ($CDCl_3$): δ 2.64 (1H, t, J = 2.74 Hz, -CH_2*OH*), 3.77 (3H, s, -$COOCH_3$), 3.78 (3H, s, -$COOCH_3$), 5.05 (2H, d, J = 2.74 Hz, -*CH_2*OH), 5.57(1H, s, bridgehead), 6.99-7.07 (4H, m), 7.37-7.43 (4H, m). Anal. Calcd. for $C_{21}H_{18}O_5$: C, 71.98; H, 5.17. Found: C, 71.81; H, 5.32% .

Ethanolysis of the lactone derivative 9a: preparation of 10a

The lactone derivative **9a** (0.5 g, 1.57 mmole) was dissolved in 20 mL ethanol[10] (by warming if necessary) and kept stirring at RT. To the solution was added 0.1 mL Conc. HCl and stirred for 80 hr at RT. The reaction-mixture remained a transparent solution. Ethanol was evaporated to about 3 mL and water was added to get a white precipitate. It was extracted with ethyl acetate, washed free from HCl and dried over anhydrous $MgSO_4$ and filtered. Evaporation of the solvent gave a mixture of the product **10c** and the starting material approximately in the ratio 4:1. The product was separated from the starting material by column chromatography (silica gel F_{254}) using ethyl acetate and hexane in the ratio 1:4 and purified by recrystallization from ethyl acetate and hexane. Yield: 56%; m.p. 134-35°C. ^{1}H NMR ($CDCl_3$): δ 1.27 (3H, t, J = 7.14 Hz, -$COOCH_2$*CH_3*), 2.80 (1H, t, J = 5.63 Hz, -CH_2*OH*), 3.76 (3H, s, -$COOCH_3$), 4.26(2H, q, *J*=7.14 Hz, -$COOCH_2CH_3$), 5.05 (2H, d, J = 5.63 Hz, -*CH_2*OH), 5.56 (1H, s, bridgehead), 7.00-7.08 (4H, m), 7.38-7.44 (4H, m). Anal. Calcd. for $C_{22}H_{20}0_5$: C, 72.50; H, 5.53. Found: C, 72.55; H, 5.21%.

Preparation of 2, 3-dichloroanthracene

A mixture of 2,3-dichloroanthraquinone[11] (10 g, 36.2 mmole), zinc dust (35.3 g, 540 mmole) and 28% aqueous ammonia (122 mL, 2.01 mmole) was taken in a 300 mL flask heated under reflux for 96 hr. The mixture was filtered and the residue was treated with Conc. HCl to dissolve the unreacted zinc when a grey precipitate containing mostly the anthracene was obtained. The precipitate was filtered off, washed with water, sodium bicarbonate solution and then with water and was allowed to dry in the air. The residue was extracted with methylene chloride (300 mL) in a soxhlet extractor (96 hr) when light yellow shining crystals of pure 2,3-dichloroanthracene were obtained. Yield: 84%; m.p. 262-63°C (lit Ref.12, 261°C). ^{1}H

NMR ($CDCl_3$): δ 7.48-7.52 (2H, m), 7.96-8.02 (2H, m), 8.13 (2H, s), 8.33 (2H, s).

Preparation of 2,3-dichloro-9-anthracenealdehyde

In a three necked round bottomed flask was placed 2,3-dichloroanthracene (3.5 g, 14.17 mmole) in 100 mL of dichloromethane and was kept stirring on ice-bath. To the mixture was introduced anhydrous $SnCl_4$ (2.5 mL, 21 mmole) dropwise (2-3 minutes) and then dichloromethyl methyl ether[13] (2.1 mL, 23.74 mmole) was added dropwise (2-3 minutes). The reaction-mixture was allowed to attain RT in about half an hr and then was refluxed for 2 hr. (On addition of dichloromethyl methyl ether, the colour of the reaction-mixture changed from pale yellow to yellow to brown and on heating became dark pink. Some dark pink precipitate deposited on the walls of the flask).

The reaction-mixture was cooled in ice-bath and then 1*N* HCl was added to decompose the complex when 2, 3-dichloro-9-anthracenealdehyde appeared as yellow precipitate. The precipitate was filtered off, washed with water, sodium bicarbonate solution and water and was allowed to dry in the air. The product was reasonably pure and was used for next reaction. (The methylene chloride layer of the filtrate after washing free from HCl and drying over anhydrous $MgSO_4$ was evaporated to yield 300 mg of the product but it was contaminated with traces of anthracene). The analytical sample was recrystallized from ethylacetate. Yield: 84.8%; m.p. 175.5-76.5°C. ^{1}H NMR ($CDCl_3$): δ 7.58-7.61 (1H, m), 7.69-7.74 (1H, m), 8.05 (1H, d, *J* = 7.8 Hz), 8.14 (1H, s), 8.58 (1H, s), 8.83 (1H, d, *J* = 8.4 Hz), 9.31 (1H, s) 11.42 (1H, s). Anal. Calcd. for $C_{15}H_8Cl_2O$: C, 65.48; H, 2.93. Found:C, 65.67; H, 2.77%.

Preparation of 2,3-dichloro-9-anthracenemethanol 7b

2,3-Dichloro-9-anthracenealdehyde (4 g, 14.5 mmole) was kept stirring in 40 mL of tetrahydrofuran at RT. A solution of $NaBH_4$ (0.56 g, 14.8 mmole) in 2 mL THF and 8 mL of water was then introduced dropwise in about 10 minutes. The reaction-mixture was stirred for 1 hr and then was poured into 100 mL of ice-water when the desired product was obtained as pale yellow precipitate.

(The aldehyde remained as suspension in THF but on addition of $NaBH_4$ dissolved completely to give a light tan transparent solution). Yield: 99%; m.p. 165-66°C.

(The analytical sample was recrystallized from benzene. The compound underwent some transformation on standing in chloroform).^{1}H NMR ($CDCl_3$): δ 1.78 (1H, t, *J* = 5.5Hz,-CH_2*OH*), 5.6 (2H, d, *J* = 5.5 Hz, -*CH*$_2$ OH), 7.52-7.61 (2H, m), 8.00 (1H, d, *J* = 9.5 Hz), 8.35 (1H, s), 8.40 (1H, d, *J* = 8.9 Hz), 8.55 (1H, s). Anal.Calcd. for $C_{15}H_{10}Cl_2O$: C, 64.98; H, 3.64. Found: C, 64.89; H, 3.64%.

Diels-Alder Reaction of 2, 3-dichloro-9-anthracene-methanol with dimethyl acetylene dicarboxylate (DMAD); formation of the lactone 9b

2,3-Dichloro-9-anthracenemethanol **7b** (4.2 g, 15.15 mmole), dimethyl-acetylene dicarboxylates (3.8 mL, 30.9 mmole) in 20 mL of toluene was refluxed under nitrogen for 24 hr. After removing the solvent under reduced pressure, the residue was chromatographed on a silica gel (Wakogel 200, 60 g) using hexane-ethylacetate (4:1 v/v) as the eluent. The product is a lactone derivative **9b.** Yield: 81%; m.p.132-35°C. ^{1}H NMR ($CDCl_3$): δ 3.89 (3H, s, -$COOCH_3$), 5.53, 5.43 (2H, ABq, *J* = 10.68Hz, -CH_2OCO), 5.76 (1H, s, bridgehead), 7.12-7.16 (2H, m), 7.33-7.36 (1H, m), 7.40 (1H, s), 7.47-7.50 (1H, m), 7.56 (1H, s); IR (cm^{-1}): 1772 (C=O, lactone), 1720 (C=O, ester). Anal. Calcd. for $C_{20}H_{12}O_4Cl_2$ for $C_{20}H_{12}O_4Cl_2$: C,62.02; H, 3.12. Found: C, 62.56; H, 3.48%.

Methanolysis of the lactone derivative 9b: preparation of 10b

The lactone derivative **9b** (4.5 g, 11.61 mmole) was treated with 25 mL methanol and 0.3 mL Conc. HCl and was stirred at RT for 30 hr (in the beginning, the reaction-mixture was a suspension which became a clear transparent solution in 1 hr of stirring. As stirring continued the ester alcohol derivative appeared as a curdy white precipitation in about 3 hr). The reaction-mixture was diluted with 10 mL water, allowed to stand for 2 hr and filtered. The product was washed with 50% aqueous methanol and dried in the air. It was dissolved in ethyl acetate, treated with decolourizing charcoal and filtered. The filtrate was diluted with hexane (to about 50%) and was allowed to stand overnight when crystals of **10b** appeared at the bottom of the flask. Yield: 80%; m.p. 217-19°C. ^{1}H NMR ($CDCl_3$): δ 2.62 (1H, t, *J* = 4.9Hz, -CH_2*OH*), 3.78 (3H, s,-$COOCH_3$), 3.79 (3H, s, -$COOCH_3$), 4.99 (2H, AB of ABX, J_{AB} = 11.21Hz, J_{AX}, J_{BX} = 4.90 Hz, -*CH*$_2$OH), 5.52 (1H, s, bridge-

head), 7.05-7.09 (2H, m), 7.34-7.40 (2H, m), 7.46 (1H, s), 7.55 (1H, s); IR (cm^{-1}): 3520(-OH), 1708 (>C=O). Anal. Calcd. for $C_{21}H_{16}O_5Cl_2$: C, 60.16; H, 3.84. Found: C, 60.43; H, 4.04%.

Ethanolysis of the lactone derivative 9b: preparation of 10d

The lactone derivative **9b** (1.0 g, 2.58 mmole) was treated with 10 mL ethanol and 0.1 mL Conc. HCl and was stirred for 72 hr at RT. The reaction-mixture remained as clear solution for about 36 hr but as stirring continued white precipitate began to appear later. The mixture was diluted with 10 mL water and filtered. The precipitate was dissolved in ethyl acetate; the solution was dried over anhydrous $MgSO_4$ and then filtered. The filtrate was diluted with hexane to about 50% and was allowed to stand overnight when the desired product appeared as colourless crystals. In fact, this is a regiospecific adduct of the Diels-Alder reaction of 9-anthracenemethanol with the unsymmetrical ethyl methyl acetylene dicarboxylate. Yield: 71%; m.p. 206-08°C. ^{1}H NMR ($CDCl_3$): δ 1.28 (3H, t, J = 7.17 Hz, $–CO_2CH_2\mathit{CH_3}$), 2.77 (1H, brs, $-CH_2\mathit{OH}$), 3.77 (3H, s, $-CO_2CH_3$), 4.27 (2H, q, J = 7.17 Hz, $–CO_2\mathit{CH_2}CH_3$), 4.99 (2H, brm, $-\mathit{CH_2}OH$), 5.51 (1H, bridgehead), 7.06-7.11 (2H, m), 7.36-7.40 (2H, m), 7.46 (1H, s), 7.57 (1H, s). Anal. Calcd. for $C_{22}H_{18}O_5Cl_2$: C, 60.98; H, 4.18. Found: C, 60.23; H, 4.26%.

Oxidation of the alcohol derivative 10b to the corresponding carboxylic acid 11b derivative using Jone's Reagent

A 100 mL double necked round bottomed flask was kept stirring containing the alcohol derivative **10b** (1.0 g, 2.38 mmole) in 60 mL of acetone at RT and 2.0 mL of Jone's reagent was added dropwise from a dropping funnel in about 10 minutes. Within ½ hr, the solution became bluish green and some greenish precipitate appeared sticking to the walls of the flask. On checking with TLC the starting material disappeared, giving spots at the bottom. The reaction was stopped in about one hr and the acetone solution was decanted off from the insoluble material. The volume of the acetone was reduced to about 5 mL on a rotavapor and then 50 mL of ether was added. The solution was washed with 20 mL of water 3 times and then with 20 mL of saturated $NaHCO_3$ solution and finally washing the alkaline solution with ether followed by acidification of the aqueous solution. The acid was extracted with ether and the ethereal solution after drying over anhydrous magnesium sulfate was treated with decolourizing charcoal. Evaporation of the solvent gave the acid **11b** as colourless residue. Yield: 90%; m.p. 202-05°C .The analytical sample was recrystallized from carbon tetrachloride-hexane (1:4). ^{1}H NMR ($CDCl_3$): δ 3.79 (3H, s, $-COOCH_3$), 3.82 (3H, s, $-COOCH_3$), 5.58 (1H, s, bridgehead), 7.13-7.15 (2H, m), 7.43-7.4 6(1H, m), 7.49 (1H, s,), 7.57-7.60 (1H, m), 7.96 (1H, s). Anal. Calcd. for $C_{21}H_{14}O_6Cl_2$: C, 58.22; H, 3.25. Found: C, 58.47; H, 3.18%.

(Jone's Reagent was prepared by mixing 2.7g of Cr^{+6} oxide, 2.3 mL of sulfuric acid and 7.0 mL of water)[15].

Oxidation of the alcohol derivative 10a to the corresponding carboxylic acid 11a derivative using Jone's Reagent

The compound **11a** was also prepared following the same procedure as in the preparation of **11b.** Yield: 90%; m.p. 198-200°C. ^{1}H NMR ($CDCl_3$): δ 3.78 (s, 3H, $-COOCH_3$), 3.82 (s, 3H, $-COOCH_3$), 5.65 (s, 1H, bridgehead), 7.09-7.12 (m, 4H), 7.42-7.45 (m, 2H), 7.72-7.75 (m, 2H). Anal. Calcd. for $C_{21}H_{16}O_6$: C, 69.22; H, 4.42. Found: C, 69.35; H, 4.21%.

Preparation of acid chloride 12b

The acid derivative **11b** (2.0 g, 4.6 mmole) was taken in 10 mL of benzene and to the solution was added 1.5 mL oxalyl chloride and it was stirred at 55°C for 30 hr. Evaporation of the solvent under reduced pressure followed by drying under vacuum yielded the acid chloride **12b**. (The reaction-mixture remained a curdy white suspension for about 12 hr but became a clear solution later when the formation of acid chloride was complete). Yield: 96%; ^{1}H NMR ($CDCl_3$): δ 3.81 (3H, s, $-COOCH_3$), 3.84 (3H, s, $-COOCH_3$), 5.46 (1H, s, bridgehead), 7.15-7.18 (2H, m), 7.42-7.45 (1H, m), 7.46 (1H, s), 7.71-7.75 (1H, m), 8.06 (1H, s).

Preparation of acid chloride 12a

The compound **12a** was also prepared following the same procedure as in the preparation of **12b**.Yield: 94%; ^{1}H NMR ($CDCl_3$): δ 3.79 (3H, s, $-COOCH_3$), 3.83 (3H, s, $-COOCH_3$), 5.52 (1H, s, bridgehead), 7.10-7.15 (4H, m, aromatic), 7.40-7.43 (2H, m, aromatic), 7.83-7.86 (2H, m, aromatic).

Conclusion

The reaction demonstrates that the 9-anthracenemethanol can undergo Diels-Alder reaction with

acetylenic esters without protecting the hydroxyl group. It also provides a route for the synthesis of regiospecific adducts of 9-substituted anrthracenes with unsymmetrical acetylenic esters without undertaking the trouble of getting unsymmetrical acetylenes.

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References and Notes

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6 When the reaction was carried out at a lower temperature, e.g. in refluxing benzene or dioxane, the products were found to be a mixture of **9a** and **10a** which could be separated by chromatography on silica gel.

7 Lactones are easily opened by treatment with alcohols to give open-chain hydroxyl esters[8].

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10 If alcohols having alkoxy groups different from that of the acetylenic esters are used for ring opening, there is possibility of transesterification. This is avoided by carrying out the reaction at RT. If the ring opening is done in refluxing solvent, transesterification, in fact, took place, along with the ring opening.

11 A sample of 2,3-dichloroanthraquinone (about 20 g) was obtained as a gift from the laboratory of Prof M Oki, Department of Chemistry, Okayama University of Science, Okayama, Japan, where one of the authors (MDS) was a visiting Scientist (1997-1999) for which the authors are grateful to Prof M Oki.

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13 Formylation of aromatic rings using dichloromethyl methyl ether in the presence of Friedel-Crafts catalysts is well known[14].

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