Molecular Design by Cycloaddition Reactions. Part XII.[1] Syntheses of Fluoranthene and Diazafluoranthene Derivatives

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The cycloaddition reaction of acenaphthylene with coumalic acid, its methyl ester, or 4,6-dimethylcoumalic acid, with loss of carbon dioxide from the bridge, afforded a 2:1 adduct and a fluoranthene-8-carboxylic acid. The corresponding reaction with 3,6-disubstituted *s*-tetrazines gave 8,9-diazafluoranthene derivatives. Mechanisms are discussed.

THE use of 2-pyrones in Diels–Alder reactions is well known,[2] and has been much studied in recent years.[3] With alkyl coumalates, the reactions of electron-rich dienophiles (*i.e.*, dienophiles with inverse electron demand) readily give cycloadducts as was suggested from extended Hückel MO calculations of the net charge distribution on methyl coumalate.[4] Similarly the use of 3,6-diaryl-*s*-tetrazines in the Diels–Alder reaction is also well known.[5] We have also described the ready cycloaddition reactions of cycloheptatriene with 2-pyrone derivatives to give novel bridged cage adducts.[6] As a continuation of our previous work,[6] we now describe the cycloaddition reactions of coumalic acid derivatives and symmetric tetrazines having electron-poor double bonds with acenaphthylene as an electron-rich dienophile.

Coumalic acid (1a), methyl coumalate (1b), and 4,6-dimethylcoumalic acid (1c) were each heated with an equimolar amount of acenaphthylene (2) in xylene at 180—200° in a sealed tube to afford the 1 : 2 adducts (3a—c), formed with loss of carbon dioxide from the bridge, in 25—30% yields.

Structural elucidation for these adducts was based on spectral data, elemental analyses, and mechanistic considerations. The high field shift of the methyl proton signal (δ 3·05) influenced by the naphthalene diamagnetic ring current effect indicated the *endo–endo* 1 : 2 adduct as depicted in Scheme 1. Similarly, the structure of compound (3c) was assigned from the n.m.r. spectrum of its methyl ester (3d) [obtained on treatment of (3c) with diazomethane]. The reaction of an excess of (1a) and (1b) with acenaphthylene in dimethylformamide afforded fluoranthene derivatives (4a) and (4b) in 30—35% yields.† The methoxy-protons in compound (4a) appear at δ 3·9 as a result of the diamagnetic ring current effect.

† In this reaction no 1 : 2 adduct (3c) or (3d) was detected even under more drastic conditions at 180—200°.

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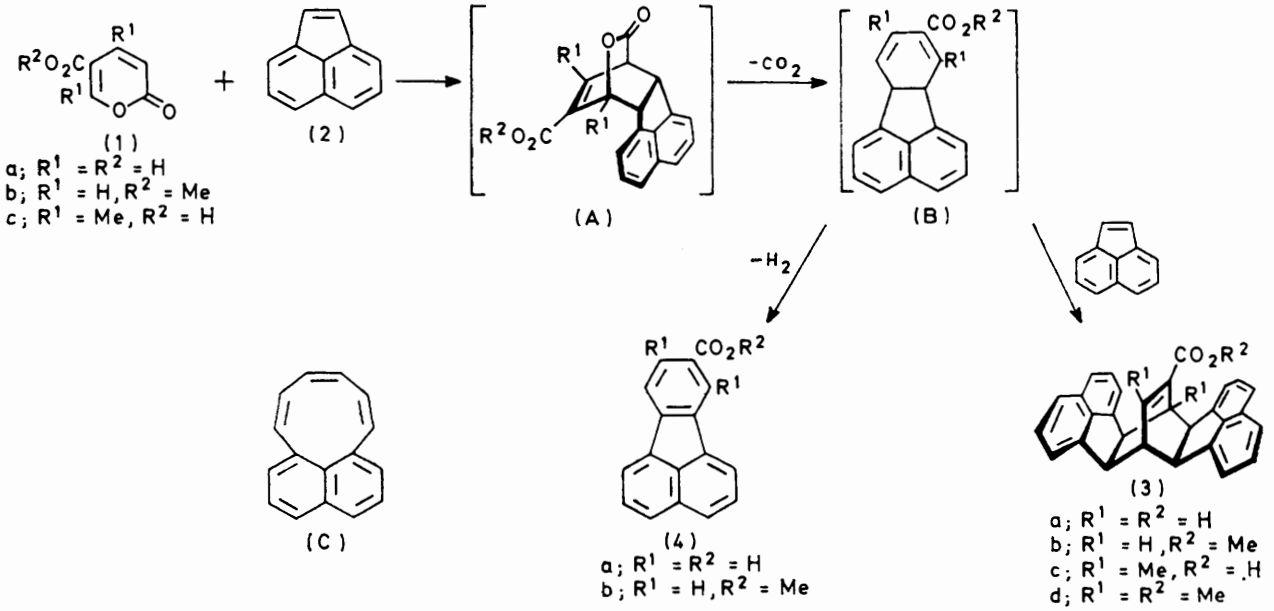
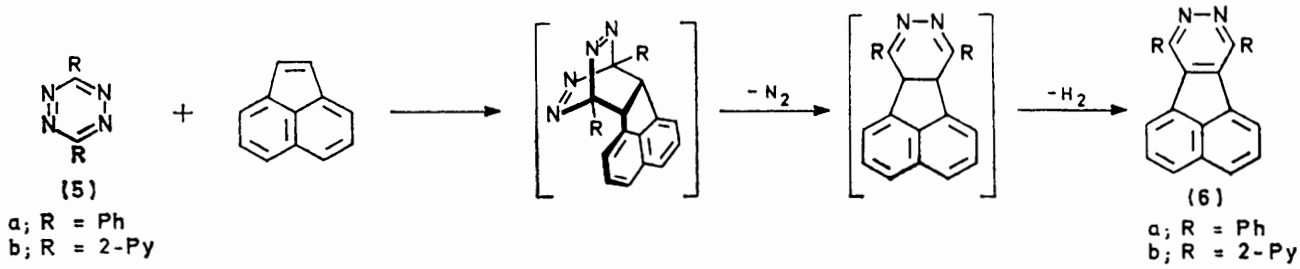
From the foregoing results, the cycloaddition reactions of (1) and (2) seem to be dependent on the solvents, but the effect could not be investigated fully because of the insolubility of both compounds in a number of polar and non-polar solvents. However, it is evident that compound (3) was formed by loss of carbon dioxide from the initially produced 1 : 1 adduct (A) followed by successive addition of acenaphthylene to an intermediate (B) which

EXPERIMENTAL

M.p.s were measured with a Yanagimoto micromelting point apparatus. Microanalyses were performed on a Perkin-Elmer 240 Elemental Analyser. N.m.r. spectra were taken with a JE C-60-XL spectrometer with Me_4Si as internal standard. U.v. spectra were determined with a Jasco ORD/UV-5 recorder. I.r. spectra were taken with a Jasco IR-S spectrophotometer.



SCHEME 1



SCHEME 2

can be explained in terms of a double Diels–Alder mechanism with inverse electron demand. Compound (4) was produced by dehydrogenation (presumably by air) of the intermediate (B) as shown in Scheme 1. The intermediate (B) seems to be an attractive synthetic precursor for a peripheral 14π-annulene (C). However, attempts to isolate the intermediate (B) were unsuccessful, even under milder conditions.

Similar reactions of 3,6-diphenyl- (5a) and 3,6-di-(2-pyridyl)-*s*-tetrazines (5b) with acenaphthylene in xylene or dimethylformamide at 180—200° in a sealed tube afforded (6a) and (6b) in 60—80% yields. The n.m.r. data (no olefinic protons) and elemental analyses support the novel 8,9-diazafluoroanthene structures.

Coumalic Acid–Acenaphthylene 1 : 2 *Adduct* (3a).—*Method A*. A solution of coumalic acid (1a) (540 mg, 4 mmol) and acenaphthylene (2) (610 mg, 4 mmol) in xylene (15 ml) was heated in a sealed tube at 180° for 20 h. The solvent was removed under reduced pressure and the residue was purified by column chromatography (silica gel) with benzene as eluant to give 6b,7,7a,13b,14,14a-*hexahydro*-7,14-*etheno*-*acenaphtho*[1,2-k]*fluoranthene*-15-*carboxylic acid* (3a) (30%) as a white solid, recrystallized from methanol, m.p. 293—295°, $\nu_{max.}$ (KBr) 1675 (C=O) cm^{-1} (Found: C, 86·8; H, 5·1. $C_{29}H_{20}O_2$ requires C, 86·95; H, 5·05%).

To a solution of (3a) (200 mg, 0·5 mmol) in chloroform (15 ml) was added ethereal diazomethane (0·5—0·7 mmol) at 0°. The solvent was removed under reduced pressure and the residue was recrystallized from methanol to give the

methyl ester, identified by mixed m.p. with the adduct (3b), m.p. 257—258°.

Coumalic Acid–Acenaphthylene 1 : 1 *Adduct* (4a).—*Method B.* A solution of coumalic acid (1a) (1·5 g, 0·01 mol) and acenaphthylene (2) (450 mg, 3 mmol) in dimethylformamide (15 ml) was heated in a sealed tube at 160° for 7·5 h. The solution was poured into water and extracted with chloroform, and separation by column chromatography (silica gel) with benzene as an eluant gave *fluoranthene-8-carboxylic acid* (4a) as a white solid (30%), m.p. 164—165°, $\nu_{max.}$ (KBr) 1670 (C=O) cm^{-1}. When the reaction of equimolar amounts of (1a) and (2) was carried out, the yield of the adduct (4a) was decreased, but (3a) could not be detected.

Compound (4a) was treated with ethereal diazomethane as described above. The residue was recrystallized from n-hexane to give the methyl ester of (4a) which was identified by i.r. and mixed m.p. with the adduct (4b); m.p. 87—89°, $\nu_{max.}$ 1710 cm^{-1} (C=O).

Methyl Coumalate–Acenaphthylene 1 : 2 *Adduct* (3b).—Similar work-up to method A of a mixture of methyl coumalate (1b) (620 mg, 4 mmol) and acenaphthylene (2) (610 mg, 4 mmol) yielded *methyl* 6b,7,7a,13b,14,14a-*hexahydro-7,14-ethenoacenaphtho*[1,2-k]*fluoranthene-15-carboxylate* (3b) as white needles (30%), m.p. 257—259°, $\nu_{max.}$ (KBr) 1700 (C=O) cm^{-1}, δ ($CDCl_3$) 3·05 (3H, s), 3·75 (1H, dt, *J* 7·0 and 2·0 Hz), 4·1—4·35 (5H, m), 6·18 (1H, d, *J* 7·0 Hz), 7·1—7·5 (12H, m), $\lambda_{max.}$ (EtOH) 321 (log ε 3·35), 317 (3·48), 307 (4·09), 302 (4·14), 292 (4·26), 284 (4·14), and 220 nm (4·97) (Found: C, 86·7; H, 5·5. $C_{30}H_{22}O_2$ requires C, 86·95; H, 5·35%).

4,6-*Dimethylcoumalic Acid–Acenaphthylene* 1 : 2 *Adduct* (3c).—A similar work-up to method A of 4,6-dimethylcoumalic acid (1c) (680 mg, 4 mmol) with acenaphthylene (2) (610 mg, 4 mmol) at 200° yielded 6b,7,7a,13b,14,14a-*hexahydro-14,16-dimethyl-7,14-ethenoacenaphtho*[1,2-k]-*fluoranthene-15-carboxylate* (3c) (25%) as needles, m.p. >300°, $\nu_{max.}$ (KBr) 1680 (C=O) cm^{-1} (Found: C, 86·75; H, 5·55. $C_{31}H_{24}O_2$ requires C, 86·9; H, 5·65%).

Compound (3c) was treated with ethereal diazomethane at 0°. The residue was recrystallized from methanol to give the *methyl ester* (3d) as needles, m.p. 286—287°, $\nu_{max.}$ (KBr) 1700 (C=O) cm^{-1}, δ ($CDCl_3$) 1·05 (3H, s), 2·00 (3H, s), 3·00 (3H, s), 3·55 (t, *J* 3·0 Hz), 3·80 (1H, d, *J* 7·0 Hz), 4·15 (1H, dd, 7·0 and 3·0 Hz), 7·1—7·6 (11H, m), $\lambda_{max.}$ (EtOH) 322 (log ε 3·30), 318 (3·52), 310 (4·14), 295 (4·30), 284 (4·15), and 223 nm (5·03) (Found: C, 86·6; H, 6·1. $C_{32}H_{26}O_2$ requires C, 86·85; H, 5·9%).

Coumalate–Acenaphthylene 1 : 1 *Adduct* (4b).—Similar work-up to method B of a mixture of methyl coumalate (1·6 g, 0·01 mol) with acenaphthylene (450 mg, 3 mmol) yielded *methyl fluoranthene-8-carboxylate* (4b) as plates (35%), m.p. 87—89°, $\nu_{max.}$ (KBr) 1710 (C=O) cm^{-1}, *m/e* 260 (M^+), $\lambda_{max.}$ (EtOH) 370 (log ε 4·00), 352 (3·97), 294 (4·54), 284 (4·32), 264 (4·23), and 230 nm (4·60), δ (CCl_4) 3·9 (3H, s), 7·4—8·01 (9H, m) (Found: C, 83·0; H, 4·8. $C_{18}H_{12}O_2$ requires 83·05; H, 4·65%).

Reaction of 3,6-*Diphenyl-1,2,4,5-tetrazine* (5a) *with Acenaphthylene* (2).—A solution of the tetrazine (5a) (470 mg, 2 mmol) and acenaphthylene (320 mg, 2 mmol) in xylene (10 ml) or dimethylformamide (10 ml) was heated in a sealed tube at 180° for 1 h. After cooling, the yellow solid was filtered off and recrystallized from chloroform to give 7,10-*diphenyl-8,9-diazafluoranthene* (6a) as yellow crystals (80%), *m/e* 356 (M^+), $\lambda_{max.}$ (EtOH) 370 (log ε 3·07), 325 (4·00), 310 (4·00), 265 (4·30), and 240 nm (4·71) (Found: C, 87·5; H, 4·4; N, 8·0. $C_{26}H_{16}N_2$ requires C, 87·6; H, 4·55; N, 7·85%).

Reaction of 3,6-*Di-(2-pyridyl)-1,2,4,5-tetrazine* (5b) *with Acenaphthylene* (2).—Similar work-up of a mixture of 3,6-di-(2-pyridyl)-1,2,4,5-tetrazine (5b) [7] (240 mg, 1 mmol) with acenaphthylene (160 mg, 1 mmol) afforded 7,10-*di-(2-pyridyl)-8,9-diazafluoranthene* (6b) (60%) as yellow needles, m.p. >300°, $\lambda_{max.}$ (EtOH) 365 (log ε 4·10), 325 (4·05), 268 (4·42), and 238 nm (4·62), δ ($CDCl_3$) 7·5—8·7 (14H, m) (Found: C, 80·15; H, 4·2; N, 15·65. $C_{24}H_{14}N_4$ requires C, 80·45; H, 3·95; N, 15·65%).

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