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Synthesis of 6-(trifluoromethyl)-8,13,13d-triazadibenzo[def,qr] chrysenes

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Abstract

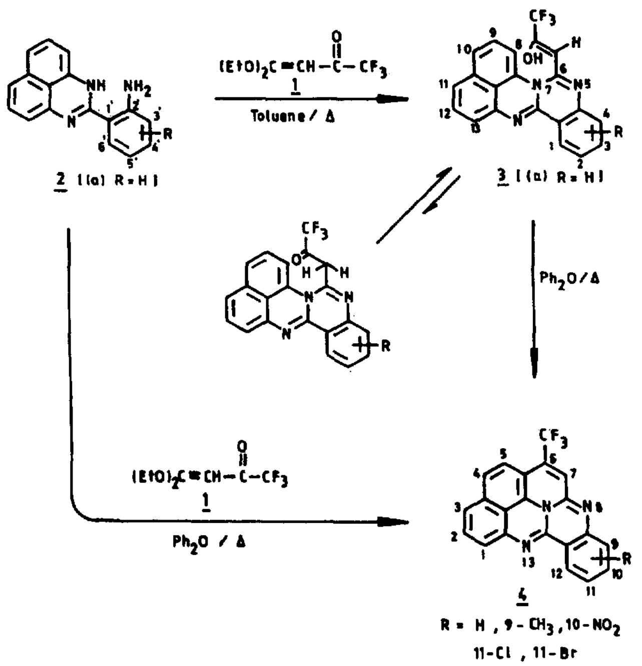
Trifluoroacetyl ketene diethylacetal reacts thermally with 2-(2′-aminoaryl)perimidines **2** in diphenyl ether to give 6-(trifluoromethyl)-8,13,13d-triazadibenzo[def,qr]chrysenes **4**.

Keywords: Synthesis; Trifluoromethyl triazadibenzo-chrysenes; NMR spectroscopy; IR spectroscopy; Mass spectrometry

1. Introduction

Trifluoroacetyl ketene diethylacetal (**1**) condenses with a variety of *ortho*-substituted amino compounds to provide access to 2-(1,1,1-trifluoroacetonyl)-imidazoles, -oxazoles, -quinazolines and -perimidines [1]. We have now extended this work to provide a useful route to 6-(trifluoromethyl)triazadibenzochrysenes from perimidines.

The reaction between the ketene acetal 1 and 2-(2′-aminophenyl)perimidine (**2a**, R = H) in toluene at reflux proceeds as shown in Scheme 1. The compound thus formed (**3a**: R = H, yield 70%) exhibited IR (KBr disc) absorptions at 3000 cm^{-1} (OH; broad) and 1624 cm^{-1} (C=N), and its ^{1}H NMR spectrum (in $CDCl_3$) showed absorptions at δ 6.2 (vinylic C–H) and δ 14.25 (HO–C=) ppm, compatible with the presence of the $-CH=C(OH)-CF_3$ group. The mass spectrum showed peaks at m/z 379 ($M^{+\bullet}$) and m/z 361 ($M^{+\bullet}-H_2O$; base peak). These data confirm the formation of 6-(1,1,1-trifluoroacetonyl)quinazolino[3,4-*a*]perimidine (**3a**), predominantly present in its enol form. Dehydrative cyclisation of **3a** (R = H) occurs in boiling (259 °C) diphenyl ether over 3 h to give the title compound (**4a**) in 80% yield. The IR and ^{1}H NMR spectrum of **4a** showed the absence of an OH group, and the mass spectrum contained a molecular ion peak (m/z 361) of 100% relative abundance. The IR spectrum showed an absorption at 1614 cm^{-1} arising from the C=N group. The ^{1}H NMR spectrum also contained a signal at δ 6.85 (s, 1H) ppm assignable to C_7–H of 6-(trifluoromethyl)-8,13,13d-triazadibenzo[def,qr]chrysene (**4a**).



Scheme 1.

In order to explore the possibility of obtaining **4a** (R = H) in a single step, the condensation of **1** with **2a** (R = H) was carried out in diphenyl ether at reflux temperature (259 °C). The compound thus obtained was identical in every respect with 6-(trifluoromethyl)-8,13,13d-triazadibenzo[def,qr]chrysene (**4a**), produced in stepwise fashion via **3a**. The reaction of **1** with other 2-(2′-aminoaryl)perimidines **2b–e**

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Table 1
Spectral and physical data for 6-(trifluoromethyl)-8,13,13d-triazadibenzo[def,qr]chrysenes **4**

Compound No.	R	M.p. (°C)	Yield (%)	IR (KBr) (cm^{-1})	MS (m/z)	^1H NMR ($CDCl_3$) δ (ppm)				
				ν(C=N)	M^+	C_1–H (d)	C_7–H (s)	Aromatic (m)	C_{12}–H (d)	Other
4a	H	265	80	1614	361	6.9	6.85	7.0–7.3	8.05	–
4b	9-CH_3	260	75	1627	375	6.85	6.95	7.0–7.35	7.85	2.35 (s, 3 H, –CH_3)
4c	10-NO_2	256	70	1624	407	6.7	6.75	6.9–7.4	8.1	
4d	11-Cl	255	70	1620	–	6.9	6.85	7.05–7.4	8.2	
4e	11-Br	260	65	1624	–	–	–	–	–	

gave analogues (**4b–e**) of **4a** (R=H) in good yield (65%–80%). All the compounds were adequately characterised by IR, ^1H NMR and MS data (Table 1).

2. Experimental details

2.1. Preparation of trifluoroacetyl ketene diethylacetal (1) [2]

To a stirred solution of ethyl orthoacetate (8.1 g, 0.05 mol) and pyridine (9.03 g, 0.114 mol) in chloroform (150 ml), trifluoroacetic anhydride (21.3 g, 0.10 mol) was added dropwise with cooling and the mixture stirred at room temperature (RT) for 24 h. It was then washed with 10% aqueous sodium carbonate solution (80 ml) and finally with water (2×80 ml) and dried over anhydrous sodium sulphate. The solvent and pyridine were removed under vacuum.

2.2. Preparation of 6-(1,1,1-trifluoroacetonyl)quinazolino[3,4-a]perimidine (3a)

1,1,1-Trifluoroacetyl ketene diethylacetal (**1**, 1 mmol) was added to a solution of 2-(2′-aminophenyl)perimidine [3] (**2a**, 1 mmol) in toluene and the mixture refluxed for 6 h. The solvent was removed under reduced pressure and the crude product chromatographically purified on a column of neutral alumina to afford 6-(1,1,1-trifluoroacetonyl)-quinazolino[3,4-*a*]perimidine (**3a**).

2.3. Pyrolysis of 6-(1,1,1-trifluoroacetonyl)quinazolino[3,4-a]perimidine (3a)

A solution of 6-(1,1,1-trifluoroacetonyl)quinazolino[3,4-*a*]perimidine (**3a**, 0.2 g) in diphenyl ether (10 ml) was refluxed for 3 h. The reaction mixture was cooled and chromatographed on neutral alumina to yield diphenyl ether (eluent; pet. ether) and 6-(trifluoromethyl)-8,13,13d-triazadibenzo[def,qr]chrysene (**4a**, eluent; pet. ether/benzene 10:2).

2.4. Condensation of 2-(2′-aminoaryl)perimidine (2) with trifluoroacetyl ketene diethylacetal (1) in diphenyl ether: formation of 6-(trifluoromethyl)-8,13,13d-triazadibenzo[def,qr]chrysenes 4. General procedure

2-(2′-Aminoaryl)perimidine (**2**, 1 mmol) was added to a solution of trifluoroacetyl ketene diethylacetal (**1**, 1 mmol) in diphenyl ether (10 ml) and the mixture refluxed for 6 h. The reaction mixture was cooled and chromatographed (neutral alumina) to yield diphenyl ether (eluent; pet. ether) and 6-(trifluoromethyl)-8,13,13d-triazadibenzo-[def,qr]-chrysenes (**4**, eluent; pet. ether/benzene).

2.5. Details of spectroscopic equipment

Mass spectra were recorded on a V.G. Micromass VG7070H Perkin-Elmer instrument and ^1H NMR spectra on a Varian Gemini 200 MH instrument, IR spectra were measured on a Perkin-Elmer FT-IR spectrometer and melting points were determined using a sulphuric acid bath.

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