Diels-Alder Reaction of Dehydrohydantoins with Dibenzo[*b,n*]perylene; The Synthesis of Dibenzo[*c,i*]phenanthro[1,10,9,8-*anmlk*]phenanthridine

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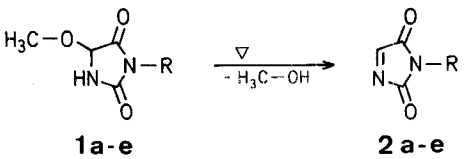
In continuation of our work[1,2,3] on the application of cycloaddition reactions in the synthesis of highly condensed heterocyclic compounds, we report a new preparation of dibenzo[*c,i*]phenanthro[1,10,9,8-*anmlk*]phenanthridine (**6**). The [4+2]-cycloaddition of a conjugated diene to an imine was widely used for the synthesis of nitrogen containing heterocycles[4]. However, the addition of an imine to a fused polycyclic hydrocarbon has hitherto not been reported. 3-Substituted 5-methoxyhydantoins (**1**) are known to lose methanol to form dehydrohydantoins (**2**) at elevated temperatures[5,6].

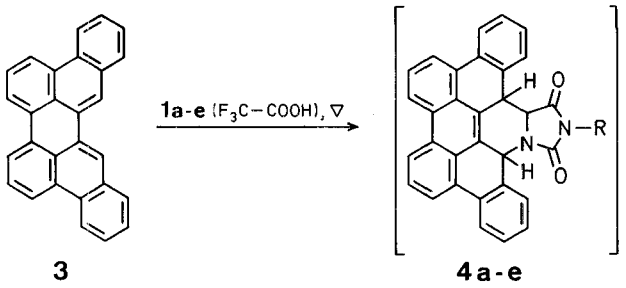


1a-e **2a-e**

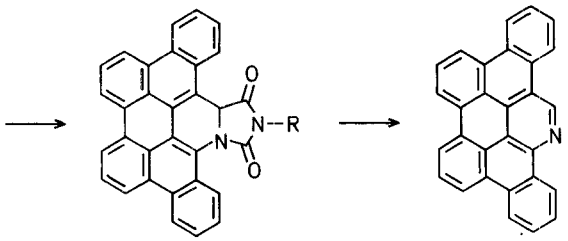
1,2	
a	
b	$-CH_2-$ 
c	$-C_4H_9$-*n*
d	$-C_3H_7$-*n*
e	$-C_2H_5$

We selected five hydantoins (**1**) as precursors of the corresponding dehydrohydantoins (**2**), and the reaction of **1** with dibenzo[*b,n*]perylene (**3**) was studied. When 5-methoxy-3-phenylhydantoin (**1a**) was heated with **3** in *p*-xylene in an autoclave at 160°C for 72 h, the cycloaddition product was obtained in 23% yield. The mass spectrum of this product showed a molecular ion peak at $m/e = 524$, which was smaller than the calculated value for the expected adduct **4a** by two mass units. The ^{1}H-N.M.R. spectrum did not show absorptions of methine groups at $\delta = 3.5$–4.5 ppm, which are typical in Diels-Alder type adducts of dehydrohydantoins[6]. The product showed a high melting point (325–331°C with decomposition). It retained the hydantoin carbonyl absorptions but lacked the imine absorption at 3400–3500 cm^{-1} in the I.R. spectrum. From these results, it was assigned as **5a**, which has a dehydrogenated structure of **4a**.

Either thermally or in the presence of trifluoroacetic acid, hydantoins **1** proved to react with **3** to give dehydrogenated adducts **5** (Tables 1, 2). Under acid-catalyzed conditions, phenyl- (**1a**) and benzylhydantoin (**1b**) gave **5a** and **5b** quantitatively (Runs 6 and 7).



3 **4a-e**



5a-e **6**

There are several reports[7,8] on the Diels-Alder reactions of cyano compounds, in which dehydrogenated products are obtained. However, the addition of imino dienophiles involving oxidative dehydrogenation has not been reported.

The reactivities of the above hydantoins with perylenes were not so high compared with those of cyclic azodienophiles[2] derived, for example, from 1,4-dioxo-1,2,3,4-tetrahydrophthalazine and lead(IV) acetate. Thus, perylene did not give any adduct with **1a** or **1b** under similar conditions as described in Method A or B in Table 2.

Treatment of **3** with an excess of *N*-(2,2,2-trichloroethylidene)ethoxycarbonylamine[9] in xylene at 130°C for 10 h resulted only in the recovery of **3**. The reaction of **3** with *N*-(2,2,2-trichloroethylidene)-*p*-toluene sulfonamide[10] in an autoclave at 160°C for 24 h gave a very complex mixture, in which the corresponding Diels-Alder adduct could not be detected.

Hydrolyses and decarboxylations of adducts **5** were performed according to our previous method[1]. The title compound **6** was obtained in 58–64% yield.

3-Substituted 5-Methoxyhydantoins 1a-e:

Compounds **1a** and **1b** are prepared from the corresponding hydantoins, bromine, and methanol in acetic acid according to Refs.[11,12]. This procedure is more convenient than the preparation of **1a**[5] from phenylurea and dibutyl oxalate[13,14]. Similarly, the 3-butyl, 3-propyl, and 3-ethyl derivatives **1c-e** are prepared from the corresponding alkylhydantoins.

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Table 1. Compounds **5a–e** prepared

Product	m.p. [°C] (dec.)	Molecular Formula[a]	M.S. *m/e* (M^+)	I.R. (KBr) ν [cm^{-1}]	^{1}H-N.M.R. (DMSO-d_6/TMS) δ [ppm]
5a	325–331°	$C_{37}H_{20}N_2O_2$ (524.6)	524	3070, 1780, 1720, 1400, 755	6.44 (s, 1H); 7.55 (m, 5H); 7.65–8.2 (m, 8H); 8.4–9.1 (m, 6H)
5b	350–356°	$C_{38}H_{22}N_2O_2$ (538.6)	538	3070, 1775, 1710, 1440, 755	4.77 (s, 2H); 6.30 (s, 1H); 7.5 (m, 5H); 7.65–8.0 (m, 8H); 8.5–9.0 (m, 6H)
5c	265–268°	$C_{35}H_{24}N_2O_2$ (504.6)	504	3060, 2930, 1775, 1705, 1410, 750	0.96 (t, 3H); 1.0–1.9 (m, 4H); 3.55 (t, 2H); 6.11 (s, 1H); 7.5–8.1 (m, 8H); 8.3–9.0 (m, 6H)
5d	180–182°	$C_{34}H_{22}N_2O_2$ (490.6)	490	3070, 2970, 2940, 1776, 1710, 1415, 754	0.95 (t, 3H); 1.2–1.95 (m, 2H); 3.44 (t, 2H); 6.20 (s, 1H); 7.6–8.1 (m, 8H); 8.5–9.0 (m, 6H)
5e	192–194°	$C_{33}H_{20}N_2O_2$ (476.5)	476	3050, 2910, 1767, 1700, 1419, 747	1.25 (t, 3H); 3.58 (q, 2H); 6.16 (s, 1H); 7.6–8.0 (m, 8H); 8.5–9.0 (m, 6H)

[a] Satisfactory microanalyses obtained: C ±0.43, H ±0.27, N ±0.33.

Table 2. Reaction of **3** with **1a–e**

Run	Hydantoin	Method	Product	Yield [%]
1	**1a**	A	**5a**	23
2	**1b**	A	**5b**	60
3	**1c**	A	**5c**	62
4	**1d**	A	**5d**	47
5	**1e**	A	**5e**	13
6	**1a**	B	**5a**	95
7	**1b**	B	**5b**	96
8	**1c**	B	**5c**	74
9	**1d**	B	**5d**	51
10	**1e**	B	**5e**	48

N-Benzyl-15,16-dihydrodibenzo[*c,i*]phenanthro[1,10,9,8-*anmlk*]phenanthridine-dicarboximide (5b); Typical Procedure:

Method A, Dibenzo[*b,n*]perylene (**3**; 100 mg, 0.28 mmol), 5-methoxy-3-benzylhydantoin (**1b**; 625 mg, 2.8 mmol), and *p*-xylene (2 ml) are heated at 160°C for 72 h in a stainless-steel autoclave. After cooling, the mixture is filtered and washed with methanol. The product is then chromatographed on an alumina column with xylene/ethanol (200/1) as eluent; yield: 92 mg (60%).

Method B: To a stirred, boiling solution of dibenzo[*b,n*]perylene (**3**; 100 mg, 0.28 mmol) and 5-methoxy-3-benzylhydantoin (**1b**; 625 mg, 2.8 mmol) in benzene (60 ml), trifluoroacetic acid (1.5 g, 13 mmol) is added dropwise. Stirring is continued under reflux for 24 h. The solvent is then removed on a rotary evaporator and the residue is chromatographed as above; yield: 142 mg (95%).

Dibenzo[*c,i*]phenanthro[1,10,9,8-*anmlk*]phenanthridine (6); Typical Procedure:

Sodium hydroxide pellets (93% pure; 175 mg, 4.0 mmol) are added in one portion to a stirred solution of compound **5b** (108 mg, 0.20 mmol) in benzyl alcohol (30 ml) at 90°C. Stirring is continued at 90–100°C for 30 min. After cooling, the mixture is acidified with a solution of concentrated hydrochloric acid (2.5 ml) in methanol (7.5 ml), and then evaporated. The precipitated product is filtered with methanol (10 ml), washed with water and methanol. Sublimation at 300–350°C/2 torr (6 h) gives a yellow powder (59 mg). Recrystallization of the sublimate from a 1500-fold amount of bis[2-hydroxyethyl] ether affords **6** as pale yellow needles; yield: 48 mg (64%): m.p. 396–400°C (dec.).

$C_{29}H_{15}N$	calc.	C 92.28	H 4.01	N 3.71
(377.4)	found	91.90	3.77	4.13

M.S.: $m/e = 377$ (M^+).

I.R. (KBr): $\nu = 3070, 1600, 1410, 750$ cm^{-1}.

^{1}H-N.M.R. (FSO_3H/TMS): $\delta = 8.1–9.6$ ppm (m).

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