Tetrahedron Letters,Vol.24,No.31,pp 3273-3276,1983 0040-4039/83 $3.00 + .00
Printed in Great Britain

DIENOPHILIC ANTHRACENES: FORMATION OF NOVEL TRIPTYCENES via THERMAL AND PHOTOCHEMICAL INTRAMOLECULAR DIELS-ALDER REACTIONS OF DIANTHRYLETHANES

Hans-Dieter Becker* and Kjell Andersson
Department of Organic Chemistry, Chalmers University of Technology
and University of Gothenburg, S-412 96 Gothenburg, Sweden

Abstract: 1,2-Di(9-anthryl)ethanes, accessible by thermolysis of lepidopterenes, undergo thermal and photochemical intramolecular Diels-Alder reactions to give 1,2-dihydroanthracenes whose aromatization leads to novel derivatives of triptycene.

1,2-Di(9-anthryl)ethanes 2 are of photochemical interest, as their excited state reactivity and the thermodynamic properties of their [4+4] cycloaddition products 1 are affected by the substituent R.[1] Unfortunately, the conventional synthesis of dianthrylethanes from 9-anthrylmethyl halides by treatment with Grignard reagents is impaired by the concomitant formation of isomeric lepidopterenes 4 which are difficult to separate.[2] On the other hand, lepidopterenes are easily obtained in high yield by reaction of 9-anthrylmethyl halides with stannous chloride.[3]

Lepidopterenes in solution have previously been shown to be in equilibrium with their [4+2] cycloreversion products, i.e. 9-anthrylmethyl α,p-dimers 3. We have now found that lepidopterenes at, or slightly above, the temperature of their melting points are smoothly converted into dianthrylethanes 2. The yields of isolated products are 80-90% (See Table 1).

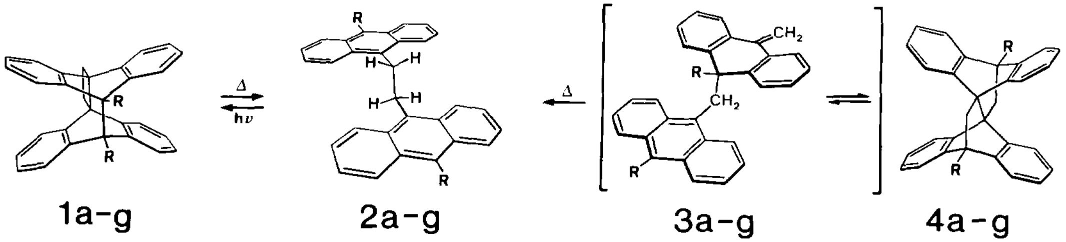


TABLE 1. Thermolytic Conversion of Lepidopterenes 4 into Dianthrylethanes 2.

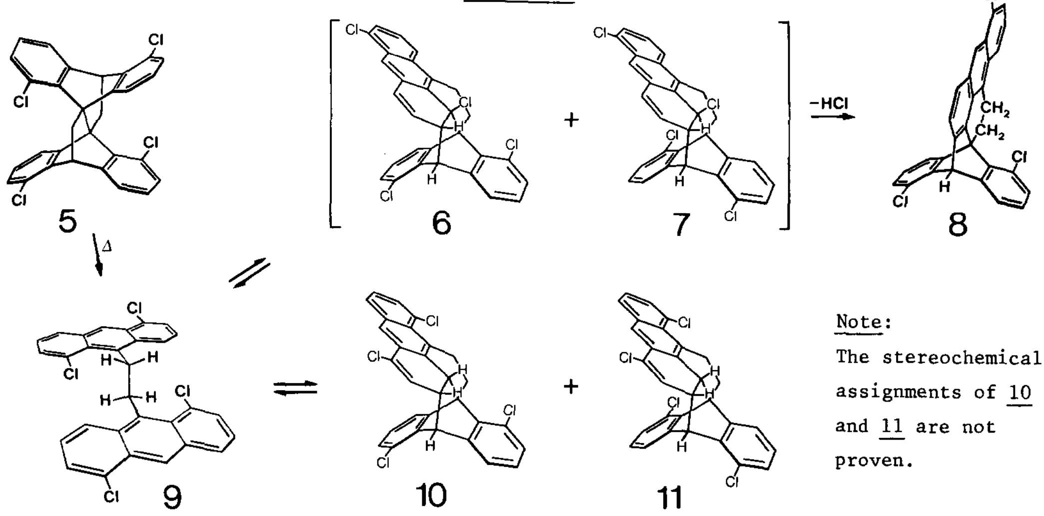
2,4	a	b	c	d	e	f	g
R	H	CH_3	C_2H_5	benzyl	phenyl	t-β-styryl	α-naphthyl-CH_2
mp of 4	317-23	308-12	292-95	256-60	273-77	270-73	293-96 °C
mp of 2	328-30	281-82	264-67	267-69	323-26	300-04	340-43 °C
yield (%)	82	80	82	90	82	78	82

Surprisingly, thermolysis of tetrachlorolepidopterene 5 at 320 °C for 2 min was found to result in the evolution of hydrogen chloride and the formation of a crystalline product (mp 315 °C; 86% yield) for which MS, ^{1}H-NMR, and electronic absorption spectrum (see Fig. 1) are in agreement with the novel triptycene derivative 8 (cf. Tables 2 and 3).[4]

The formation of triptycene 8 can be rationalized by invoking an intramolecular Diels-Alder reaction of the intermediate 1,1',5,5'-tetrachloro-substituted dianthrylethane 9, in which one anthryl moiety reacts as a diene, and the 1,2-bond of the other serves as a dienophile. The resulting two isomeric 1,2-dihydroanthracenes 6 and 7 are assumed to aromatize by way of dehydrohalogenation (cf. Scheme I).

In search of direct evidence for the unprecedented thermal isomerizarion of a dianthrylethane by intramolecular Diels-Alder reaction, we have synthesized 9 by an unambiguous route[5] and confirmed its smooth thermal conversion into 8 at 210 °C. Moreover, by carrying out the thermolysis of 9 in refluxing toluene, we have obtained as major products those two conceivable 1,2-dihydroanthracenes 10 and 11, which derive from an intramolecular Diels-Alder reaction involving the unsubstituted 7,8-bond of 9 as a dienophile.

Scheme I

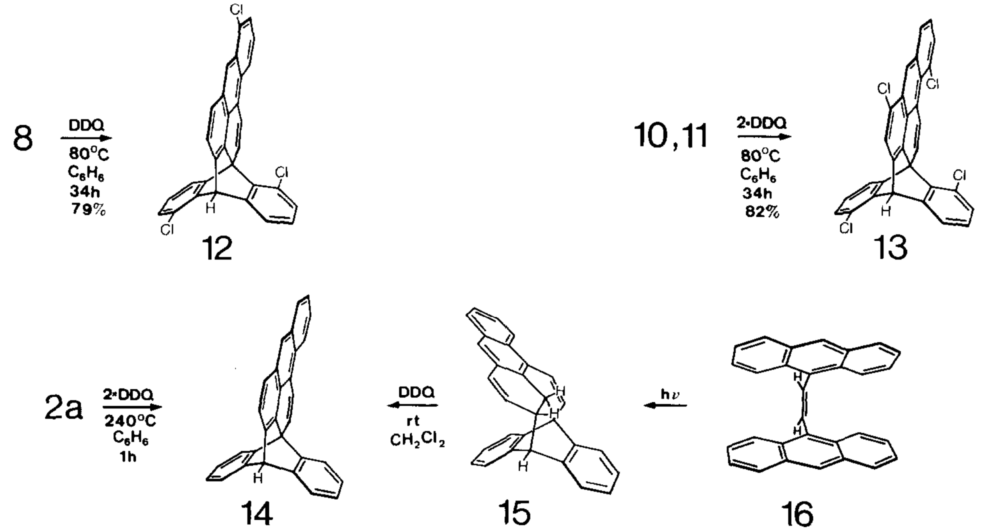


Note:
The stereochemical assignments of 10 and 11 are not proven.

TABLE 2. Thermal Conversions of 5, 9, 10, and 11.

	°C	solvent	time	product		°C	solvent	time	product
5	320	-	2 min	8(86%)	9	210	-	5 min	8(88%)
5	240	xylene	60 min	8(92%)	9	173	decane	15 min	8(100%)
10/11	230	-	2 min	8(92%)	9	110	toluene	90 min	8(27%), 9(8%) 10(42%), 11(23%)

Dehydrogenation of 8 and 10/11 with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) leads to triptycene derivatives 12 and 13, respectively. The parent hydrocarbon 14, previously[6] hard to come by from cis-1,2-di(9-anthryl)ethylene (16) via its photo-isomer 15, was now obtained in 70% yield by a simple one-pot procedure which involves keeping a solution of dianthrylethane 2a and two molar equivalents of DDQ in benzene in a sealed tube at 240 °C for 1 h.[7] The electronic absorption spectra of triptycenes 12-14 are of interest because they are characteristic of the planar 9-vinylanthracene chromophore (see Fig. 2).[8] Consequently, 12-14 fluoresce with high quantum yields of 85, 89, and 96%, respectively; (Φ_F of 8 is 18%).



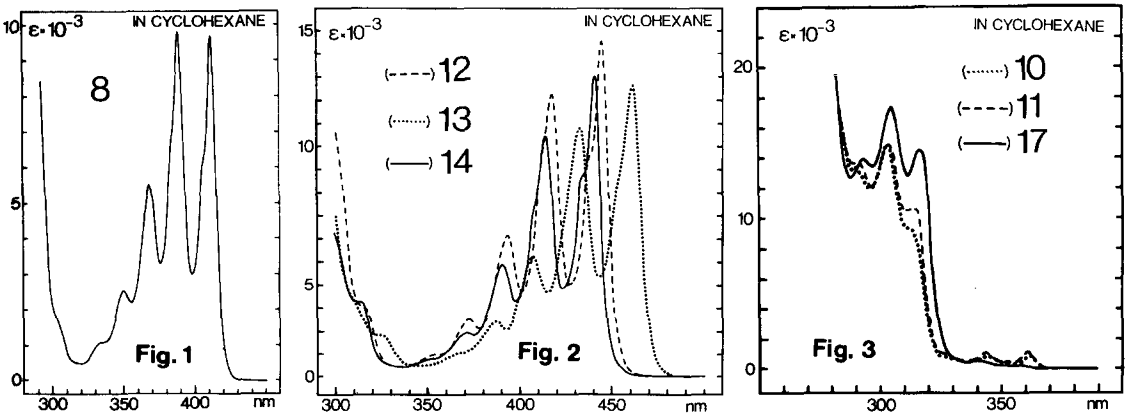
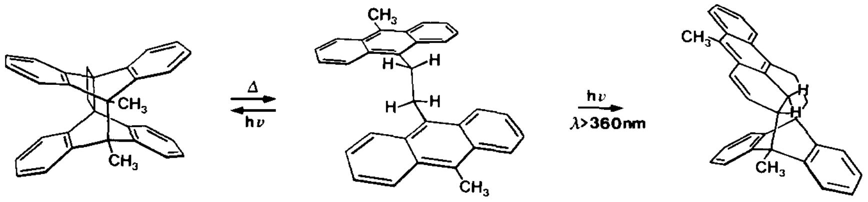


Fig. 1-3. Electron spectra of triptycenes (8, 12, 13, 14) and Diels-Alder adducts (10, 11, 17).

We have found during the course of the present investigation that dianthrylethanes 2 also can undergo photochemical isomerization by intramolecular Diels-Alder reaction, though this mode of cycloaddition generally will be obscured by the more efficient [4+4] cyclomerization leading to 1. However, when the cycloadducts 1 are characterized by low thermal stability and undergo cycloreversion, the photochemical route to intramolecular [4+2] cycloadducts from dianthrylethanes 2 becomes feasible. For example, 1,2-bis(10-methyl-9-anthryl)ethane (2b) upon irradiation isomerizes with a quantum efficiency of 0.14 to give 1b, whose half-life at 25 °C is as short as 33 min.[1] However, irradiation of 2b (100 mg; 125 W high-pressure mercury lamp; λ_{exc} >360 nm) in benzene (300 mL) at 70 °C for 16 h leads to the Diels-Alder isomer 17, which was isolated in 68% yield. Its UV absorption spectrum is in agreement with the 1,2-dihydroanthracene chromophore which also characterizes the absorption spectra of Diels-Alder products 10 and 11 (see Fig. 3). The ^{1}H-NMR spectral data of Diels-Alder adducts 10, 11, and 17 as well as those of triptycenes 8, and 12-14 are summarized in Table 3.



1b 2b 17

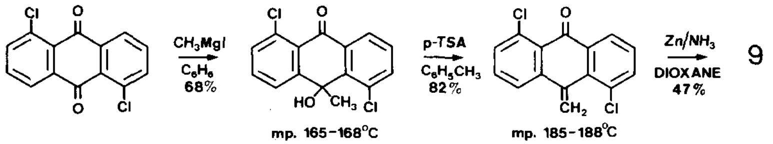
TABLE 3. Characterization of Diels-Alder Products and Triptycenes by ^{1}H NMR and MS

	mp ^{o}C	arom./olef. H	bridgehead H	aliphatic H	formula	requires	found
8	315	8.79-6.82	6.05	4.47-3.07	$C_{30}H_{17}Cl_3$	482.0398	482.0382
10	192,dec.	7.68-6.08	5.03	4.73-2.21	$C_{30}H_{18}Cl_4$	518.0165	518.0165
11	223,dec.	7.63-6.20	4.71	5.15-2.96	$C_{30}H_{18}Cl_4$	518.0165	518.0159
12	329-31	8.73-6.92	6.24	-	$C_{30}H_{15}Cl_3$	480.0242	480.0239
13	>350	9.40-6.92	6.18	-	$C_{30}H_{14}Cl_4$	513.9852	513.9836
14	293	8.45-6.94	5.74	-	$C_{30}H_{18}$	378.1409	378.1411
17	262-66	8.01-5.96	-	3.87-2.84 CH_3:2.43;2.04	$C_{32}H_{26}$	410.2036	410.2046

In conclusion, the experiments described above verify the dienophilic character of the anthracene 1,2-bond whose remarkably short bond length had previously been established by X-ray diffraction.[9,10,11]

References and Notes

1. H.-D- Becker, T. Elebring, and K. Sandros, J. Org. Chem. 47, 1064 (1982).
2. G. Felix, R. Lapouyade, A. Castellan, H. Bouas-Laurent, J. Gaultier, and C. Hauw, Tetrahedron Lett. 1975, 409.
3. H.-D. Becker, K. Andersson, and K. Sandros, J. Org. Chem. 45, 4549 (1980).
4. For a triptycene review, see V.R. Skvarchenko, V.K. Shalaev, and E.I. Klabunovskii, Russ. Chem. Rev. 43, 951 (1974).
5. 9: mp 205 °C (dec); proton NMR (δ):4.64, br s, 4H; 6.78-8.55, m, 14 H (in chloroform). The synthesis of 9 involves the following straightforward reactions [cf. R. Lapouyade, J.-P. Desvergne, and H. Bouas-Laurent, Bull. Soc. Chim. France, 1975, 2137; H.-D. Becker, D. Sanchez, and A. Arvidsson, J. Org. Chem. 44, 4247 (1979)]:



6. H.-D. Becker, K. Sandros, and K. Andersson, Angew. Chem. 95, in press (1983).
7. A minor by-product of the thermolysis of 2a in the presence of DDQ was di(9-anthryl)-acetylene which was removed by column chromatography (silica gel, toluene:hexane 10:3).
8. Cf. H.-D. Becker and K. Andersson, J. Org. Chem. 48, submitted (1983).
9. The reaction of anthracene with hexachlorocyclopentadiene gives in low yield a 1:2 adduct [A.A. Danish, M. Silverman, and Y.A. Tajima, J. Am. Chem. Soc. 76, 6144 (1954)] whose formation conceivably involves the anthracene 1,2-bond in a Diels-Alder addition (cf. E. Clar, Polycyclic Hydrocarbons, Vol. 1, p. 296, Academic Press/Springer, New York/Berlin, 1964).
10. D.W.J. Cruickshank, Acta Crystallogr. 9, 915 (1956).
11. Concerning the molecular geometry of a dianthrylethane, see H.-D. Becker, S.R. Hall, B.W. Skelton, and A.H. White, Aust. J. Chem. 35, 2357 (1982).

(Received in UK 5 May 1983)