

A NOVEL PHOTOCYCLIZATION, STARTING FROM  
1,4-DIARYLBUTENYNES

A.H.A. Tinnemans and W.H. Laarhoven

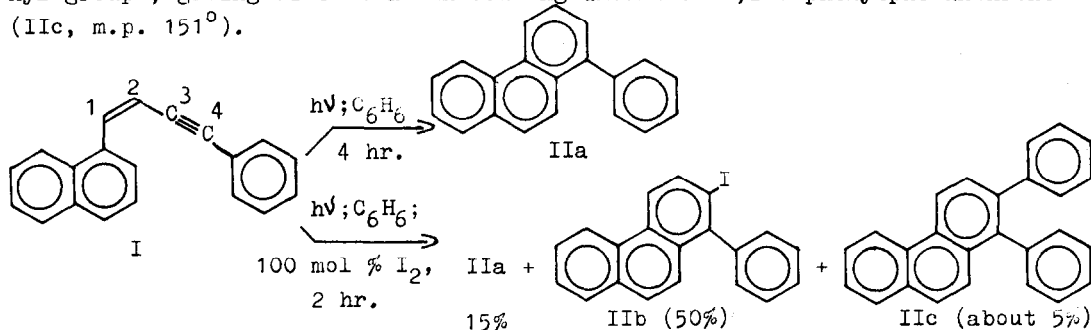
Department of Organic Chemistry, Catholic University,  
Toernooiveld, Nijmegen, The Netherlands

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Cis-trans isomerization is the only known photochemical reaction of arylbutenyne<sup>1</sup> until now. We found, however, that irradiation under nitrogen of a dry and deaerated solution ( $5 \cdot 10^{-4}$  molar) of 1-( $\alpha$ -naphthyl)-4-phenylbut-1-en-3-yn<sup>2</sup>(I) in benzene with a 360 nm fluorescence lamp (Sylvania blacklite F8T5) during four hours converted the solute into 1-phenylphenanthrene (IIa), 45%.

Although no oxidation step is involved the cyclization is slightly faster in the presence of air; in a solution saturated with oxygen or supplied with a small amount of iodine ( $3 \cdot 10^{-5}$  molar) the rate is about twice as fast as in a deaerated and iodine-free solution.

The main irradiation product in a deaerated solution of I containing an equimolar amount of iodine is an iodo derivative, 1-phenyl-2-iodophenanthrene (IIa). On prolonged irradiation of this solution iodine is replaced by a phenyl group<sup>3</sup>, giving rise to an increasing amount of 1,2-diphenylphenanthrene (IIc, m.p. 151°).



The cyclization is a light-induced reaction. Refluxing a benzene solution of I in the dark or heating of pure I in an evacuated tube at 300° during four hours did not yield any cyclization product.

Irradiation under nitrogen of an iodine-free solution of I ( $5 \cdot 10^{-4}$  molar) in hexane in the presence of triplet-sensitizers like 2-methylantraquinone, benzophenone, benzil or acetophenone ( $0-1.2 \cdot 10^{-2}$  molar) did not lead to higher yields of IIa. Also the presence of the triplet-quencher azulene did not influence the result of the photoreaction.

The radical scavenger di-tert.butylnitroxide<sup>4</sup> ( $10^{-3}$ - $4 \cdot 10^{-4}$  molar) had no influence upon the cyclization of I into IIa. However, on irradiation a solution of I containing iodine as well as this radical scavenger only IIa and not IIb and IIc was formed.

From these results it may be concluded that IIa arises from a singlet excited state of I. It is known that acetylenes in the first excited state have non-linear trans configurations<sup>5</sup>, which should be very favourable for the ring-closure observed. The formation of the new C-C bond and the 1,5-hydrogen shift may be a concerted. In the presence of iodine cyclization product IIb is apparently formed via a radical intermediate, possibly formed by the addition of an iodine atom to the triple bond of I.

The new photocyclization reaction has been investigated on several other diarylbutenyne (Table).

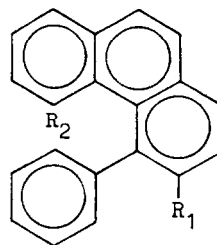
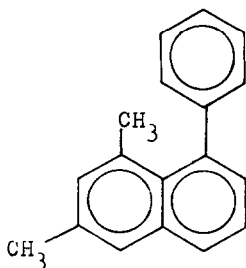
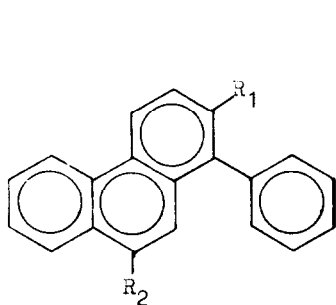
Table

Irradiation products from diarylbutenyne<sup>2</sup>,  
 $\text{Ar}^1-\text{CH}=\text{CH}-\text{C}\equiv\text{C}-\text{Ar}^2$

Ar <sup>1</sup>	Ar <sup>2</sup>	without iodine			with iodine		
		pro-duct	yield %	m.p. °C	pro-duct	yield %	m.p. °C
1 $\alpha$ -naphthyl	phenyl	IIa	45	74-76	IIb	50	166-168
2 phenyl	phenyl	-			-		
3 p. methoxyphenyl	phenyl	-			-		
4 3,5-dimethylphenyl	phenyl	IIIa	44	liquid	*)		
5 $\beta$ -naphthyl	phenyl	IVa	55	82-84	IVb	44	160-162
6 $\alpha$ -(4-methylnaphthyl)	phenyl	IIId	54	89-92	IIe	19	93-95
7 $\beta$ -(8-phenylnaphthyl)	phenyl	IVc	65	169-171	IVd	16	135-140
8 3-phenanthryl	phenyl	Va	50	109-113	Vb	32	131-133
9 2-benzo [c]phenanthryl	phenyl	-**			-		
10 9-(1-phenylphenanthryl)	phenyl	VIa	60	150-152	VIb	44	254-260
11 phenyl	$\alpha$ -naphthyl	-			-		
12 $\alpha$ -naphthyl	$\alpha$ -naphthyl	VIIa	22	116-118	*)		
13 $\beta$ -naphthyl	$\alpha$ -naphthyl	VIIIa	38	150-152	VIIIb	38	137-140

\*) Irradiation had to be carried out with a high pressure mercury lamp in hexane; under these circumstances carbon-iodine bonds are broken.

\*\*\*) Only a mixture of dimers had been formed.



IIa:  $R_1 = R_2 = H$

b:  $R_1 = I, R_2 = H$

c:  $R_1 = C_6H_5, R_2 = H$

d:  $R_1 = H, R_2 = CH_3$

e:  $R_1 = I, R_2 = CH_3$

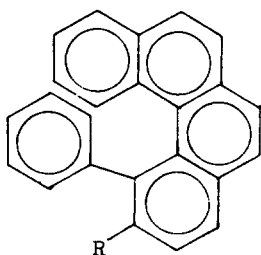
IIIa

IVa:  $R_1 = R_2 = H$

b:  $R_1 = I, R_2 = H$

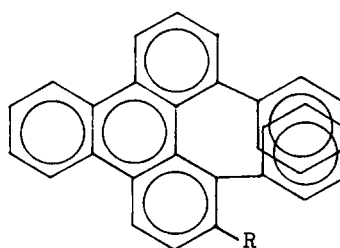
c:  $R_1 = H, R_2 = C_6H_5$

d:  $R_1 = I, R_2 = C_6H_5$



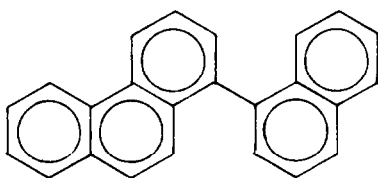
Va:  $R = H$

b:  $R = I$

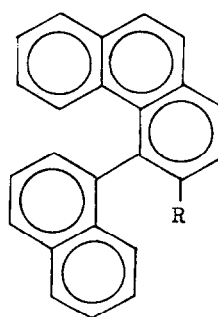


VIa:  $R = H$

b:  $R = I$



VIIa



VIIIa:  $R = H$

b:  $R = I$

The negative results in the experiments 2, 3 and 11 compared with the cyclization in 4 suggest that some factor related to the electron-distribution in the relevant ring is of decisive importance for the cyclization. The failure of cyclization in experiment 9 may be due to the strong tendency of the starting compound to dimerization, even in dilute solutions. In all other cases only one type of cyclization product was obtained; bond formation occurs always between an acetylenic carbon ( $C_4$  in I) and the aromatic ring at  $C_1$ . In this respect the reaction is clearly different from photocyclizations in diarylbutadienes<sup>6</sup>, which lead to two products if different arylresidues are present in the starting compound<sup>7</sup>. The experiments 7, 8 and 10 reveal that even highly crowded polycyclic aromatics can be obtained quite specifically and in good yields from properly chosen diarylbutenyne.

Full experimental details concerning the syntheses and spectroscopic data and properties of the products will be given elsewhere.

#### Acknowledgement:

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#### References and notes

1. G. Quinkert, M. Hintzmann, P. Michaelis, P. Jürges, H. Appelt and U. Krüger, *Ann.* **748**, 38 (1971).
2. The butenyne were synthesized by Wittig reactions from arylpropargylaldehydes and triphenylphosphonium salts of appropriate bromomethyl aromatics in methanol or DMF as solvent and with sodium methoxide as base.
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5. J. Dale in H.G. Viehe, *Chemistry of Acetylenes*, Marcel Dekker, New York, **1969**, p. 52.
6. R.J. Hayward, A.C. Hopkinson and C.C. Leznoff, *Tetrahedron* **28**, 439 (1972).
7. Although Leznoff mentioned high specificity in photocyclizations of 1,4-diarylbutadienes we found in general more than one product. This discrepancy may be due to the very low yields (about 10%) in Leznoff's experiments.