Photocyclisations of 1,4-Diarylbut-1-en-3-ynes. Part II.[1] Mechanism of the Reaction

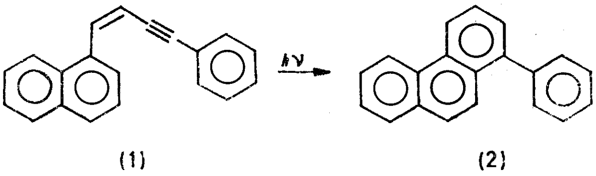
By **Alois H. A. Tinnemans** and **Wim H. Laarhoven,*** Department of Organic Chemistry, Catholic University, Toernooiveld, Nijmegen, The Netherlands

The photocyclisation of 1,4-diarylbutenynes into aromatic compounds (Scheme 1) proceeds in aprotic solvents as a radical reaction in which the singlet excited *cis*-isomer of the parent compound abstracts a hydrogen atom from the solvent or some other hydrogen donor, and the resulting radical undergoes intramolecular ring closure (Scheme 3). With methanol as the solvent the same end product arises *via* ionic intermediates, formed by photoprotonation of the starting compound and subsequent, intramolecular, electrophilic substitution (Scheme 4).

A PRELIMINARY report[1] on photocyclisation of 1,4-diarylbutenynes and several applications[2,3] of this reaction for the preparation of aryl-substituted polycyclic aromatic compounds have been published. Only very few examples of intramolecular photocyclisations in which an acetylenic bond is involved are known. Templeton[4] isolated phenanthrene on irradiation of diphenylacetylene in ethanol, but only dimers are found in other solvents.[5] Kaplan[6] observed formation of fulvene and benzene on irradiation of *cis*-hexadienyne in the gas phase at 253.7 nm; isomerisation into benzene also occurs by heating[7] above 275 °C. Mechanisms have not been proposed for these reactions.

In this paper the results of our investigations into the mechanism of the photocyclisation of diarylbutenynes is reported, and in the following paper the scope and limitations of the reaction will be compared with the conclusions of this mechanistic study.

Nature of the Reactive State.—The possible influence of triplet sensitizers or quenchers on the yield of the photocyclisation product of 1-(α-naphthyl)-4-phenylbut-1-en-3-yne (Scheme 1) was measured in two series of parallel experiments performed in a ' merry-go-round ' apparatus (Rayonet RPR-100 reactor). The yields were determined by n.m.r. spectroscopy. Table 1 gives the results of the experiments with several sensitizers at various concentrations and with the quencher azulene. Cyclisation *via* the triplet state appears to be very improbable because neither sensitizers nor quenchers have the expected effect on the reaction; the presence of oxygen even causes acceleration instead of retardation. The occurrence of triplets in the irradiation mixture of (1) could equally not be detected by measurement of its absorption spectrum by flash photolysis.† Ring closure



SCHEME 1

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† The experiment was carried out by Dr. G. P. de Gunst, Gorleaus Laboratory, Leiden.

[1] Part I, A. H. A. Tinnemans and W. H. Laarhoven, *Tetrahedron Letters*, 1973, 817.

[2] A. H. A. Tinnemans and W. H. Laarhoven, *J. Amer. Chem. Soc.*, 1974, **96**, 4617.

[3] W. H. Laarhoven and P. G. F. Boumans, *Rec. Trav. chim.*, 1975, **94**, 114.

[4] W. Templeton, *Chem. Comm.*, 1970 1412.

[5] G. W. Büchi, C. W. Perry, and E. W. Robb, *J. Org. Chem.* 1962, **27**, 4106.

[6] L. Kaplan, S. P. Walch, and K. E. Wilzbach, *J. Amer. Chem. Soc.*, 1968, **90**, 5646.

[7] H. Hopf and H. Musso, *Angew. Chem.*, 1969, **81**, 704.

of (1) in a hot ground state reached by internal conversion of the S_1 state also seems rather improbable. Such a process might be acceptable for the cyclisation of hexadienyne in the gas phase[6] which also proceeds thermally.[7] In solutions of diarylbutenynes, however, hot ground states would rapidly lose excessive energy by collisions with solvent molecules. Moreover, we found that the cyclisation of this type of compound does not occur on heating. Therefore, we assume that the photocyclisation of diarylbutenynes occurs in the first excited singlet state. This assumption is attractive because acetylenes have a non-linear *trans*-configuration[8] in the S_1 state which should be very suitable for the observed cyclisation reaction.

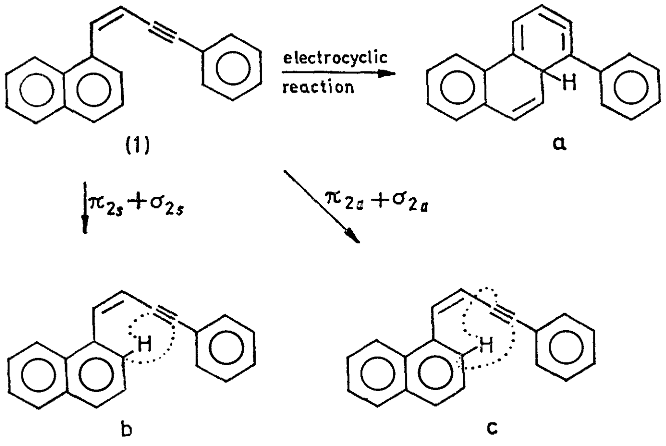
TABLE 1

Influence of sensitizers and quenchers on the photocyclisation of 1-(α-naphthyl)-4-phenylbutenyne (1) in hexane

λ/nm	Atmosphere	10^4 [Butenyne]/M	10^4 [Sensitizer] or [quencher]/M		E_T/ kcal mol^{-1}	Yield[c] (%)
300	N_2	6				39
300	Air	6				50
300	O_2	6				67
300	N_2	6	Benzophenone	30	69[a]	33
300	N_2	6	Benzophenone	120	69	32
300	N_2	6	Benzophenone	180	69	37
300	N_2	6	Methylanthraquinone	120	62[a]	35
300	N_2	6	Acetophenone	180	74[a]	36
300	N_2	6	Benzil	30	54[a]	37
300	N_2	6	Benzil	120	54	39
360	N_2	4				25
360	N_2	4	Azulene	3	31—39[b]	23
360	N_2	4	Azulene	6	31—39	23

[a] W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Amer. Chem. Soc.*, 1964, **86**, 4537. [b] A. A. Lamola, W. G. Herkstroeter, J. C. Dalton, and G. S. Hammond, *J. Chem. Phys.*, 1965, **42**, 1715. [c] See Experimental section.

Nature of the Reaction.—*A priori* the photocyclisation of diarylbutenynes might be a concerted, a radical, or an ionic reaction. Of these the concerted process might be either an electrocyclic reaction followed by a [1,5]sigmatropic hydrogen shift, or a $[_\sigma 2 + {}_\pi 2]$cycloaddition. Both possibilities for a concerted process are extremely improbable, because an electrocyclic reaction of (1) would lead to the sterically unfavourable allene structure



SCHEME 2

(a), whereas symmetry rules for cycloaddition predict a product having either a hydrogen atom inside the newly formed ring or the newly formed carbon–carbon bond inside the ring of the naphthyl residue, as indicated in b and c in Scheme 2. A concerted reaction as the main pathway in the photocyclisation of diarylbutenynes could definitely be ruled out by experiments with a deuteriated compound, 1-(2-[1-^{2}H]naphthyl)-4-phenylbutenyne (3b). A concerted photocyclisation of this compound should lead to 4-phenyl[3-^{2}H]phenanthrene (4b). Comparison of the n.m.r. spectra of the products from the unlabelled compound (3a) and from 90% deuteriated (3b) revealed, however, that almost all the deuterium was present at C-3 but the percentage of the isotope (mass spectrometry) was always much lower than in the starting compound (Table 2). Moreover, photocyclisations of diarylbutenynes having a substituent at the ring atom involved in the cyclisation [*e.g.* 1-(2-methyl-1-naphthyl)-4-phenylbutenyne (5) and 1-(1-bromo-2-naphthyl)-4-phenylbutenyne (3c)] gave only unsubstituted products [(2) and (4a), respectively]. The substituents were completely lost during the reaction.

TABLE 2

Percentage of deuteriated 4-phenyl[3-^{2}H]phenanthrene (4b) relative to the total amount of 4-phenylphenanthrene (4a + b) on irradiation of 1-(2-[1-^{2}H]naphthyl)-4-phenylbutenyne (3b) under various conditions

	Solvents		
Atmosphere	Hexane	Benzene	Methanol
Nitrogen	30 ± 5	35 ± 5	
Oxygen	15 ± 5	5 ± 5	5 ± 5

Of the other possibilities, a radical or an ionic reaction, the latter is very unlikely in aprotic solvents such as hexane and benzene. In fact we found two strong indications for a radical mechanism. (i) Irradiation of (3a) in benzene under nitrogen gave rise to the formation of a small amount of biphenyl which does not arise on irradiation of pure benzene under the same circumstances; the side-product arises from the reaction of

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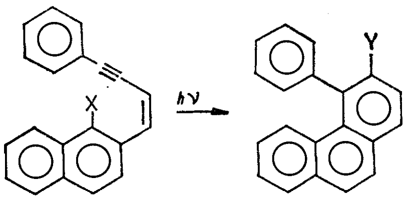
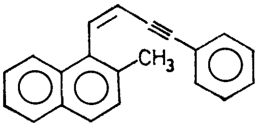
[8] J. Dale in 'Chemistiy of Acetylenes,' H. G. Viehe, Marcel Dekker, New York, 1969, p. 72.

phenyl radicals with benzene.[9] (ii) Irradiation (λ <300 nm) of (1) in carbon tetrachloride in the probe of an n.m.r. instrument resulted in a small CIDNP emission signal at the frequency of chloroform.* As we have shown above that the reaction starts from the singlet excited state, we assume that the CIDNP emission is due to diffusive encounters of free CCl_3 radicals. The same experiment in methanol or benzene did not give rise to a CIDNP signal.



(3)
a; X = H
b; X = D
c; X = Br

(4)
a; Y = H
b; Y = D

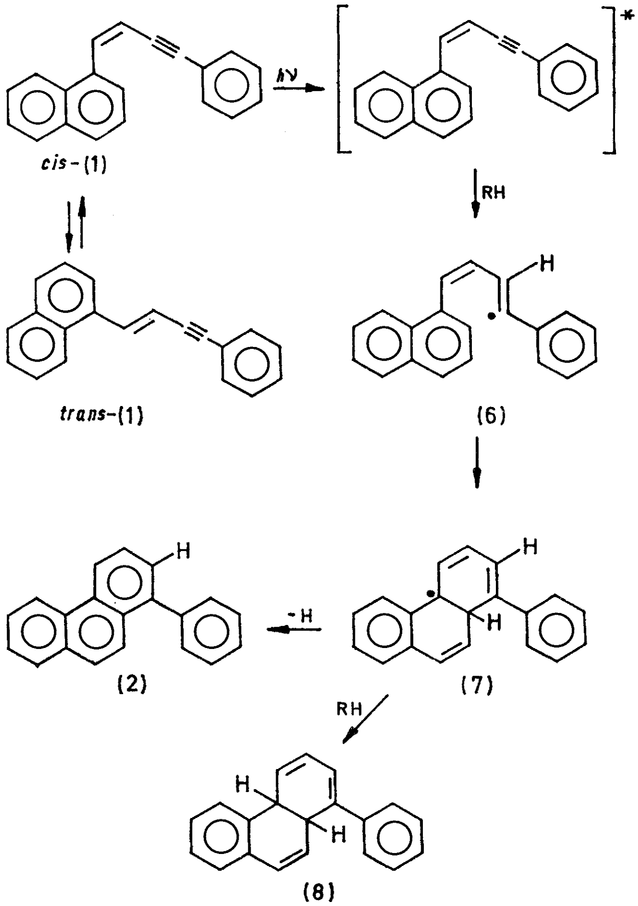


(5)

Mechanism in Aprotic Solvents.—In accordance with this radical mechanism the photocyclisation of (1) proceeds about twice as fast in hexane as in benzene; the C–H bond dissociation energy of hexane is *ca.* 4 kcal mol^{-1} lower than that of benzene.[10] The accelerating influence of oxygen, already mentioned in Table 1, is also observed in the photocyclisation of other butenynes. Simultaneous irradiation of the methyl derivative (5) in hexane at 300 nm under nitrogen and in air gave (2) in 15 and 80% relative yield, respectively (see Experimental section).

A reasonable reaction pathway, analogous to that previously proposed[11] for the photocyclisation of stilbene-α-carboxylic acid, is given in Scheme 3. For stereochemical reasons it may be accepted that the product (2) arises from the *cis*-isomer in the photochemical equilibrium mixture of (1). Singlet excited *cis*-(1) picks up a hydrogen atom from some hydrogen donor giving the radical (6) which undergoes ring closure by intramolecular radical addition to the naphthyl residue giving (7). The hydrogen donor can be a solvent molecule, as is apparent from the formation of biphenyl in benzene solutions, but it can also be the radical (7), as may be deduced from the partial labelling of the end-product in experiments with a deuteriated starting compound. The ring-closed radical (7) can be converted into a stable end product by addition or by abstraction of a hydrogen atom. Energetically the latter process is preferred, and in the presence of a suitable oxidant (*e.g.* oxygen) (7) will be completely converted into (2). The high velocity of the oxidation step under these conditions reduces the participation of (7) as a hydrogen donor in the formation of the primary radical (6) (see Table 2). The addition of a hydrogen to (7) with formation of the dihydro-product (8) has never been observed, not even under nitrogen.

Additional evidence for the proposed radical mechanism was obtained from irradiation experiments in the presence of iodine. On irradiation of a benzene solution of (1) to which 5 mol % iodine had been added, the normal cyclisation product (2) was obtained as the main product (45%) but small amounts of 2-iodo- (9) and 2-phenyl-substituted 1-phenylphenanthrene (10) also appeared to be formed (total *ca.* 10%).



Scheme 3

In the presence of 100 mol % iodine (2), (9), and (10) were formed in 15, 50, and 5% yield, respectively. The

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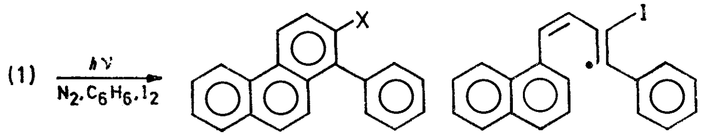
* The experiment was performed by Dr. R. Kaptein, Shell Laboratories, Amsterdam.

[9] G. H. Williams, 'Homolytic Aromatic Substitution,' Pergamon Press, Oxford, 1960, ch. 4.

[10] C. Walling, 'Free Radicals in Solution,' Wiley, New York, 1957, p. 50.

[11] R. Srinivasan and J. N. C. Hsu, *J. Amer. Chem. Soc.*, 1971, **93**, 2816.

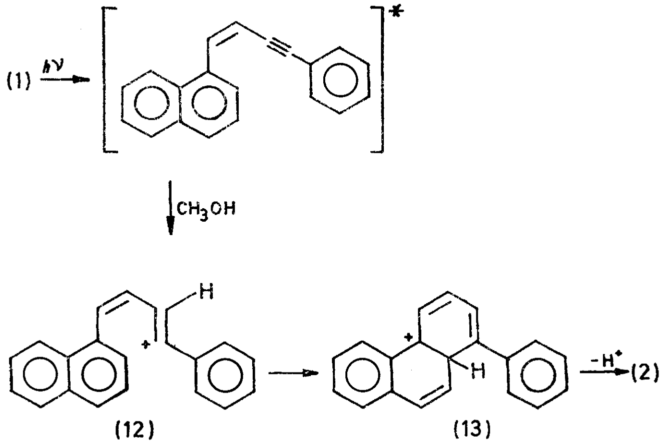
formation of (10) is due to photolysis of the corresponding iodo-derivative (9) followed by reaction of the resulting aryl radical with the solvent.[12,13] Indeed, irradiation of pure (9) in benzene gave (10) in very high yield. The iodinated product (9) itself, however, cannot have arisen *via* addition of thermally formed iodine atoms, since heating of a solution of (1) with iodine led only to *cis–trans*-isomerisation and not to cyclisation. Apparently the iodinated end-product arises *via* an iodinated radical (11) corresponding to (6), which is formed from the excited starting compound and molecular iodine.



(2) X = H
(9) X = I
(10) X = C_6H_5

(11)

Mechanism in Methanol.—The photocyclisation of (1) in methanol proceeds only slightly faster than in an aprotic solvent. Simultaneous experiments in methanol and hexane yielded 50 and 42% of (2) respectively. Irradiation of a 5 × 10^{-3}M solution of (3a) in methan[^{2}H]ol yielded the product (4b) containing one deuterium atom, *m/e* 255 (M^+, 89%), 254 ($M^+ - 1$, 100), 253 ($M^+ - 2$, 68), 252 ($M^+ - 3$, 15), 251 ($M^+ - 4$, 21), and 240 ($M^+ - 15$, 10). The n.m.r. spectrum of the product



(12) (13)

Scheme 4

showed an AB signal, δ 7.49 (2-H) and 7.76 (1-H), (J_{AB} 8.3 Hz) instead of the ABC pattern in the spectrum of the unlabelled product, δ 7.73 (1-H), 7.48 (2-H), and 7.32 (3-H). Apparently, hydrogen at C-3, δ 7.32, had been exchanged for deuterium, and integration revealed that deuterium was present in at least 95%. The transfer of the oxygen-bound hydrogen from the solvent into the product points to transfer as a proton,[14] and the cyclisation in this solvent must therefore be an ionic reaction. Without light, product (2) is not formed from (1) even in solutions containing acetic acid. Therefore, the cyclisation of (1) in methanol apparently proceeds *via* a vinylic cation (12) formed by photoprotonation of the parent compound (Scheme 4).

Light-induced protonation of unsaturated compounds, followed by reactions of the resulting carbonium ions in the ground-state has previously been observed in irradiation of cyclohexenes and cycloheptenes in protic solvents.[14,15] With unsubstituted and phenyl-substituted cyclohexenes the photoprotonation of the ethylenic bond only occurs in the presence of a mineral acid. However, with alkyl-substituted cyclohexenes such an acid is not necessary. The difference has been ascribed to the higher basicity of alkyl substituted cyclohexenes in the excited state. By similar reasoning the easy photoprotonation of (1) leading to (12) may be ascribed to the greater basicity of acetylenes in the excited state in comparison with ethylenes.

EXPERIMENTAL

Spectroscopic measurements were made with a Varian MAT SM2B mass spectrometer, a Cary 15 or Beckman DK2A u.v. spectrophotometer, a Perkin-Elmer 257 i.r. apparatus, and a Varian HA-100 or XL-100 n.m.r. instrument. M.p.s were measured on a Leitz m.p. microscope and are uncorrected.

Irradiations were carried out in a Rayonet RPR-100 reactor fitted with 300 or 360 nm lamps, in quartz or Pyrex tubes of 1 000 ml surrounded by four Sylvania ' black-lite ' F8T5 lamps, or in a cooled quartz tube surrounding a Philips HPK 125 mercury lamp.

The synthetic procedure for the preparation of the starting compounds [(1), (3a, c), (5)] and physical data for these compounds and the products (2), (4), (9), and (10) is given in ref. 16.

The yields of the cyclisation product in irradiation experiments with (1) (Table 1) were calculated from the n.m.r. spectra of the irradiation mixtures by comparison of the intensities of the olefinic H-2 signal in *cis*- and *trans*-(1), δ 6.04 and 6.34, respectively, and the H-4 and -5 signals in the product, δ 8.59. Percentages are relative to the total amounts of (1) and (2) present in the mixture.

1-(2-[1-^{2}H]*Naphthyl)-4-phenylbutenyne* (3b).—A 20% solution of n-butyl-lithium in hexane (30 ml) was dropped into

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[12] W. Wolf and N. Kharasch, *J. Org. Chem.*, 1965, **30**, 2493.

[13] R. K. Sharma and N. Kharasch, *Angew. Chem.*, 1968, **80**, 69.

[14] P. J. Kropp, *J. Amer. Chem. Soc.*, 1969, **91**, 5783.

[15] P. J. Kropp, E. J. Reardon, jun., Z. L. F. Gaibel, K. F. Williard, and J. H. Hattaway, *J. Amer. Chem. Soc.*, 1973, **95**, 7058.

[16] A. H. A. Tinnemanns and W. H. Laarhoven, preceding paper.

a solution of 1-bromo-2-methylnaphthalene[17] (0.03 mol) in absolute ether (100 ml) under nitrogen. The solution was stirred for 30 min at room temperature and then slowly supplied with D_2O. After completion of the reaction water was added and the mixture was extracted with ether. The extract was washed to neutral pH, dried ($MgSO_4$), and evaporated. The resulting 2-methyl[1-^{2}H]naphthalene was converted into (3b) in the same way as described elsewhere for the unlabelled compound (3a).

[5/1359 *Received, 9th July,* 1975]

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[17] M. S. Newman and A. I. Kosak, *J. Org. Chem.*, 1949, **14**, 375.