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PHOTOCHEMICAL AND THERMAL TRANSFORMATIONS OF AZOMETHINE IMINES

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Abstract—The thermal and photochemical fragmentations of a few bisazoalkenes have been investigated. 2-Phenyl-4, 5-disubstituted-1, 2, 3-triazoles were obtained both in the thermolysis and photolysis of 1, 2-bisphenylazo-(4, 4'-dichloro) stilbene, 1, 2-bisphenylazo(4, 4'-dimethoxy)stilbene, 1, 2-bisphenylazocyclohexene and *o*-(phenylazo) phenyldiazocyanide. Both 2, 3-bisphenylazo-2-butene and 1, 2-bisphenylazoethylene failed to undergo either photolysis or thermolysis in the expected manner. However, 2, 3-bisphenylazo-2-butene underwent an acid-catalysed valence isomerisation to anhydro 1-phenylimino-2-phenyl-4, 5-dimethyl-1, 2, 3-triazolium hydroxide, which on photolysis gave 2-phenyl-4, 5-dimethyl-1, 2, 3-triazole. The same iminotriazolium intermediate gave a cycloadduct, 2, 6-diphenyl-3, 3a-dimethyl-4, 5-dicarbomethoxypyrazolino [2.3.c][1.2.3] triazole, on treatment with dimethyl acetylenedicarboxylate, whereas treatment with carbon disulphide gave 2-phenyl-4, 5-dimethyl-1, 2, 3-triazole. Both photolysis and thermolysis of C-biphenylene-N$^\alpha$-(4-chlorophenyl)-N$^\beta$-cyanoazomethine imine gave 9-fluorenone-N- (4-chlorophenyl) anil. Photolysis of 1, 2-bisphenylazo-acenaphthylene in methanol gave acenaphthenequinone monophenylhydrazone.

In an earlier paper[1] we had reported that the formation of 2, 4, 5-triphenyl-1, 2, 3-triazole (**3a**) in the photolysis of N,C-diphenylsydnone is proceeding through the intermediate formation of 1, 2-bisphenylazostilbene (**1a**), which subsequently undergoes valence isomerisation to the mesoionic anhydro 1 phenylimino - 2, 4, 5 - triphenyl - 1, 2, 3 - triazolium hydroxide (**2a**). Further photochemical fragmentation of **2a** has been assumed to be the pathway for the formation of the triazole **3a** (Scheme 1). Our subsequent studies have shown that the bisphenylazostilbene (**1a**), formed separately through the oxidation of benzil osazone undergoes valence isomerisation to the corresponding phenyliminotriazolium derivative **2a** and that **2a** behaves like an azomethine imine, undergoing 1, 3-dipolar cycloadditions with different dipolarophiles.[2,3] The object of the present investigation was to study the photochemical and thermal transformations of several bisazoalkenes which are capable of undergoing valence isomerisation to the corresponding iminotriazolium derivatives. Although bisazoalkenes are conveniently prepared through the oxidation of the corresponding bisphenylhydrazones, it has been observed that the nature of the products in these oxidations depends to a large extent on the structure and stereochemistry of the starting bisphenylhydrazones.[4] Also, since only the cis-isomers of 1,2-bisazoalkenes would be expected to undergo ready valence isomerisation to the cyclic iminotriazolium intermediates, we hoped to draw some correlation between the photochemical and thermal behaviour of different bisazoalkenes, derived from various 1,2-diketone bisphenylhydrazones and the structure and stereochemistry of the parent bisphenylhydrazones.

In our preliminary studies, it has been shown that the direct heating of 1,2-bisphenylazostilbene (**1a**) to around 175–180° gives an 85% yield of the triazole (**3a**).[1] The same triazole was formed in appreciable yields when a solution of **1a** was photolysed in benzene.[1,5] In the present investigation we have examined the photochemical and thermal behaviour of two bisphenylazoalkenes namely, 1, 2-bisphenylazo-(4, 4'-dichloro) stilbene (**1b**) and 1, 2-bisphenylazo-(4, 4'-dimethoxy) stilbene (**1c**). Direct heating of **1b** to around 205–210° for 1 h resulted in the formation of a 55% yield of the triazole **3b**. The same triazole was formed in nearly the same yield when a benzene solution of **1b** was irradiated for 1 h. Similarly, the thermolysis and photolysis of **1c** resulted in the formation of the corresponding triazole **3c** in 89% and 60% yields, respectively (Scheme 1).

The formation of the triazoles (**1a–c**) in these reactions can be rationalized in terms of the thermal and photochemical fragmentation of the corresponding phenyliminotriazolium derivatives, (**2a–c**), respectively, resulting in the loss of phenylnitrene. However, our attempts to trap the phenylnitrene in these reactions have not been successful. As, for example, the photolysis of **1a** in presence of

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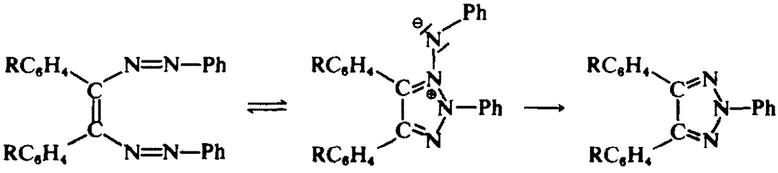


1a: R = H
b: R = *p*-Cl
c: R = *p*-CH_3O

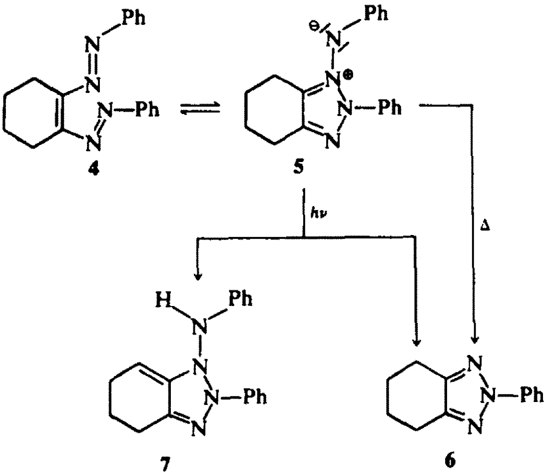
2a,b,c

3a,b,c

SCHEME 1

either cyclohexene or aniline resulted in the formation of the triazole **3a**, together with small amounts of benzil-1, 2-bisphenylhydrazone.

The valence isomerisation of bisphenylazoalkenes to the corresponding iminotriazolium isomers would be expected to be more feasible in cases where the starting bisazoalkenes have the *cis*-geometry. With a view to testing this assumption, we have examined the thermal and photochemical transformations of a bisphenylazoalkene, which is known to have a *cis*-geometry as in the case of *cis*-1, 2-bisphenylazocyclohexene (**4**). By direct heating of **4** around 125–130° for 1 h, a 14% yield of 2-phenyl-4, 5-tetramethylene-1, 2, 3-triazole (**6**) was obtained. The photolysis of **4**, on the other hand, gave a mixture of products consisting of a 28% yield of the triazole **6** and 5% yield of a product identified as 1-anilino-2-phenyl-1, 4, 5, 6-tetrahydrocyclohexa-[d] [1.2.3] triazole (**7**). The identity of **7** was established on the basis of analytical results and spectral data.

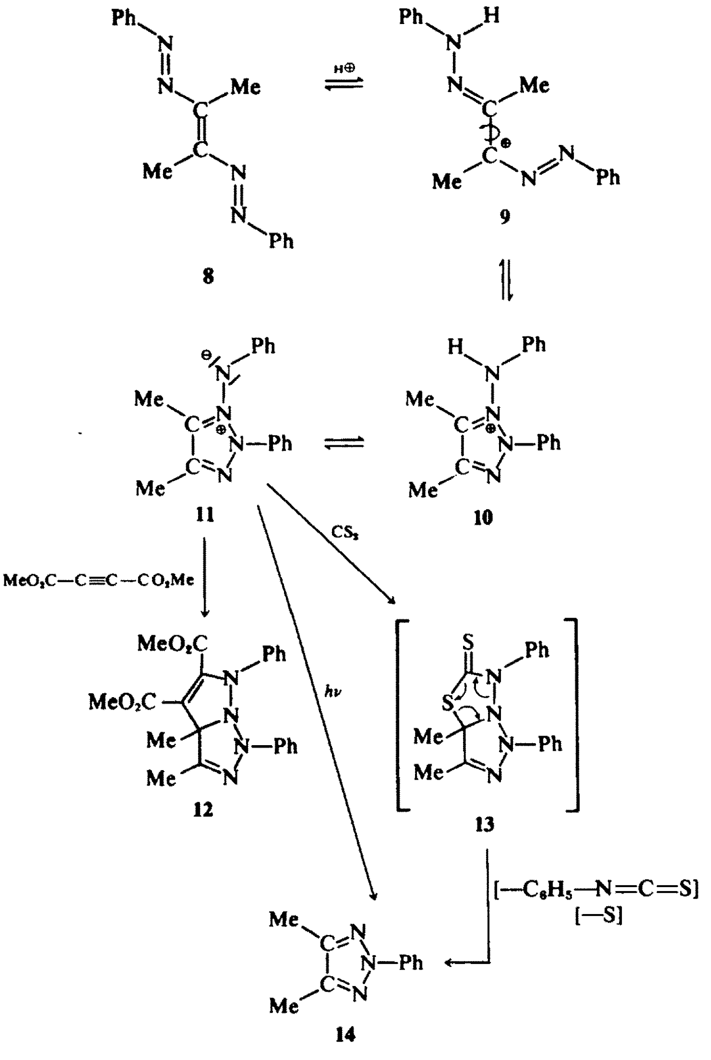


SCHEME 2

The NMR spectrum of **7** showed two multiplets centered around $2{\cdot}15\delta$ (4H) and $2{\cdot}95\delta$ (2H) due to the methylene protons, a multiplet around $4{\cdot}35\delta$ (1H), due to the vinyl proton and a broad peak centered around $3{\cdot}75\delta$ (1H) due to the NH proton. In addition, a complex multiplet around $7{\cdot}50\delta$ (10H) was present in the spectrum, assigned to the phenyl protons. Further confirmation of the presence of an NH group in **7** was derived from the fact that the peak at $3{\cdot}75\ \delta$ disappeared when the spectrum was determined in presence of D_2O. In addition, the IR spectrum of **7** showed an absorption band at 3325 cm^{-1}, characteristic of an NH group. A probable route to the formation of **7** in the photolysis of **4** is through the iminotriazolium intermediate **5**, which can subsequently isomerise through a prototropic shift (Scheme 2).

It is interesting to note that when a bisphenylazoalkene like 2, 3-bisphenylazo-2-butene (**8**), which is analogous to **4**, as far as substituents are concerned, is subjected either to thermolysis or photolysis under conditions similar to those employed in the case of **4**, does not give any triazole. It is quite probable that the most stable form of **8** has a *trans*-geometry across the C=C bond and that the isomerisation of **8** to its iminotriazolium analogue (**11**) may not be taking place readily under these conditions. With a view to observing whether the isomerisation of **8** to **11** may be taking place under acid-catalysed conditions we have examined the NMR spectrum of **8**, both in presence of some added HCl and also without any acid catalyst. The NMR spectrum of **8** showed a sharp singlet at $2{\cdot}65\delta$, due to the Me protons (6H) and two sets of multiplets centered around $8{\cdot}6\delta$ (6H) and $8{\cdot}1\delta$ (4H), due to the phenyl protons. When a drop of HCl was added to the solution of **8**, the spectrum changed drastically in the region of the phenyl protons. The phenyl protons now appeared as a complex multiplet spread over the range of $6{\cdot}8\delta$–$8{\cdot}1\delta$. The Me protons still appeared as a singlet at $2{\cdot}55\delta$. In addition, the spectrum showed a broad singlet centered at $8{\cdot}7\delta$, which is assigned to an NH proton. The fact that an NH proton signal is observed in the spectrum would suggest that **8** may be undergoing protonation in presence of HCl leading, perhaps, to the formation of the protonated iminotriazolium derivative **10** (Scheme 3). The exact reason for the equivalence of the two Me protons in **10** is not very clear. It may, however, imply that the structure **10** is in rapid equilibrium with an isomeric form which would make the two Me groups equivalent.

If the protonation of **8** is leading to an imino-



SCHEME 3

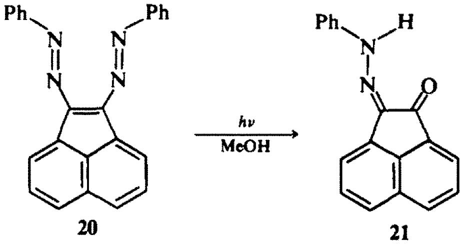
triazolium derivative such as **10**, then it would be reasonable to assume that cycloadditions characteristic of the azomethine imine **11**, would take place, if the reaction of **8** with any dipolarophile is carried out in presence of an acid catalyst. Thus, when dry HCl gas was passed through an equimolar mixture of **8** and dimethyl acetylenedicarboxylate in dry benzene, for 5 min, a 62% yield of a product identified as 1, 6-diphenyl-3, 3a-dimethyl-4, 5-dicarbomethoxypyrazolino [2.3.c] [1.2.3] triazole (**12**) was formed. Similarly, passing dry HCl gas, through a mixture of **8** and carbon disulphide for 5 min resulted in the formation of a 60% yield of 2-phenyl-4, 5-dimethyl-1, 2, 3-triazole (**14**). In addition, a 76% yield of elemental sulphur was also isolated from this reaction. The formation of the cycloadduct **12**, and the triazole **14** in the reactions of **8** with dimethyl acetylenedicarboxylate and carbon disulphide, respectively can be rationalized in terms of the azomethine imine intermediate **11**, formed through the protonated species **10** (Scheme 3). The triazole **14** is assumed to be formed through the fragmentation of the initially formed adduct **13** and the isolation of elemental sulphur in this reaction is in support of this view. A similar fragmentation of an adduct formed in the reaction of **1a** with carbon disulphide has been reported by us earlier.[3]

Having shown the existence of a dipolar species like anhydro 1-phenylimino-2-phenyl-4,5-dimethyl-1,2,3-triazolium hydroxide (**11**) in a solution of **8**, in presence of an acid catalyst, we then subjected such a solution to photolysis. Irradiation for nearly 5 min gave a 70% yield of the triazole. It was shown, in a blank experiment, that merely keeping a solution of **8** in presence of HCl for even 30 min, no appreciable yield of the triazole is formed. However, it has been observed that by refluxing a solution of **8** with aqueous HCl for 30 min, leads to the formation of 74% of the triazole **14**.[6] In this connection, it might be mentioned that the generally observed reaction of the acid-catalysed conversion of bisazoalkenes to triazoles may in fact be proceeding through a protonated species like **10**.

It is interesting to note that a bisphenylazoalkene such as 1,2-bisphenylazoethylene failed to undergo either cycloaddition reactions, or photolysis to give the expected 2-phenyl-1, 2, 3-triazole, even when these reactions were carried out in presence of HCl. It would be reasonable to assume that in this case the intermediate azomethine imine may not be formed in any appreciable yields.

In continuation of our studies we have examined the thermal and photochemical fragmentations of *o*-(phenylazo) phenyldiazocyanide (**15**) and an azomethine imine like C - biphenylene - N$^\alpha$ - (4 - chlorophenyl)-N$^\beta$-cyanoazomethine imine (**18**). Irradiation of a benzene solution of **15** for 2 h resulted in the formation of a 55% yield of the benzotriazole **17**. The same product was obtained in a 47% yield when **15** was heated alone to around 150–160° for 3 h. Similarly, the photolysis of **18** in benzene for 2 h gave a 32% yield of 9-fluorenone-(4-chlorophenyl) anil (**19**), as the only isolable product. Direct heating of **18** to around 200–210°, for 1 h, on the other hand, gave a mixture of products consisting of **19** (11%) and fluorenone (12%) (Scheme 4). It appears that azomethine imines like **15** and **18** undergo thermal and photochemical transformations, similar to those observed in the case of azomethine imines, derived from bisphenylazoalkenes. It is interesting to note, however, that azomethine imines like the 1-iminopyridinium betaines have been reported to undergo ring-expansion reactions, leading to the formation of diazepines.[7,8]

In our studies we have observed that a bisphenylazoalkene like 1,2-bisphenylazoacenaphthylene (**20**) does not yield any triazole, either under photochemical or thermal conditions. However, when **20** was photolysed in a 1 : 1 mixture of methanol and methylene dichloride, a 17% yield of acenaphthenequinone monophenylhydrazone was obtained (Scheme 5). The exact mechanism of this transformation is not very clear.



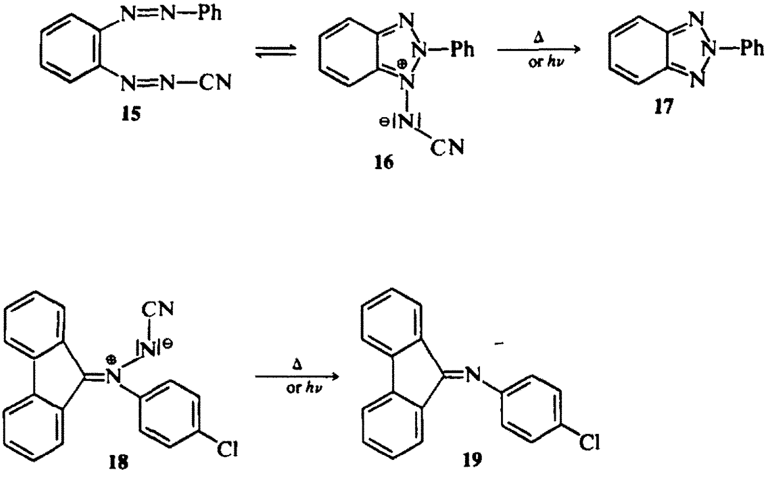
SCHEME 5

EXPERIMENTAL

All m.ps are uncorrected. Irradiation experiments were carried out using a Hanovia, medium pressure, mercury lamp (450 W). NMR spectra were recorded on a Varian A-60D NMR spectrometer and IR spectra, on a Perkin-Elmer, Model 521, Infrared Spectrometer.

Starting materials. Compounds **1b**, m.p. 205°, **1c**, m.p. 175°, **8**, m.p. 159° and 1,2-bisphenylazoethylene, m.p. 149° were prepared by the oxidation of the corresponding 1,2-diketone bisphenylhydrazones through the nickel peroxide oxidation, as reported.[4] Compounds **15**,[9] m.p. 158°, and **18**,[10,11] m.p. 194–195°, were prepared by known procedures.

Preparation of 1, 2-*bisphenylazocyclohexene* (**4**). A mixture of cyclohexane-1, 2-dione bisphenylhydrazone (4 g; 0·013 mol) and nickel peroxide (12 g) in 200 ml benzene was stirred at room temp for 4 h. Removal of the inorganic material and solvent gave a viscous mass which



SCHEME 4

was recrystallized from a mixture (1:1) of light petroleum (b.p. 60–80°) and benzene to give 3·2 g (82%) of 1, 2-bisphenylazocyclohexene, m.p. 127–128°. (Found: C, 74·61; H, 6·29; N, 19·57. $C_{18}H_{18}N_4$ requires: C, 74·48; H, 6·21, N, 19·31%).

Thermolysis of 1, 2-*bisazoalkenes.* In a typical experiment, the bisazoalkene (0·5 mmol) was heated around its m.p. in an oil-bath and the product was chromatographed over alumina. Elution with light petroleum (b.p. 60–80°) gave the triazole in each case.

Heating **1b** for 1 h around 205–210° gave a 55% yield of **3b**, m.p. 155° (m.m.p.). A 60% yield of **3c**, m.p. 134° (m.m.p.) was obtained on heating **1c** around 170–180° for 1 h.

Thermolysis of **4** gave a 14% yield of **6**, m.p. 90°, after recrystallization from a mixture (2:1) of light petroleum (b.p. 60–80°) and benzene. (Found: C, 72·24; H, 6·1; N, 20·75; Mol wt., 199 (Mass spectrometry). $C_{12}H_{13}N_3$ requires; C, 72·36; H, 6·53; N, 21·12%; Mol. wt., 199). The NMR spectrum ($CDCl_3$) showed multiplets around 1·90δ (4H) and 2·81δ (4H) due to the methylene protons and at 7·45δ (5H) due to the phenyl protons.

On heating **15** for 3 h around 150–160° gave a 47% yield of **17**, m.p. 110° (m.m.p.).

Photolysis of 1,2-*bisazoalkenes.* In a representative run, the bisazoalkene (0·5 mmol) was irradiated in 175 ml dry benzene till the intense deep violet colour of the soln changed to light yellow. On removal of the solvent under vacuum, the mixture was chromatographed over alumina using solvents like light petroleum and benzene to give the products.

Irradiation of **1b** for 1 h gave **3b** in 55% yield, m.p. 155° (m.m.p.).

Photolysis of **1c** in benzene for 2 h gave a 89% yield of **3c**, m.p. 134° (m.m.p.) and a 17% yield of biphenyl, m.p. 70° (m.m.p.).

When a solution of **4** was photolysed for 8 h, a 28% yield of **6**, m.p. 90° (m.m.p.) and a 10% yield of biphenyl, m.p. 70° (m.m.p.) were obtained. In addition, 5% of **7**, m.p. 136° after recrystallization from a mixture (1:1) of benzene and light petroleum (b.p. 60–80°) was also obtained. (Found: C, 74·70; H, 5·9; N, 19·3; Mol. wt., 290 (Mass spectrometry). $C_{18}H_{18}N_4$ requires: C, 74·48; H, 6·20; N, 19·17%; Mol. wt., 290). The NMR spectrum ($CDCl_3$) of **7** showed multiplets around 2·15δ (4H) and 2·95δ (2H) due to the methylene protons, 4·35δ (1H) due to the vinylic proton and 7·50δ (10H) due to the phenyl protons. A broad signal was observed around 3·75δ (1H) due to the NH proton which disappeared on D_2O exchange.

Photolysis of **15** in benzene soln for 2 h gave a 55% yield of **17**, m.p. 110 (m.m.p.).

Reaction of 2,3-*bisphenylazo*-2-*butene* (**8**) *with dimethyl acetylenedicarboxylate in presence of dry hydrogen chloride gas.* Dry HCl gas was passed into a mixture of **8** (0·26 g; 1 mmol) and dimethyl acetylenedicarboxylate (0·14 g; 1 mmol) in 10 ml dry benzene for 5 min, until the intense deep violet colour of the soln had finally disappeared. The soln was washed free of HCl with water and removal of the solvent from the organic layer gave a product which was recrystallized from a mixture (1:1) of light petroleum (b.p. 60–80°) and benzene to give 0·25 g (62%) of 2,6-diphenyl-3,3a-dimethyl-4,5-dicarbomethoxypyrazolino [2.3c] [1.2.3]-triazole, m.p. 136°. (Found: C, 65·11; H, 5·45; N, 13·74. $C_{22}H_{22}N_4O_4$ requires: C, 65·08; H, 5·42; N, 13·79%). IR spectrum (KBr) showed peaks at 1745 (C═O), 1690 (C═O), 1575, 1565, 1490, 1460, 1405, 1370, 1345, 1322, 1250, 1215, 1170, 1095, 1050, 980, 760, 740, 695, and 677 cm^{-1}. NMR spectrum ($CDCl_3$) showed the following signals at: 1·55δ (3H, s) and 1·90δ (3H, s) due to the Me protons, 3·75δ (3H, s) and 3·85δ (3H, s) due to the Me protons and 7·50δ (10H, m) due to the phenyl protons.

Reaction of 2,3-*bisphenylazo*-2-*butene* (**8**) *with carbon disulphide in presence of dry hydrogen chloride gas.* Into a mixture of **8** (0·52 g; 2 mmol) in freshly distilled CS_2 (3 ml) was passed a stream of dry HCl gas for 5 min. The unchanged CS_2 was removed under vacuum and the residue was treated with a mixture (1:1) of light petroleum (b.p. 60–80°) and benzene to remove the organic fractions. The residue (50 mg) was identified as elemental sulphur (76%) through comparison with an authentic sample.

From the filtrate, the solvent was removed under vacuum and the residue was digested with dil HCl for 30 min to remove the phenyl isothiocyanate, present as one of the constituents and the mixture was then repeatedly extracted with ether. Removal of the solvent from the ether extract under vacuum gave 0·21 g (60%) of **14**, m.p. 35° (b.p. 162° (60 mm)), identified through a comparison of its IR spectrum with that of an authentic sample.[6]

Photolysis of 2,3-*bisphenylazo*-2-*butene* (**8**) *in presence of dry hydrogen chloride.* A soln of **8** (0·26 g; 1 mmol) in 175 ml dry benzene was irradiated for 10 min while a continuous stream of dry HCl gas was passed through the soln, until the intense colour of the solution disappeared completely. The soln was washed free of HCl with water and after removal of the solvent, the residue was chromatographed over alumina. Elution with light petroleum (b.p. 60–80°) gave 0·11 g (60%) of **14**, b.p. 160° (60 mm), identified by comparison of its IR spectrum with that of an authentic sample.[6]

Photolysis of C - *biphenylene* - N^{α} - (4 - *chlorophenyl*) - N^{β} - *cyanoazomethine imine* (**18**). A soln of **18** (0·15 g, 0·45 mmol) in 175 ml benzene was irradiated for 2 h. Removal of the solvent under vacuum gave a dark material which was repeatedly extracted with hot benzene. Removal of the solvent from the benzene-extract under vacuum gave a product which was chromatographed over alumina. Elution with light petroleum (b.p. 60–80°) gave 42 mg (32%) of **19**, m.p. 150 (m.m.p.), after recrystallization from benzene.

Thermolysis of C-*biphenylene*-N^{α}-(4-*chlorophenyl*)-N^{β}-*cyanoazomethine imine* (**18**). Heating **18** (0·15 g; 0·45 mmol) around 200–210° for 1 h followed by chromatography of the product mixture over alumina using light petroleum (b.p. 60–80°) gave 15 mg (11%) of **19**, m.p. 150° (m.m.p.).

Continued elution of the column with a mixture (1:1) of benzene and light petroleum (b.p. 60–80°) gave 10 mg (12%) of 9-fluorenone, m.p. 83–84° (m.m.p.).

Photolysis of 9,10-*bisphenylazocenaphthylene* (**20**). A soln of **20** (0·44 g; 1·33 mmol) in 175 ml of a mixture (1:1) of CH_2Cl_2 and MeOH was irradiated for 6 h. Removal of the solvent gave a viscous material which was chromatographed over alumina to give 55 mg (17%) of 9,10-acenaphthenequinone monophenylhydrazone, m.p. 179–180° (m.m.p.), after recrystallization from MeOH.

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REFERENCES

[1] C. S. Angadiyavar and M. V. George, *J. Org. Chem.* **36**, 1589 (1971)

[2] C. S. Angadiyavar, K. B. Sukumaran and M. V. George, *Tetrahedron Letters* 633 (1971)

[3] K. B. Sukumaran, C. S. Angadiyavar and M. V. George, *Tetrahedron* **28**, 3987 (1972)

[4] K. S. Balachandran, I. Hiriyakkanavar and M. V. George, Unpublished Results

[5] C. Wintner, *Tetrahedron Letters* 2275 (1970)

[6] H. von Pechmann, *Ber. Dtsch. Chem. Ges.* **21**, 2751 (1888)

[7] J. Streith and J. M. Casal, *Angew. Chem.* **80**, 117 (1968)

[8] J. Streith and J. M. Casal, *Tetrahedron Letters* 4541 (1968)

[9] H. Bauer, G. R. Bedford and A. R. Katritzky, *J. Chem. Soc.* 751 (1964)

[10] R. Huisgen, R. Fleischmann and A. Eckel, *Tetrahedron Letters* 1 (1960)

[11a] A. Eckel, R. Huisgen, R. Sustmann, G. Wallbillich, R. Grashey and E. Spindler, *Chem Ber.* **100**, 2192 (1967); [b] A. Eckel, Ph.D. Thesis, Universität München (1963)