J. Org. Chem. **1980**, *45*, 1668–1672

Syntheses and Reactions of Spiroanthronetriazolines

Kiyoichi Hirakawa,* Tsutomu Ito, Yoshiji Okubo, and Sho Nakazawa

Department of Chemistry, Faculty of Textile Science and Technology, Shinshu University, Ueda, Nagano 386, Japan

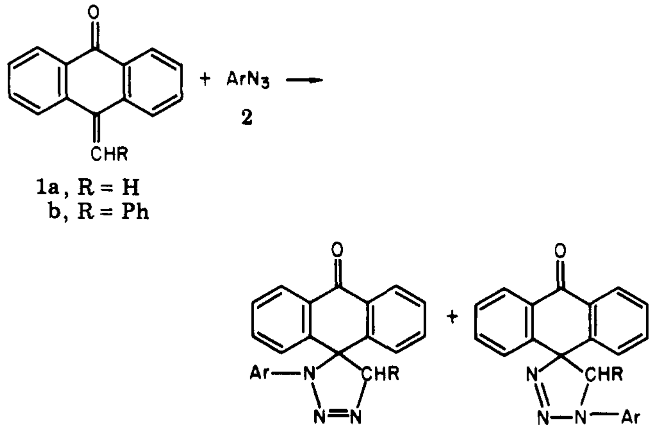
Received July 17, 1979

Quinone methide **1a** reacts with aryl azides **2** to give the corresponding spiroanthronetriazolines **3** along with byproducts, collected in Table I, which are formed by the thermal reaction of **3** or **1a**. Quinone methide **1b** adds to azides **2** to give spiroanthronetriazolines **5** or their subsequent products. Pyrolysis of **3** regenerates the starting quinone methide **1a** and azide **2**, and their photolysis leads to **1a**. Pyrolysis and photolysis of **5** yield aryliminoanthrone **7**, arylaminodibenzo[*a*,*d*]cycloheptenone **12**, or its isomer **19**. Attempts to convert **3** and **5** into spiroanthroneaziridines **14** and **15**, respectively, were unsuccessful. Reactions of **3** and **5** with acid catalysts give the rearrangement products dibenzo[*a*,*d*]cycloheptenediones **23** and **24**, respectively, in high yields. These reactions are discussed in mechanistic terms.

In connection with our interest in highly strained spiroanthrones[1] and in the ring-enlargement reactions of spiro compounds, we have further examined the chemistry of spiroanthrones. Although ring-enlargement reactions of spiro compounds have been studied in detail, the enlargements of spirotriazolines and spiroaziridines have been reported only for azaspiro[2.2]pentenes,[2] triazaspiro[2.4]heptenes,[2] triazaspiro[4.5]decenes,[3] and triazadispiro[2.0.5.3]dodecenes.[3] Since photolysis, pyrolysis, or acid-induced reactions of these heterocycles generally give ring-expanded compounds in good yields, the reactions of their analogues are available as a method of ring enlargement. The reactions of quinone methides and aryl azides would be expected to give spiroanthronetriazolines containing both a triazoline ring and a quinone moiety in a spiro configuration. This heterocyclic system is expected to be highly reactive because of the possibility that highly strained spiroanthroneaziridines or reactive intermediates are obtained from it by elimination of nitrogen. We have, therefore, investigated the products from reactions of *p*-quinone methides with aryl azides.

Results and Discussion

Reactions of Quinone Methides with Aryl Azides. Reaction of 10-methyleneanthrone (**1a**) with an excess of aryl azides **2a–g** and **2i** under nitrogen at 90 °C without solvent gave the corresponding spiroanthronetriazolines **3a–g** and **3i** in yields of 16–48%. No **3h** was formed in the reaction with **2h**. The byproducts 10-aryliminoanthrone (**7**), 1′,3′-arylspiro[anthrone-10,4′-imidazolidine] (**8**), and 1′-aryldispiro[anthrone-10,2′-pyrrolidine-3′,10″-anthrone] (**9**) were found in widely differing amounts, as shown in Table I. The dimer of **1a**, 2,3-dihydrospiro[benz[*de*]anthrone-3,10′-anthrone] (**10**), was the principal product from the reaction of **1a** with **2b** and a minor product in the reactions with **2a** and **2i**; it was identified by comparison with an authentic sample.[1a] Anthraquinone (**11**) was isolated in all runs in yields of 0.4–4%. TLC of the reaction mixtures before the workup procedure showed the absence of **11**. Anthraquinone was formed by autoxidation of **1**, **3**, and unidentified reactive products during chromatographic separation on silica.



1a, R = H
b, R = Ph

3, R = H
5, R = Ph

4, R = H
6, R = Ph

a, Ar = Ph; **b**, Ar = 4-MeC$_6$H$_4$; **c**, Ar = 3-MeC$_6$H$_4$; **d**, Ar = 2-MeC$_6$H$_4$; **e**, Ar = 4-MeOC$_6$H$_4$; **f**, Ar = 4-ClC$_6$H$_4$; **g**, Ar = 3-ClC$_6$H$_4$; **h**, Ar = 2-ClC$_6$H$_4$; **i**, Ar = 4-NO$_2$C$_6$H$_4$

The spiroanthronetriazolines were obtained as sharp-melting crystalline solids whose homogeneity and gross structure are supported by ^{1}H NMR spectra which show a sharp singlet methylene absorption at δ ca. 4.8. The assignments of the spiroanthronetriazolines as **3** rather than as its regioisomer **4** rest on the observation that reaction of the spirotriazolines with acid catalysts gives the enlargement product dibenzo[*a*,*d*]cycloheptenedione in high yields (see below). If these spirotriazolines have structure **4**, their enlargement reaction would have to proceed by an improbable path.[3] However, structure **4** cannot be rigorously excluded.

10-Benzylideneanthrone (**1b**) reacted with **2a**, **2b**, and **2e** to give spiroanthronetriazolines **5** in 11–35% yields. The only other product isolated was anthraquinone (**11**, 1–4%), which could not be detected prior to chromatography and was formed during workup. However, reaction of **1b** with **2f–i** gave no triazolines but rather the corresponding compounds **7** and **12** plus **11**. The rate of thermal decomposition of the spirotriazolines from **1b** and **2f–i** exceeds their rate of formation, thus precluding isolation. The spirotriazolines formed from **1b** and **2a**, **2b**, and **2e** are assigned the structure **5** on the same basis as for structures **3**; the alternative structure **6** cannot be excluded.

The aryliminoanthrones **7** were identified by comparison with authentic samples prepared independently by reactions of 10,10-dibromoanthrone with substituted anilines. The structures shown for **8**, **9**, and **12** are consistent with their analytical and spectral data.

Two pathways are conceivable for the formation of **7**. One is thermal fragmentation of **3** or **5** into diazo compound and **7**. Examples of such a fragmentation are known

---

[1] (a) K. Hirakawa and S. Nakazawa, *J. Org. Chem.*, **43**, 1804 (1978); (b) S. Nakazawa, K. Hirakawa, S. Fujimori, and K. Iwasaki, *J. Chem. Soc., Perkin Trans. 1*, 2052 (1979).

[2] (a) D. H. Aue, R. B. Lorens, and D. S. Helwig, *Tetrahedron Lett.*, 4705 (1973); (b) J. K. Crandall and W. W. Conover, *J. Chem. Soc., Chem. Commun.*, 33 (1973); *J. Org. Chem.*, **39**, 63 (1974).

[3] J. E. McMurry and A. P. Coppolino, *J. Org. Chem.*, **38**, 2821 (1973).

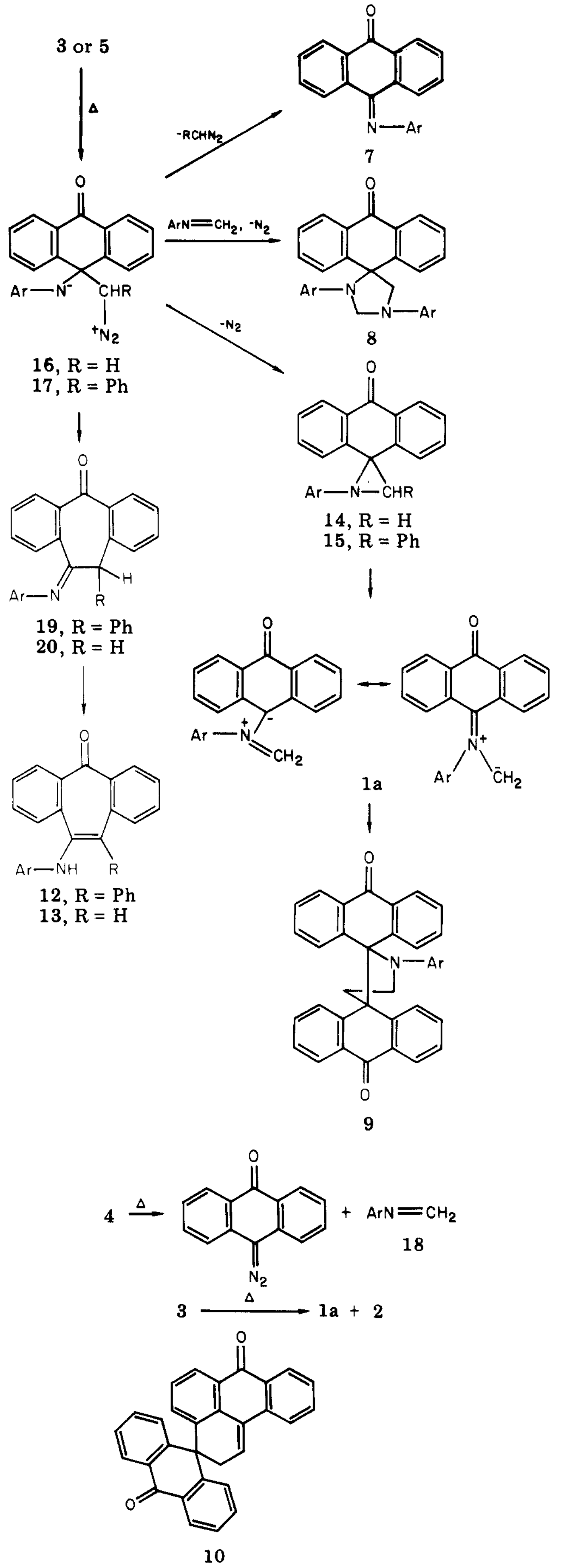
0022-3263/80/1945-1668$01.00/0

Table I. Reactions of Quinone Methides 1 with Aryl Azides 2

reaction conditions			relative yield, %, of product[a]					total yield, %[b]
reactant		time,						
methide	azide	h	3	7	8	9	10	
1a	2a	3^{c}	53	28	11	0	8	38
1a	2b	25^{c}	43	0	10	0	47	42
1a	2c	6^{c}	39	0	22	39	0	70
1a	2d	11^{c}	32	0	0	68	0	50
1a	2e	15^{c}	100	0	0	0	0	34
1a	2f	7^{c}	79	17	4	0	0	61
1a	2g	4^{c}	79	13	8	0	0	42
1a	2h	4^{c}	0	11	0	89	0	37
1a	2i	2^{c}	77	0	0	0	23	31
			5	7	12			
1b	2a	30^{d}	100	0	0			11
1b	2b	35^{d}	100	0	0			16
1b	2e	20^{d}	98	2	0			36
1b	2f	30^{d}	0	100	0			18
1b	2g	30^{d}	0	14	86			23
1b	2h	30^{d}	0	45	55			31
1b	2i	50^{d}	0	42	58			44

[a] The products except slightly soluble 9 were isolated by chromatography. Anthraquinone 11, which could not be detected prior to chromatography, was found in all runs. Further eluate afforded a complex mixture of colored products of which isolation could not be achieved. [b] Yields of the isolated products based on 1 consumed. [c] Approximate time required for disappearance of 1a. [d] Percent recovery of 1b was 45-55%.

Scheme I



in the literature.[4] The other possibility is fragmentation of the spiroanthroneaziridines 14 or 15, formed by pyrolysis of the spiroanthronetriazolines, into 7 and carbene. However, the thermal fragmentation of aziridines into imines and carbenes has not been observed previously.[5] It seems reasonable that 7 was formed by the former pathway involving the formation of 3 (5), followed by its thermal fragmentation via diazonium zwitterionic intermediate 16 (17). In practice, only pyrolysis of 5e gave 7e (see below). Although pyrolysis of other spirotriazolines gave no aryliminoanthrones 7, it is conceivable that the thermal cycloreversion of 3 to 1a and 2 and rearrangement of 5 (except 5e) to dibenzo[*a*,*d*]cycloheptenones 19 (see below) are much more favorable than the conversion of 3 (5) to 7 and diazo compound. For the formation of 7, the pathway involving addition of nitrene, which arises from 2, with 10-diazoanthrone formed by pyrolysis of the regioisomers 4 or 6 was also considered, but 7 was not obtained from the reaction of 10-diazoanthrone with 2. From previous work with related triazolines[4,6] and aziridines,[7] the formation of 8 can be accounted for by the formation of diazonium zwitterionic species 16 followed by addition of 16 to aryliminomethylene 18 formed by the fragmentation of 4; it is probable that addition of 14, formed from 16, to 1a gives 9 (see Scheme I). However, there is no concrete evidence at present relative to the possibility of

---

[4] P. Scheiner, "Selective Organic Transformations", Vol. 1, B. S. Thyagarajan, Ed., Wiley-Interscience, New York, 1971, p 327, and references cited therein.

[5] G. W. Griffin and N. R. Bertoniere, "Carbenes", Vol. 1, M. Jones, Jr., and R. A. Moss, Ed., Wiley-Interscience, New York, 1971, p 332, and references cited therein.

[6] G. Bianchi, C. De Micheli, and R. Gandolfi, "The Chemistry of Double Bonded Functional Groups", S. Patai, Ed., Wiley-Interscience, New York, 1977, Chapter 6, and references cited therein.

[7] (a) J. W. Lown and K. Matsumoto, *J. Synth. Org. Chem. Jpn.*, 29, 760 (1971); (b) H. C. van der Plas, "Ring Transformations of Heterocycles", Vol. 1, Academic Press, New York, 1973, pp 51 and 79, and references cited therein.

Scheme II

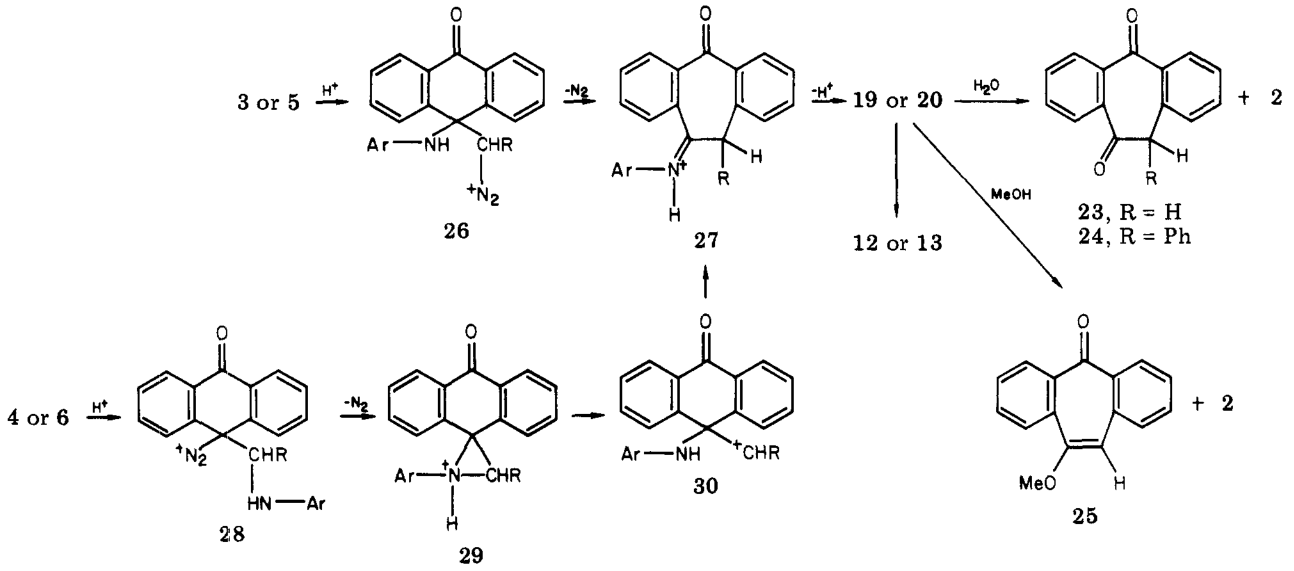


Table II. Melting Points of the Products from the Reactions of Quinone Methides 1 with Aryl Azides 2

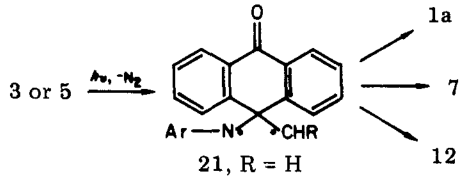
compd	mp, °C	compd	mp, °C
3a	198-199 dec	8a	271-272
3b	230-231 dec	8b	235
3c	182-183 dec	8c	210-211
3d	164-165 dec	8f	261
3e	207-208 dec	8g	230-231
3f	180-182 dec	9c	295
3g	197-198 dec	9d	233-237
3i	225-226 dec	9h	266-267
5a	191-192 dec	10	297-298[b]
5b	172-174 dec		
5e	181-182 dec	12g	229-231
7a	116-118[a]	12h	216-218
7f	191-192	12i	118-121
7g	158-159		
7h	171-173		
7i	210-211		

[a] Lit.[16] mp 115-118 °C. [b] Lit.[1a] mp 298-300 °C.

these mechanisms, since 4 has not been isolated in the reaction of **1a** with **2** and the thermal reaction of **3** with **1a** did not give **9**. Thermal cycloreversion of **3** occurs predominantly during pyrolysis. The products **12** probably arise from the thermal rearrangement of **17** formed from **5**.[3]

Pyrolysis of Spiroanthronetriazolines. Although heat treatment of triazolines generally gives mixtures of imines and aziridines,[4] heating **3a-g** in refluxing xylene under nitrogen gave **1a** (10-25%) and a trace of **2**. The thermal conversion of **3** to **1a** and **2** also occurred very slowly in refluxing benzene, indicating that the 1,3-cycloaddition of **1a** and **2** is reversible. The reversion of triazolines to olefins and azides has been reported in two other cases: 4-cyano-5-aminotriazolines[8] and 5-amino-1-tosyltriazolines.[9] Pyrolysis of **3i** gave, in addition to **1a** (5%) and **2i** (trace), the rearrangement product 10-(4-nitroanilino)-5*H*-dibenzo[*a*,*d*]cyclohepten-5-one (**13i**, 11%); this structure is consistent with analytical and spectral data. Pyrolysis of **5a** and **5b** in refluxing xylene yielded 11-(arylimino)-10,11-dihydro-10-phenyl-5*H*-dibenzo[*a*,*d*]cyclohepten-5-ones (**19a**, 8%, and **19b**, 17%). The infrared spectra of **19** support the presence of the C=N group. Similar pyrolysis of **5e** afforded only **7e** (32%). As mentioned above, the spiroanthronetriazolines in this study undergo three types of thermal reactions: cycloreversion to azides and quinone methide, fragmentation to anils and perhaps diazo compounds, and elimination of nitrogen followed by rearrangement to 5*H*-dibenzo[*a*,*d*]cyclohepten-5-ones. The similarities of thermal behavior of **3** and **5** are remarkable.

Photolysis of Spiroanthronetriazolines. Photolysis of triazolines generally gives aziridines in high yields.[4] However, irradiation of **3** in benzene under nitrogen gave complex mixtures that contained **1a** (shown by TLC) from which **1a** and anthraquinone could be isolated. The path to **1a** may be photochemical deamination of the biradical **21**.[10] Similar photolysis of **5a** and **5e** gave **12a** (6%) and **7e** (69%), respectively. The photolytic formation of **7e** and **12a**, respectively, is accounted for by the photofragmentation and rearrangement of the biradical **22**[4] arising from **5**.



21, R = H
22, R = Ph

Ring-Enlargement Reactions of Spiroanthronetriazolines. Treatment of **3** and **5** with hydrochloric acid in acetone resulted in rapid evolution of nitrogen and formation of 10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene-5,10-dione (**23**, 80-95%) and the 11-phenyl analogue (**24**, 90-95%), respectively, along with arylamines. Likewise, treatment of **3** with hydrogen chloride in methanol gave 10-methoxy-5*H*-dibenzo[*a*,*d*]cyclohepten-5-one (**25**) in ca. 85% yield. These acid-induced reactions of spiroanthronetriazolines offer a synthetic route to dibenzo[*a*,*d*]tropolones. A plausible mechanism for the ring enlargement is shown in Scheme II. The reactions might actually be catalyzed by acid in a process involving the following steps: protonation of the basic triazoline nitrogen (the formation of diazonium ion **26**),[4] rearrangement of **26** to **27** with loss of nitrogen,[3] deprotonation, and hydrolysis or alcoholysis of **19** and **20**.[11] The one uncertainty in this

---

[8] F. Texier and J. Bourgois, *J. Heterocycl. Chem.*, 12, 505 (1975).

[9] D. Pocar, M. C. Ripamonti, R. Stradi, and P. Trimarco, *J. Heterocycl. Chem.*, 14, 174 (1977).

[10] A. Padwa and L. Hamilton, *J. Am. Chem. Soc.*, 87, 1821 (1965).

mechanism involves the timing of nitrogen loss and bond migration, but we feel that this is probably concerted for the following reason. Mechanistically, the ring-enlargement process is analogous to the triazaspirocycloalkane–iminoalkane rearrangement;[3] in this reaction, loss of nitrogen is concerted with rearrangement. Treatment of **3i** and **5a** with hydrogen chloride in dry benzene gave **13i** (55%) and **12a** (63%), respectively. The presumptive intermediates **20i** and **19a** were not found. Similar treatment of other spiroanthronetriazolines afforded complex mixtures.

Finally, if the spiroanthronetriazolines formed from **1** and **2** have structure **4** (**6**) rather than **3** (**5**), their ring-enlargement reactions have to proceed by alternate path [**4** (**6**) → **28** → **29** → **30** → **19** (**20**)]. Although the path of **29** to **19** (**20**) is probable,[2] the one of **4** (**6**) to **29** is not. Therefore, the structures of the spiroanthronetriazolines are **3** and **5**.

Experimental Section

General Procedures. Melting points were determined with a Yanagimoto hot-stage apparatus and are uncorrected. Microanalyses were performed on a Perkin-Elmer Model 240 elemental analyzer. Infrared spectra were recorded on a JASCO IRA-1 spectrophotometer (KBr disk), ^{1}H NMR spectra on JEOL JNM-3H-60 (60 MHz) and JNM-FX100 (100 MHz) spectrometers for solutions in deuteriochloroform (tetramethylsilane as standard), and mass spectra on a JEOL JMS-01SG-2 spectrometer (at 75 eV). For analytical TLC, Wakogel B-10 (Wako Pure Chemical Industries) was used. Components were detected either by staining with iodine vapor or by spraying with 50% sulfuric acid in methanol followed by heating. Column chromatography was carried out with Wakogel C-200. Irradiations were carried out with an Ushio UM102 100-W high-pressure mercury lamp through a Pyrex filter. All compounds used as starting materials in the synthetic procedures were obtained either from commercial sources or by known procedures. Purity of products was checked by TLC and spectral analyses. The yields reported are based on amounts of isolated products of adequate purity and on amounts of starting materials consumed.

The following compounds were prepared according to previously described procedures: 10-methyleneanthrone (**1a**),[12] 10-benzylideneanthrone (**1b**),[13] and aryl azides **2a–i**.[14]

Reaction of 1a with 2. A mixture of **1a** (1.03 g, 5 mmol) and **2a–i** (15 mmol) was stirred under nitrogen at 90 ± 2 °C until TLC showed disappearance of the starting quinone methide. After the reaction was complete, the excess aryl azide was removed under reduced pressure, except that excess **2i** was removed by chromatography, and then the residue was chromatographed on silica (benzene or chloroform as eluant). Results and melting points of the products are summarized in Tables I and II, respectively. Spectral and analytical data of the representative products are given below. See the supplementary material for characterization data of the other products.[15]

1′-Phenylspiro[anthrone-10,5′-(1′,2′,3′-triazacyclopent-2′-ene)] (3a): light yellow microcrystals from benzene–hexane; R_f 0.30 (benzene); IR 1660 (C=O) cm^{-1}; ^{1}H NMR δ 4.83 (s, 2 H, CH_2) and 6.73–8.50 (m, 13 H, aromatic H); mass spectrum, *m/e* (relative intensity) 297 (M$^+$ – 28, 100), 269 (91), 206 (13), 194 (65), 178 (14), and 165 (15). Anal. Calcd for $C_{21}H_{15}N_3O$: C, 77.52; H, 4.65; N, 12.92. Found: C, 77.58; H, 4.72; N, 12.95.

10-(4-Chlorophenyl)iminoanthrone (7f): red needles from benzene–hexane; R_f 0.70 (benzene); IR 1668 (C=O), 1625 (C=N) cm^{-1}; ^{1}H NMR δ 6.55–8.45 (m, 12 H, aromatic H); mass spectrum, *m/e* (relative intensity) 319/317 (M$^+$, 36/100), 282 (24), 163 (10), 152 (16), 127 (17), and 126 (30). Anal. Calcd for $C_{20}H_{12}ClNO$: C, 75.59; H, 3.80; Cl, 11.15; N, 4.41. Found: C, 75.75; H, 3.66; Cl, 11.01; N, 4.36.

The iminoanthrone **7f** was prepared independently by the method of Meek and Koh[16] from 10,10-dibromoanthrone and 4-chloroaniline in 27% yield.

1′,3′-Diphenylspiro[anthrone-10,4′-imidazolidine] (8a): light yellow microcrystals from chloroform; R_f 0.70 (benzene); IR 1650 (C=O) cm^{-1}; ^{1}H NMR δ 3.73 (s, 2 H, CH_2), 5.45 (s, 2 H, NCH_2N), and 6.21–8.42 (m, 18 H, aromatic H); mass spectrum, *m/e* (relative intensity) 402 (M$^+$, 25), 297 (100), 278 (27), 195 (27), 178 (12), and 165 (17). Anal. Calcd for $C_{28}H_{22}N_2O$: C, 83.55; H, 5.51; N, 6.96. Found: C, 83.44; H, 5.67; N, 7.01.

1′-(3-Tolyl)dispiro[anthrone-10,2′-pyrrolidine-3′,10″-anthrone] (9c): colorless microcrystals; IR 1660 (C=O) cm^{-1}; ^{1}H NMR δ 2.10 (s, 3 H, CH_3), 3.34 (t, 2 H, J = 7.5 Hz, CH_2), 4.82 (t, 2 H, J = 7.5 Hz, NCH_2), and 5.75–8.05 (m, 20 H, aromatic H); mass spectrum, *m/e* (relative intensity) 517 (M$^+$, 44), 311 (90), 310 (100), 297 (19), 296 (12), 282 (16), 206 (10), 194 (14), 178 (10), and 165 (13). Anal. Calcd for $C_{37}H_{27}NO_2$: C, 85.85; H, 5.26; N, 2.71. Found: C, 85.58; H, 5.06; N, 2.83.

Reaction of 1b with 2. A mixture of **1b** (1.42 g, 5 mmol) and **2** (15 mmol) was stirred under nitrogen at 90 ± 2 °C until approximately one-half of the amount of **1b** was consumed. The excess aryl azide was then removed under reduced pressure, and the residue was chromatographed on silica (benzene as eluant). Results and melting points of the reaction products are summarized in Tables I and II, respectively. Data for representative products are given below. See the supplementary material for characterization data of the other products.[15]

1′,4′-Diphenylspiro[anthrone-10,5′-(1′,2′,3′-triazacyclopent-2′-ene)] (5a): colorless microcrystals from benzene–hexane; R_f 0.33 (benzene); IR 1668 (C=O) cm^{-1}; ^{1}H NMR δ 5.78 (s, 1 H, CH) and 6.90–8.56 (m, 18 H, aromatic H); mass spectrum, *m/e* (relative intensity) 373 (M$^+$ – 28, 66), 344 (50), 282 (100), 281 (73), 267 (40), 266 (28), 254 (42), 252 (61), and 165 (45). Anal. Calcd for $C_{27}H_{19}N_3O$: C, 80.77; H, 4.77; N, 10.47. Found: C, 80.52; H, 4.95; N, 10.69.

10-(3-Chloroanilino)-11-phenyl-5*H*-dibenzo[*a*,*d*]cyclohepten-5-one (12g): yellow plates from benzene; R_f 0.75 (benzene); IR 3410 (NH), 1660 (C=O) cm^{-1}; ^{1}H NMR δ 5.90–8.05 (m, 18 H, aromatic H and NH); mass spectrum, *m/e* (relative intensity) 409/407 (M$^+$, 48/100), 379 (33), 281 (13), 270 (14), 267 (10), 252 (16), 165 (10), and 164 (9). Anal. Calcd for $C_{27}H_{18}ClNO$: C, 79.50; H, 4.45; Cl, 8.69; N, 3.43. Found: C, 79.45; H, 4.50; Cl, 8.45; N, 3.41.

Pyrolysis of 3 and 5. A. Spiroanthronetriazolines 3. A solution of **3a–g** (1 mmol) in xylene (30 mL) was refluxed under nitrogen for 2 h. The solvent was distilled off under reduced pressure, and the residue was chromatographed on silica (benzene as eluant) to give **1a** (10–25%) and **2** (trace), identical with authentic specimens. The only other product isolated was anthraquinone **11**, which could not be detected prior to chromatography and was formed during the workup procedure. Further eluate gave a complex mixture of products which could not be analyzed. The conversion of **3** was ca. 60–70%. A similar treatment of **3i** gave **1a** (5%), **2i** (trace), and 10-(4-nitroanilino)-5*H*-dibenzo[*a*,*d*]cyclohepten-5-one (**13i**, 11%): orange plates from chloroform–hexane; mp 245 °C; R_f 0.20 (benzene); IR 3380 (NH), 1650 (C=O) cm^{-1}; ^{1}H NMR δ 6.45–8.50 (m, 14 H, aromatic H, CH, and NH); mass spectrum, *m/e* (relative intensity) 342 (M$^+$, 100), 314 (10), 295 (25), 267 (22), 194 (10), and 165 (10). Anal. Calcd for $C_{21}H_{14}N_2O_3$: C, 73.67; H, 4.12; N, 8.18. Found: C, 73.52; H, 4.14; N, 8.05.

B. Spiroanthronetriazolines 5. A similar pyrolysis of **5a** and chromatography of the product gave 10,11-dihydro-10-phenyl-11-(phenylimino)-5*H*-dibenzo[*a*,*d*]cyclohepten-5-one (**19a**, 8%). Further elution afforded a complex mixture which could not be isolated and led to **11** in autoxidation during workup procedure. **19a**: light yellow microcrystals from benzene–hexane; mp 151 °C; R_f 0.32 (benzene); IR 1665 (C=O), 1653 (C=N) cm^{-1}; ^{1}H NMR δ 5.46 (s, 1 H, CH) and 6.65–8.40 (m, 18 H, aromatic

---

[11] A. Bruylants and Mrs. E. Feytmants-de Medicis, "The Chemistry of Carbon–Nitrogen Double Bond", S. Patai, Ed., Wiley-Interscience, New York, 1970, Chapter 10, and references cited therein.

[12] W. H. Starnes, Jr., *J. Org. Chem.*, **35**, 1974 (1970).

[13] J. W. Cook, *J. Chem. Soc.*, 2160 (1926).

[14] (a) R. O. Lindsay, "Organic Syntheses", Collect. Vol. III, Wiley, New York, 1955, p 710; (b) I. Ugi, H. Perlinger, and L. Behringer, *Chem. Ber.*, 91, 2330 (1958).

[15] See paragraph at end of Experimental Section regarding supplementary material.

[16] J. S. Meek and L. Koh, *J. Org. Chem.*, **35**, 153 (1970).

H); mass spectrum, *m/e* (relative intensity) 373 (M$^+$, 93), 344 (39), 281 (100), 270 (16), 267 (28), 252 (20), and 165 (11). Anal. Calcd for $C_{27}H_{19}NO$: C, 86.84; H, 5.13; N, 3.75. Found: C, 86.63; H, 5.18; N, 3.70.

A similar pyrolysis of **5b** and chromatography of the product gave 10,11-dihydro-10-phenyl-11-(4-tolylimino)-5*H*-dibenzo[*a*,*d*]-cyclohepten-5-one (**19b**, 17%), mp 181–182 °C. Further eluate gave a complex mixture which led to **11** during workup. See the supplementary material for the characterization of **19b**.[15]

A similar pyrolysis of **5e** gave 10-(4-methoxyphenylimino)-anthrone (**7e**, 32%): red needles from benzene–hexane; mp 143–145 °C; R_f 0.32 (benzene); IR 1662 (C=O) cm^{-1}; ^{1}H NMR δ 3.88 (s, 3 H, OCH$_3$) and 6.65–8.70 (m, 12 H, aromatic H); mass spectrum, *m/e* (relative intensity) 313 (M$^+$, 51), 298 (43), 279 (20), 208 (100), 180 (93), 152 (80), and 126 (14). Anal. Calcd for $C_{21}H_{15}NO_2$: C, 80.49; H, 4.83; N, 4.47. Found: C, 80.42; H, 4.69; N, 4.33.

The iminoanthrone **7e** was prepared independently by the procedure described for **7f** in a 48% yield.

C. Pyrolysis of **3** and **5** in refluxing benzene gave the same products as in xylene, but the reaction was slow. Thermal reaction of **3** with **1a** in refluxing benzene or xylene did not yield **9**.

Photolysis of 3 and 5. A solution of **3** (**5**) (1 mmol) in benzene (30 mL) was irradiated at room temperature under nitrogen with a 100-W high-pressure mercury lamp through a Pyrex filter until gas evolution ceased (~3 h). After irradiation, the resulting solution was concentrated and the residue was chromatographed on silica (benzene as eluant). TLC of the crude photolysate of **3** (**5**) showed spots of compounds which could not be isolated owing to their extreme reactivity in addition to the isolated products shown below. Anthraquinone, which could not be detected prior to workup, was formed during chromatographic separation on silica. The results of analyses of the isolated compounds are as follows. Photolysis of **3a**, **3f–g**, and **3i** gave **1a** (trace) and **11** (20–30%). **3b** and **3e**: **1a** (15–20%) and **11** (3–5%). **5a**: **11** (40%), **19a** (trace), and 10-anilino-11-phenyl-5*H*-dibenzo[*a*,*d*]cyclohepten-5-one (**12a**, 6%). **5b**: **11** (29%). **5e**: **7e** (69%). **12a**: yellow microcrystals from benzene; mp 199–200 °C; R_f 0.35 (benzene); IR 3400 (NH), 1660 (C=O) cm^{-1}; ^{1}H NMR δ 5.95–8.05 (m, 19 H, aromatic H and NH); mass spectrum, *m/e* (relative intensity) 373 (M$^+$, 100), 354 (24), 270 (12), 267 (12), and 252 (12). Anal. Calcd for $C_{27}H_{19}NO$: C, 86.84; H, 5.13; N, 3.75. Found: C, 86.71; H, 5.02; N, 3.78.

Reactions of 3 and 5 in Acetone with Hydrochloric Acid. **A. Spiroanthronetriazolines 3.** A suspension of **3** (2 mmol) in acetone (30 mL) containing hydrochloric acid (0.2 mL) was stirred at room temperature until gas evolution ceased (~30 min). The resulting solution was poured into water (100 mL), and the precipitate was collected and washed with water. Recrystallization from ethanol gave 10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene-5,10-dione (**23**) as colorless needles in 80–95% yield, mp 118 °C (lit.[17] mp 118 °C), identical with an authentic specimen. The filtrate was neutralized with sodium hydrogen carbonate and extracted with ether. The extract was dried and evaporated to give aryl amines (ca. 50–60%).

B. Spiroanthronetriazolines 5. The same reaction of **5** gave arylamines and 10,11-dihydro-11-phenyl-5*H*-dibenzo[*a*,*d*]cycloheptene-5,10-dione (**24**, 90–95%) as colorless needles, mp 135 °C (lit.[13,18] mp 134–135 °C), identical with an authentic specimen.

Reaction of 3 in Methanol with Hydrogen Chloride. A suspension of **3** (1 mmol) in methanol (15 mL) containing hydrogen chloride (0.1 g) was stirred at room temperature until gas evolution was complete (~3 h). The mixture was poured into water and the precipitate was collected. Recrystallization from methanol gave 10-methoxy-5*H*-dibenzo[*a*,*d*]cyclohepten-5-one (**25**) as colorless needles in ca. 85% yield, mp 100–101 °C (lit.[17a] mp 96–97 °C).

Reactions of 3 and 5 in Benzene with Hydrogen Chloride. A solution of **3** (**5**) (1 mmol) in benzene (20 mL) was stirred at room temperature under nitrogen while 3 mL of a saturated solution of hydrogen chloride in benzene was added. The reaction was followed by TLC, which showed disappearance of starting material. The solvent was distilled off under reduced pressure, and the residue was recrystallized from benzene–hexane. The reaction of **3i** and **6a** gave **13i** (55%) and **12a** (63%), respectively. However, isolation or identification of products from other spiroanthronetriazolines could not be achieved owing to their complexity.

Registry No. **1a**, 4159-04-0; **1b**, 14343-92-1; **2a**, 622-37-7; **2b**, 2101-86-2; **2c**, 4113-72-8; **2d**, 31656-92-5; **2e**, 2101-87-3; **2f**, 3296-05-7; **2g**, 3296-06-8; **2h**, 3296-07-9; **2i**, 1516-60-5; **3a**, 73078-95-2; **3b**, 73078-96-3; **3c**, 73078-97-4; **3d**, 73078-98-5; **3e**, 73078-99-6; **3f**, 73079-00-2; **3g**, 73079-01-3; **3i**, 73079-02-4; **5a**, 73079-03-5; **5b**, 73079-04-6; **5e**, 73079-05-7; **7a**, 10019-06-4; **7e**, 73079-06-8; **7f**, 73079-07-9; **7g**, 73079-08-0; **7h**, 73079-09-1; **7i**, 73079-10-4; **8a**, 73079-11-5; **8b**, 73079-12-6; **8c**, 73079-13-7; **8f**, 73079-14-8; **8g**, 73078-83-8; **9c**, 73078-84-9; **9d**, 73078-85-0; **9h**, 73078-86-1; **10**, 65252-95-1; **11**, 84-65-1; **12a**, 73078-87-2; **12g**, 73078-88-3; **12h**, 73078-89-4; **12i**, 73078-90-7; **13i**, 73078-91-8; **19a**, 73078-92-9; **19b**, 73078-93-0; **23**, 16174-24-6; **24**, 73078-94-1; **25**, 40976-22-5; 10,10-dibromoanthrone, 21555-13-5; 4-chloroaniline, 106-47-8.

Supplementary Material Available: Characterization data of the derivatives of **3**, **5**, **7**, **8**, **9**, **12**, and **19** (6 pages). Ordering information is given on any current masthead page.

---

[17] (a) J. Rigaudy and L. Nédélec, *Bull. Soc. Chim. Fr.*, 659 (1959); (b) W. Tochtermann, K. Oppenlaender, and U. Walter, *Chem. Ber.*, **97**, 1318 (1964).

[18] J. W. Cook, *J. Chem. Soc.*, 58 (1928).

Synthesis of Spiro[arylenedioxy] Derivatives from Hexachlorocyclotriphosphazene and Dihydroxybinaphthyls

Krystyna Brandt and Zbigniew Jedliński*

Institute of Polymer Chemistry, Polish Academy of Sciences, 41-800 Zabrze, Poland

Received October 2, 1979

Monospiro-substituted products prevail when sterically hindered aromatic ortho diols are employed in the reaction with hexachlorocyclotriphosphazene (1). Two isomeric monospiro[binaphthylenedioxycyclophosphazenes], 4 and 5, were isolated in high yields starting from equimolar amounts of 1 and 1,1′-dihydroxy-2,2′-binaphthyl (2) and 2,2′-dihydroxy-1,1′-binaphthyl (3), respectively. With the latter reagent a small amount of a corresponding bisspiro derivative 6 was also isolated. Differences in the spectral properties of the isomers 4 and 5 can be attributed to the steric and electronic effects. The appearance of a strong K-band UV absorption for (1,1′-dioxy-2,2′-binaphthyl)cyclophosphazene 4 indicates that the naphthalene rings in this compound are in extensive conjugation. The lack of remarkable resonance interaction can be inferred from the UV spectrum of the spirocyclophosphazene derivative (5) of 2,2′-dihydroxy-1,1′-binaphthyl.

It has been previously demonstrated that the reaction of hexachlorocyclotriphosphazene (1) with aliphatic glycols or ortho diphenols in the presence of a base leads to the formation of spirocyclic products. A number of trisspi-

0022-3263/80/1945-1672$01.00/0