3. o-Cyanophenol from the Sodium Salt of *syn*-o-Nitrobenzaldoxime. A reaction mixture similar to 1c employing the sodium salt of *syn*-o-nitrobenzaldoxime[8] (1.13 g, 6 mmol), o-nitrobenzonitrile (20 mg, 0.14 mmol), freshly ground potassium hydroxide (338 mg, 6 mmol), and Me_2SO (20 ml) stirred at room temperature for 8 hr and worked up as in 1c gave 500 mg (66%) of o-cyanophenol, mp 94–95° (lit.[10] mp 98°).

4. Piperonylonitrile. A. From Isolated Piperonaldoxime. The oxime employed, prepared quantitatively in aqueous ethanol, melted at 107–110° (lit.[11] syn isomer 112°, anti isomer 146°); NMR [$(CD_3)_2SO$] δ 8.07 (s, 1, HC=N), 11.01 (s, 1, NOH). A mixture of the oxime (1 g, 6 mmol), p-nitrobenzonitrile (900 mg, 6.1 mmol), freshly ground potassium hydroxide (676 mg, 12 mmol), and 20 ml of Me_2SO was stirred at room temperature for 3–4 hr. The mixture was poured into ice water (150 ml) and the solution was acidified and extracted with ether. The ethereal extract was successively washed with cold 5% aqueous sodium hydroxide and water. After drying ($MgSO_4$) and removal of the solvent in vacuo, 807 mg (92%) of the nitrile was obtained. Recrystallization from ethanol–water gave analytically pure material (645 mg, 73%), mp 87–89° (lit.[4] mp 91–93°).

Anal. Calcd for $C_8H_5NO_2$: C, 65.31; H, 3.43; N, 9.52. Found: C, 65.16; H, 3.46; N, 9.66.

B. From Piperonaldoxime Prepared in Situ. A mixture of hydroxylamine hydrochloride (462 mg, 6.5 mmol), sodium methoxide (350 mg, 6.5 mmol), and 20 ml of Me_2SO was stirred at room temperature for 15 min. Piperonal (1 g, 6.5 mmol) was added and the mixture was heated at 70° for 2 hr. Heating was then discontinued, p-nitrobenzonitrile (980 mg, 6.5 mmol) and freshly ground potassium hydroxide (758 mg, 13 mmol) were added, and the mixture was stirred at room temperature for 3–4 hr. Work-up as in part A and recrystallization from ethanol–water afforded 742 mg (78%) of piperonylonitrile, mp 87–89[10] (lit.[4] mp 92–93°).

Acknowledgment. The authors are grateful to the National Science Foundation (GP 34198X) for the support of this work.

Registry No.—I sodium salt, 56086-86-3; V, 619-72-7; p-cyanophenol, 767-00-0; potassium hydroxide, 1310-58-3; sodium carbonate, 497-19-8; p,p'-dicyanodiphenyl ether, 6508-04-9; o-cyanophenol, 611-20-1; *syn*-o-nitrobenzaldoxime sodium salt, 56086-87-4; o-nitrobenzonitrile, 612-24-8; piperonylonitrile, 4421-09-4; *syn*-piperonaldoxime, 20747-41-5; *anti*-piperonaldoxime, 20747-42-6.

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Photoreaction of Benzofurazan and Dimethyl Acetylenedicarboxylate. Synthesis of Isomeric Isoxazoles. Carbon-13 Nuclear Magnetic Resonance Spectra of Isoxazoles and Oxazoles[1]

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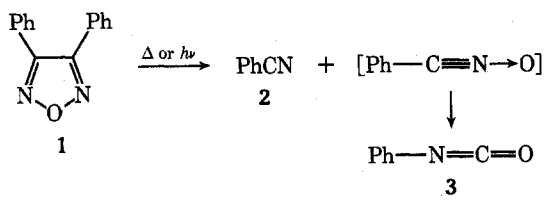
Received April 26, 1974

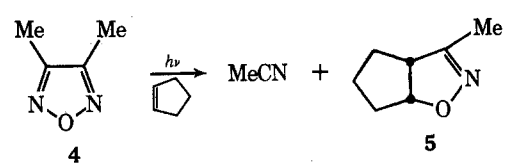
When benzofurazan is irradiated by ultraviolet light (3000 Å), a reactive nitrile oxide intermediate is produced. In order to trap this intermediate, benzofurazan has been irradiated in dimethyl acetylenedicarboxylate (DAD). The nitrile oxide reacts with DAD to produce various geometrical isomers of dimethyl 3-(4-cyanobuta-1,3-dienyl)isoxazole-4,5-dicarboxylate (8). The isoxazoles have been characterized by their ^{13}C NMR spectra. All the isomers have been degraded to the same dimethyl 3-carboxaldehydeisoxazole-4,5-dicarboxylate (9) by ozonolysis. Cis,cis, trans,cis, and trans,trans isomers of 8 have been identified.

The thermal splitting of diphenylfurazan (1) to give benzonitrile (2) and phenyl isocyanate (3) has been known since 1888.[3,4] Ultraviolet irradiation of a 5% ethereal solution of 1 produces the same two compounds.[5]



1

In order to prove the presence of the highly reactive nitrile oxide intermediate, dimethylfurazan (4) was irradiated in the presence of excess cyclopentene to yield 3-methyl-4,5-trimethylene-2-isoxazoline (5).[5] Irradiation of 1 in cyclopentene produced only 2 and 3 in yields similar to those obtained in the absence of cyclopentene. It has been suggested that this failure to trap the benzonitrile oxide by 1,3-dipolar addition is due to a rearrangement of the intermediate to the isocyanate which is faster than the ground-state 1,3-dipolar addition to cyclopentene.[5] Photolysis of 1 in benzene has yielded diphenylfuroxan, 3,5-diphenyl-1,2,4-oxadiazole, and 3.[6]



4 5

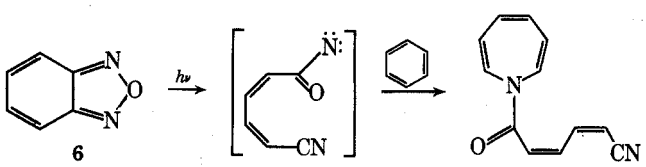
It has been shown recently that the irradiation of benzo-, naphthalo-, and phenanthrofurazan derivatives in the presence of triethyl phosphite affords 1,4-dinitrile derivatives in high yields.[7] An azepide 7 has been isolated from the reaction mixture after irradiation of benzofurazan in ben-

Table I
^{13}C Chemical Shift Data[a,d]

Assignments[b]	8a	[J(CH), Hz]	8b[c]	8c	10	11	12	13	14
CH_3O	53.1	(148.5)	53.4	53.4	53.4				
	53.8	(148.5)	53.9	53.7	53.6				
CN	114.7		114.4	113.9					114.8
CH(6)	120.9	(167.7)	125.3	124.6					
CH(7)	132.1	(163.2)	132.6	134.1					
CH(8)	145.3	(170.6)	147.6	148.6					142.8
CH(9)	103.6	(179.4)	102.5	104.0					106.2
ring C(2)							164.1	160.4	
C(3)	157.1		157.1	157.0	156.9	160.0			
C(4)	115.8		116.0	117.5	116.5	102.7	142.1	137.1	
C(5)	158.2		158.8	158.6	159.9	169.4	151.5	145.7	
C=O	160.7		161.3	161.1	161.7				
	161.7		161.8	162.1	162.3				

[a] Chemical shifts in parts per million relative to Me_4Si. [b] Suggested assignments, some may be interchanged. [c] Resonance peaks due to contamination by 8c omitted. [d] Other resonance peaks: 10 phenyl, 127.5, 128.5, 129.4 and 131.2 ppm; 11 methyl, 11.2 and 11.9 ppm; 12 methyl, 14.3 ppm; 12 benzo, 110.6, 119.8, 124.4 and 124.8 ppm; 13 phenyl, multiple peaks between 126.2 and 132.9 ppm.

zene.[8] Irradiation of 1 or 6 in methanol yields the corresponding N-substituted carbamate.[5,8]

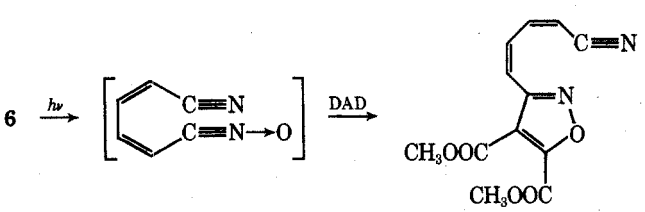


6 7

The work reported here was undertaken in order to determine the possibility of trapping the highly reactive nitrile oxide intermediate using the powerful dipolarophile dimethyl acetylenedicarboxylate. The 1,3-cycloaddition of acetylenes to nitrile oxides is well known[9] and is used here in the preparation of hitherto unknown isomeric isoxazoles.

Results

The photochemical reaction of benzofurazan (6) and DAD yields a mixture of isomeric isoxazoles 8. Chromatographic separation on a silica gel column yields three fractions of crystalline materials (8a, 8b, and 8c). The compounds 8a and 8c are pure isomers as shown by ir and NMR spectroscopy, but the intermediate product 8b could not be totally freed of contamination by 8c. TLC and column chromatography and fractional recrystallization have been employed in attempts to purify 8b but TLC of the purest fraction exhibited two distinguishable spots.

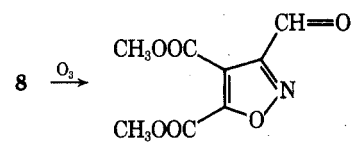


8

All the isoxazoles are white, crystalline compounds, insoluble in water but soluble in most organic solvents. Their solubility decreases in the order of their elution from the column, and their melting points increase in the same order.

The isoxazoles decolorize potassium permanganate with ease but are almost completely resistant to a solution of bromine in carbon tetrachloride. Hydrolysis in boiling 2 *N* HCl or in hot aqueous KOH affords a resinous product which could not be identified. No –C≡N stretching vibration is present in the infrared spectrum of this product.

Oxidation of the isomers with potassium permanganate,[10] osmate and periodate,[11] and permanganate and periodate[12] in all cases yields a yellow-red oil after work-up. This oil exhibits no –C≡N stretching vibration in the infrared, and its NMR spectrum includes a weak aldehydic proton resonance. The low intensity of this peak, and the presence of other peaks in the spectrum, indicated the oil to be a mixture of several compounds. Treatment with 2,4-dinitrophenylhydrazine produced a derivative with a broad melting point. Ozonolysis of the isoxazoles gives a much cleaner reaction, producing the aldehyde 9 in good yield.



9

Discussion

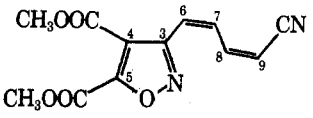
The essential structure of the isomeric photoproducts is clearly shown to be the isoxazole 8 by uv, ir, and NMR spectroscopy and mass spectrometry. The sensitivity of the compounds to permanganate oxidation, and the lack of reaction with Br_2–CCl_4 indicate the 1,4-disubstituted diene structure.[13] Although isoxazoles are known to rearrange readily under the influence of ultraviolet radiation to the corresponding oxazoles via an azirine intermediate,[14] the compounds described here are characterized as isoxazoles by ^{13}C NMR spectroscopy. The various structures of the individual isomers are deduced from their ^1H NMR spectra.

The electronic spectra of the photoproducts exhibit two bands: at ca. 205 nm due to the isoxazole ring,[15] and at ca. 273 nm due to the butadiene moiety.

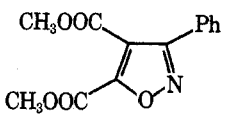
The mass spectra of the isomeric products are very similar, as expected, and confirm the molecular weight of 262. Initial fragmentations involve loss from or of the isoxazole side chains (–CN, $-OCH_3$, $-CO_2CH_3$) and in many cases are supported by metastable peaks. The molecular ion peak is absent in the spectrum of the isoxazole aldehyde. Instead, the spectrum exhibits a relatively weak M + 1 peak at *m/e* 214 (15%) due to the protonation of the isoxazole in the mass spectrometer. The ion at *m/e* 126 (100%) is assigned to a methyl 2-carboxaldehyde–azirinium-3-carboxylate ion.[16]

The resonance peaks in the ^{13}C NMR spectra of the three isomeric isoxazoles 8a, 8b, and 8c are listed in Table I

with data for related compounds. In general, an isoxazole ring is expected to exhibit two low-field peaks due to C_3 and C_5 with a *higher* field resonance due to C_4; an oxazole ring is expected to exhibit two low field peaks due to C_4 and C_5 with a *lower* resonance due to C_2. These predictions are borne out by the data in Table I.



8a



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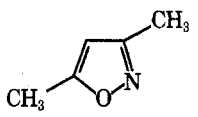

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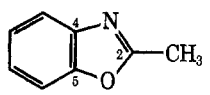
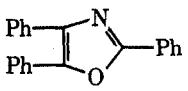


12



13

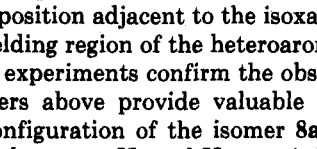
14

The ^{13}C resonances of the butadiene moiety are assigned by comparison with **14** and by examination of the $J(CH)$ coupling observed in the **8a** spectrum obtained in the absence of wide-band proton decoupling. Owing to the approximate symmetry of the 1,4-disubstituted cis,cis isomer **8a**, the coupling generates the same long-range $J(CH)$ splitting pattern for both C_6 and C_9, and for both C_7 and C_8.

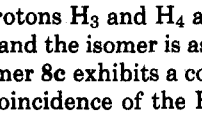
Although a cis,cis structure is expected to be the initial product obtained in the photolysis of **6**, a trans,trans structure should be the most stable configuration for the 1,4-disubstituted butadiene.[17]

Analyses of the **8a** proton spectra at 100 and 251 MHz, with limited iteration (LAOCN3), yield the best, but not unique, fit: H_1, 5.76; H_2, 7.89; H_3, 7.07; H_4, 6.92 (δ ppm) and J_{12} = 10.98; J_{23} = 11.64; J_{24} = −0.28; J_{34} = 11.60; J_{13} and $J_{14} \simeq 0$ Hz. The high-field resonance of H_1 is due to its position within the shielding cone of the anisotropic cyanide group[13] and the low-field resonance of H_2 is attributed to its position adjacent to the isoxazole nitrogen within the deshielding region of the heteroaromatic ring. Double resonance experiments confirm the observed coupling. The parameters above provide valuable information concerning the configuration of the isomer **8a**: thus, protons H_1 and H_2, and protons H_3 and H_4 are cis,[13,17,18] the conformation is s-trans, and the isomer is assigned a cis,cis structure.

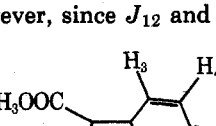
The isomer **8c** exhibits a complex second-order spectrum due to a coincidence of the H_2 and H_3 resonance frequencies. However, since J_{12} and $J_{34} \simeq 14.6$ Hz (i.e., both H_1 and H_2, and H_3 and H_4 are trans), and proton H_2 is removed from the vicinity of the isoxazole ring (indicated by the upfield shift in its resonant frequency), this isomer is assigned the trans,trans configuration.



cis,cis isomer **8a**



trans,cis isomer **8b**



trans,trans isomer **8c**

The isomer **8b** is assigned a trans,cis configuration since $J_{12} \simeq 11.5$ Hz and again proton H_2 resonates at the higher field.

Experimental Section

General. A Rayonet Srinivisan-Griffin photochemical reactor (No. RPR-100) was used for the reaction of benzofurazan and DAD. Ozonolysis was performed using a Welsbach Laboratory ozonator (T-408). Benzofurazan was prepared by reduction[19a] of benzofurazan oxide.[19b] Dimethyl acetylenedicarboxylate (DAD) was obtained from Fluka AG, Switzerland, and was rapidly distilled prior to use. Compounds **10**,[20] **11**,[21] **12**,[21] **13**,[21] and **14**[22] were prepared as previously described. Petroleum ether mentioned below was a 60–80° fraction. ^1H NMR spectra at 60 and 100 MHz were taken on Varian A-60 and HA-100 spectrometers in $CDCl_3$ solution. ^{13}C NMR spectra at 63.1 MHz and ^1H NMR spectra at 251 MHz were obtained in Professor F. A. L. Anet's laboratory at UCLA by one of us (I.Y.). Ir spectra were determined for KBr disks with a Beckman IR-20 spectrophotometer. Uv spectra were obtained in 95% ethanol solution with a Unicam SP-800 spectrometer. Mass spectra (70 eV) were obtained on an AEI MS12 spectrometer at the University of Surrey, England. Elemental analyses were performed by the University of Surrey Microanalytical unit.

Photochemical Reaction of Benzofurazan and DAD. Benzofurazan (12 g, 0.1 mol) was dissolved in DAD (14.2 g, 0.1 mol) and this solution was placed in the annular cavity between two concentric glass tubes (inner tube, Pyrex, 42 mm o.d.; outer tube, quartz, 46 mm i.d.). The solution was irradiated using lamps with principal emission at 3000 Å, when the color changed slowly from yellow to red. After 30 hr, some bright yellow crystals appeared between the tubes. By removing and reimmersing the inner tube these crystals were moved to the bottom, thus exposing more solution to the light. After 120 hr, the photoreaction was stopped and the reaction mixture was transferred to a 500-ml flask, washing the tubes with 100 ml of ethyl acetate. The mixture was dissolved in 200 ml of ethyl acetate by warming on a steam bath. Silica gel (30 g) was added and the solvent was evaporated. Dry silica gel and the residue were placed over a column of silica gel (400 g) and elution first made with petroleum ether. The first yellowish oil (2.5 g) obtained solidified after a few hours and was identified as benzofurazan. The second oily compound (3.3 g) with the characteristic smell of DAD was identified as unreacted ester (ir). Elution was continued gradually increasing the polarity of the eluent by using 75:25 and 50:50 compositions of petroleum ether and benzene. With this solvent mixture a bright yellow oil was obtained. This solidified after a few hours (4.9 g, mp 77–80°, 18.7%). Recrystallization from petroleum ether yielded white needle crystals (4.4 g, mp 82–83°). This compound is referred to as **8a**: mass spectrum *m/e* (rel intensity) 262 (70), 236 (20), 231 (18), 203 (67), 172 (19), 171 (100), 144 (18), 116 (17), 103 (26), 78 (59), 77 (26), 59 (80); ir 2200 (C≡N), 1725 and 1750 (C=O), 810, 960, 1460, and 1620 cm^{-1} (isoxazole ring[23]); uv 205 nm (log ϵ 3.93) (isoxazole ring[15]), 272 (4.29) (diene). Anal. Calcd for $C_{12}H_{10}N_2O_5$: C, 54.96; H, 3.84; N, 10.68. Found: C, 55.16; H, 3.58; N, 10.76.

Elution with pure benzene yielded a white solid compound)7.2 g, mp 101–110°, 27%). Recrystallization from benzene–petroleum ether yielded fine white needles (6.0 g, mp varies between 104 and 114°). This fraction is referred to as **8b**: ir 2200 (C≡N), 1735 and 1750 cm^{-1} (C=O); uv 205 nm (log ϵ 3.93), 273 (4.54); NMR δ 4.00, 4.06 (carboxylic CH_3); 5.60 (H_1); 6.90–7.50 ppm (H_2, H_3 and H_4).

Elution with mixtures of benzene and chloroform (75:25 and 50:50) yielded a white solid compound (3.8 g, mp 145–150°, 14.5%). Recrystallization of this compound from benzene–petroleum ether produced hard, white crystals (3.1 g, mp 156–157°). This compound is referred to as **8c**: ir 2200 (C≡N), 1732 and 1755 cm^{-1} (well resolved, C=O); uv 205 nm (log ϵ 3.93), 274 (4.52); NMR δ 3.94, 4.03 (carboxylic CH_3); 5.66 (H_1); 6.90–7.50 ppm (H_2, H_3, and H_4). Anal. Calcd as above. Found: C, 55.16; H, 3.63; N, 10.87.

The end fraction, eluted by chloroform, was an unidentified dark red oil (5.1 g) which failed to solidify even after several weeks.

Ozonolysis of the Isoxazoles. Ozone–oxygen was bubbled through a solution of the isomer **8a** (1.31 g, 5 mmol) in methylene chloride (200 ml) at −10°. The ozonolysis was continued until a deep blue color developed in the reaction solution, indicating an

excess of dissolved ozone. The reaction was assumed to be complete and oxygen was passed through the mixture for 5 min to remove excess ozone. The solution became colorless. Methanol (25 ml) was then added and the mixture was left to stand at room temperature for 1 hr. Work-up involved the addition of 50 ml of water followed by solvent removal to give a yellow oil (750 mg, 70%).[24] This yellow oil exhibited no C≡N stretching band in the ir, and the NMR spectrum exhibited an intense aldehydic proton resonance. The NMR spectrum indicated the presence of some impurities which were removed by distillation of the oil at 150° (2 mm) in a molecular still. The distillate solidified to give a white compound (550 mg, mp 74–76°, 52%, 2,4-DNP derivative mp 232–234°). Ozonolysis of the isomers **8b** and **8c** gave the same aldehyde in comparable yields: mass spectrum *m/e* (rel intensity) 214 (15), 182 (66), 138 (15), 127 (65), 126 (100), 124 (42), 94 (83), 92 (97), 81 (55), 80 (34); ir 2800 (CH aldehyde), 1707 cm^{-1} (C=O aldehyde); uv 205 nm (log ϵ 3.60), 215 (3.55, broad), 267 (3.20, broad); NMR δ 3.98, 4.04 (carboxylic CH_3); 10.65 ppm (CHO). Anal. Calcd for $C_8H_7NO_6$: C, 45.08; H, 3.31; N, 6.57. Found: C, 45.18; H, 3.26; N, 6.45.

Acknowledgments. We wish to thank Dr. G. A. Webb and the University of Surrey, England, for 100-MHz ^1H NMR spectra, mass spectra, and computing facilities. We greatly appreciate the use of Professor F. A. L. Anet's ^{13}C and ^1H NMR equipment at UCLA and we should like to acknowledge the assistance of Dr. F. H. Köhler at Technischen Universität München in taking some ^{13}C NMR spectra.

Registry No.—**6**, 273-09-6; **8a**, 56086-88-5; **8b**, 56086-89-6; **8c**, 56086-90-9; **9**, 56086-91-0; **9** 2,4-DNPH, 56086-92-1; **10**, 7710-44-3; **11**, 300-87-8; **12**, 95-21-6; **13**, 573-34-2; **14**, 1557-59-1; DAD, 762-42-5.

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Photochemical Synthesis of 6,7-Dihydro-5*H*-dibenz[*c,e*]azepine and 5,6,7,8-Tetrahydrodibenz[*c,e*]azocine Derivatives[1]

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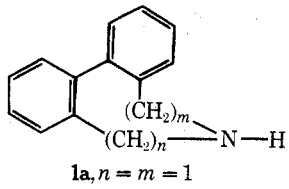
Received March 18, 1975

Photolysis of several substituted 2-iododibenzylamine hydrochlorides in aqueous solution provided convenient syntheses of the corresponding 6,7-dihydro-5*H*-dibenz[*c,e*]azepines in useful yields. Thus, irradiation of amines **2**, **3**, **4**, and **5** gave dibenzazepines **1a**, **10**, **11**, and **12** in 57, 44, 32, and 27% yield, respectively. However, irradiation of **6** yielded only biphenyl **14** together with a small amount of dibenzoxepine **15**. The formation of **14** and **15** was rationalized as originating from a photoassisted hydrolysis of the desired product **13**. Likewise, photolysis of three *N*-(2-halogenobenzyl)-β-phenethylamine hydrochlorides provided convenient syntheses of the corresponding 5,6,7,8-tetrahydrodibenz[*c,e*]azocines. Thus, irradiation of amines **7** and **8** gave dibenzazocines **1b** and **16** in 33% yield, while irradiation of **9** yielded the corresponding cyclic product in 22% yield. ^1H NMR examination of the dibenzazocines confirmed that they existed in a skewed biphenyl conformation, and that inversion of the system by rotation through the planar biphenyl was hindered.

The physiological activities manifested by certain compounds containing either the bridged biphenyl system **1a**,[3–5] **1b**,[4] or **1c**[5,6] continue to stimulate interest in the development of general synthetic routes to these ring systems. The reported synthesis of substituted biphenyls by the photolysis of aryl iodides in benzene[8] prompted us to investigate a photochemical route to the bridged biphenyl systems **1a** and **1b**. During the course of our investigation an extension of the original reaction was employed for effecting intramolecular arylations leading to phenanthrenes,[9] and later to the synthesis of aporphines.[10]



1a, $n = m = 1$
b, $n = 1; m = 2$
c, $n = m = 2$

The results of our investigation demonstrate that photochemically induced intramolecular arylation may be employed not only in the formation of six-membered rings but also for constructing some seven- and eight-membered cycles. In this paper, we summarize the synthesis of several 6,7-dihydro-5*H*-dibenz[*c,e*]azepine (**1a**) derivatives and provide further details on the synthesis of the 5,6,7,8-tetrahydrodibenz[*c,e*]azocine (**1b**) ring system.