of imine **7** (e.g., 1,3,5-trimethylhexahydro-*s*-triazine, polymeric material). The smaller proportion of oligomers seems clearly due to efficient trapping of **7** in solution by excess dimethylamine. The minimum yields of hydrazines are of less certain origin, corresponding to an unusual situation in which a radical dimer product is formed in the gas phase, but not in solution. An explanation involving intermediacy of the isomeric C-centered radicals in solution rather than **6**, an a priori possibility in light of Allan and Swan's photochemical studies of diethylamine,[12] seems incompatible with the absence of *N,N'*-dimethylethanediamine here and the known proclivity of α-aminoalkyl radicals toward recombination rather than disproportionation.[1a,12] The most likely explanation would appear to be the source of the dimethylamino radical. When **6** is generated from **2** by photolysis in solution, oxidation to imine **7**, either via autodisproportionation within the solvent cage (eq 3a) or via the hydrogen transfer sequence with solvent as hydrogen carrier (eq 3c), should be optimized, conditions favoring subsequent formation of **1**. In contrast, when **6** is generated from tetramethyltetrazene or even from **2** in the gas phase, conditions for oxidation of **6** to **7** are no longer optimal; diffusion and recombination reactions of **6** become more important.

Our observations differ superficially from those of Niu and Stenberg,[10] who reported 90% yields of imines analogous to **7** (and no diamines analogous to **1**) resulting from photodehydrogenation of several secondary amines (e.g., **10**, eq 7). Although shorter periods of irradiation were employed in the **10** → **11** (eq 7) conversion (6 hr[10] vs. 96 hr for

$$(n\text{-}C_6H_{13})_2NH \xrightarrow[\text{cyclohexane}]{h\nu,\ 6\text{ hr}} n\text{-}C_6H_{13}N{=}CHC_5H_{11} \qquad (7)$$

10 **11**

2 → **1**), unreported sample size in the earlier study[10] makes direct, meaningful comparisons difficult. It is likely, however, that the failure to detect even transient buildup of **7** from **2** during the NMR–GLC monitoring of photolyses of **2** partly reflects the higher concentrations of amine (≥ 1 *M*) used in our study than in Niu and Stenberg's work (10^{-2} *M*[10]), since higher concentrations of amine would lead to more efficient bimolecular destruction of imine (Scheme I, eq 4). Similar concentration dependence of imine yields in secondary amine photolysis has been reported by Ratcliff and Kochi.[1a] Another important factor in accounting for the differing reactivities of **2** and amines such as **10** may be stereochemical. Relative to imine **7**, the imine **11** derived from **10** may be less reactive toward nucleophilic addition of amine (as in eq 4) because of the steric hindrance posed by bulky substituents in **10** and **11**.

Finally, the origin of diamine **1**, which was once considered "obscure,"[3a] and later considered to be the reaction of methyl radicals with trimethylamine,[3c] is, in all likelihood, neither. Unlike previous mechanisms offered for formation of **1**, the one outlined in Scheme I involves only species whose presence in photolysates is now well documented.

Experimental Section

Photolysis of Dimethylamine in Nonane. In a typical experiment, a 1.3 *M* solution of dimethylamine (3.77 g, 83.7 mmol) in 65 ml of *n*-nonane in a quartz tube was degassed by three freeze–pump–thaw cycles, then sealed, and irradiated at 35° with an adjacent Vycor-filtered mercury arc lamp (Hanovia medium-pressure 450-W). Progress of reactions was monitored by NMR and by GLC on a 5 ft × 0.25 in. column of 20% w/w alkali-treated Carbowax 20M on 60/80 firebrick at 65°. After 96 hr, NMR, mass spectral, and GLC analysis indicated 68% reaction, with 27 mmol of dimethylamine remaining, formation of 18 mmol (95% yield) of *N,N,N',N'*-tetramethylmethanediamine, 6 mmol of methylamine, and traces (<2% each) of tetramethylhydrazine and *N,N,N'*-trimethylmethanediamine (identified by tandem GC–MS). Prolonged irradiation was inefficient in raising the yield of *N,N,N',N'*-tetramethylmethanediamine because of secondary photochemical reactions. Similar procedures were followed for irradiating samples containing from 2 to 100 mmol of dimethylamine, with approximately proportional irradiation times and with identical results.

Nitrogen was bubbled through the photolysate to remove most of the methylamine and some of the dimethylamine. *N,N,N',N'*-tetramethylmethanediamine was isolated from the residue by spinning-band distillation, bp 82–84° (lit.[8] bp 82–84°), of larger samples or by preparative GLC of smaller ones in ca. 85% yields; it was identified by comparison of ir, NMR, and mass spectra to those of authentic material.[2,8]

Use of pentane or cyclohexane as solvent gave comparable results by GLC analysis; however, isolation by distillation was facilitated using the higher boiling *n*-nonane as solvent (and distillation chaser).

Acknowledgment. Financial support furnished by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. We thank Professor D. H. Volman for valuable discussions.

Registry No.—**1**, 51-80-9; **2**, 124-40-3; nonane, 111-84-2.

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3-Thiabicyclo[3.2.0]hepta-1,4-dienes. Synthesis of Tetraphenyl-2,5-dithiabisnorbiphenylene

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Received December 24, 1974

3-Thiabicyclo[3.2.0]hepta-1,4-dienes are members of a class of strained heterocyclic systems which have only recently been prepared.[1-4] Two of the reported synthetic routes[1,3] involve closure of the four-membered ring as the final synthetic step, one the formation of the thiophene ring[2] and in the other formation of both rings in one reac-

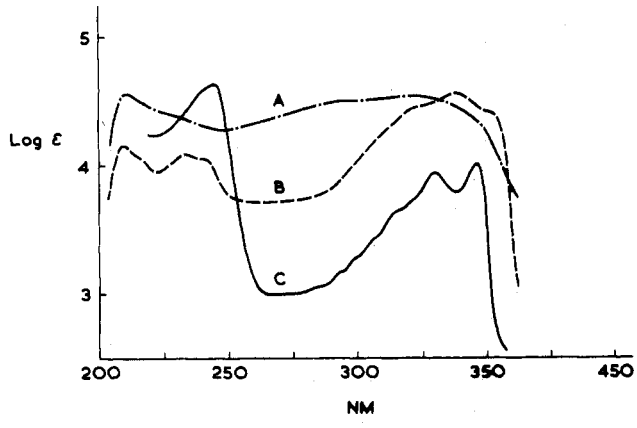
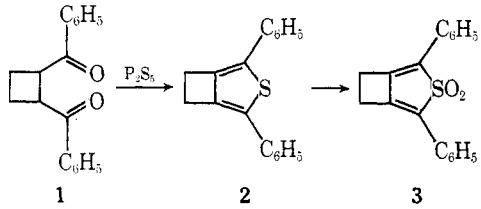


Figure 1. Electronic spectra of (A) tetraphenyl-2,5-dithiabisnorbiphenylene (**5**) in ether, (B) 2,4-diphenyl-3-thiabicyclo[3.2.0]hepta-1,4-diene (**2**) in ether, and (C) 2-thianorbiphenylene in ethanol.

tion.[4] We now report a fifth method which also involves formation of the heterocycle in the final reaction and illustrates its application by the preparation of tetraphenyl-2,5-dithiabisnorbiphenylene (**5**), the first biphenylene analog containing two five-membered heterocycles.[5]

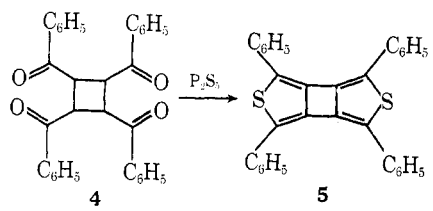
The observed stabilities of the 3-thiabicyclo[3.2.0]hepta-1,4-diene system once it is formed[1-3] encouraged us to examine the classical method of synthesizing five-membered heterocycles from 1,4 diketones. When the diketone **1**[6] was treated with P_2S_5 in tetralin or pyridine then 2,4-diphenyl-3-thiabicyclo[3.2.0]hepta-1,4-diene (**2**), mp 150–150.5°, was obtained in 6% yield. The NMR spectrum (CCl_4) showed a multiplet centred at τ 2.70 with a singlet at 6.77 (5.2) and the electronic spectrum (Figure 1) is very similar to that of the 2,4,6,7-tetraphenyl derivative.[3]

Oxidation of **2** with *m*-chloroperoxybenzoic acid gave the sulfone **3**, mp 244–246° (40%). The NMR spectrum of **3** showed the expected downfield shift of the cyclobutyl ring protons.[2]



1 2 3

When the tetraketone **4**[7] was treated with P_2S_5 in pyridine, tetraphenyl-2,5-dithiabisnorbiphenylene (**5**), mp 194–194.5°, was obtained in 3% yield.[8] The NMR spectrum ($CDCl_3$) showed only a multiplet centered at τ 2.60, and the electronic spectrum (Et_2O) showed a shoulder at 298 nm (ϵ 31,500) and a maximum at 322 (34,800).



4 5

The electronic spectrum of **5** is shown in Figure 1, together with that of **2** and 2-thianorbiphenylene.[4] The spectrum is clearly different from that of **2**, probably owing to interaction of the thiophene rings and an out-of-plane preference of the phenyl groups. The extent of the paratropic contribution of the potential cyclobutadiene in dithianorbiphenylenes must await the synthesis of less substituted derivatives.

Experimental Section

NMR spectra were obtained on either a Varian T-60 or HA-100 spectrometer. Mass spectra were taken on an AEI MS-9 spectrometer at 70 eV. Infrared spectra were recorded on a Unicam SP 200 spectrophotometer and only strong and medium bands are reported. Electronic spectra were determined on a Unicam SP-800 recording spectrophotometer. Melting points were measured on a Kofler hot stage microscope.

Silica for preparative thin layer chromatography was Merck Kieselgel PF_{254} (type E). Solvents were purified and dried by standard methods.

Synthesis of 2,4-Diphenyl-3-thiabicyclo[3.2.0]hepta-1,4-diene (2). A mixture of phosphorus pentasulfide (250 mg, 1.0 mmol), sand (0.5 g), and tetralin (15 ml) was stirred and heated to 150°. *trans*-1,2-Dibenzoylcyclobutane (528 mg, 2.0 mmol) was dissolved in hot tetralin (10 ml) and the hot solution was added dropwise to the stirred mixture over 5 min. The mixture was stirred for a further 15 min at 150–155°, the resulting red solution was filtered, and the filtrate was extracted with hot water (50 ml), 5% NaOH solution (50 ml), and dried ($MgSO_4$). The solution was passed through alumina (150 g), eluting with dichloromethane–petroleum ether (60–80) (1:1), and the solvent and eluted tetralin were removed by distillation under reduced pressure. Preparative TLC of the oily residue on silica, eluting with dichloromethane–pentane (1:9), gave **2** (30 mg, 0.11 mol, 6%): white crystals (EtOH); mass spectrum *m/e* 262.081 (calcd for $C_{18}H_{14}S$, 262.082); ir (KBr) 3025, 2920, 1598, 1539, 1484, 1450, 1360, 1180, 1079, 1020, 925, 908, 760, 744, 698, 670 cm^{-1}; for nmr, see discussion; for electronic spectrum, see discussion.

Anal. Calcd for $C_{18}H_{14}S$: C, 82.39; H, 5.38. Found: C, 82.56; H, 5.45.

Oxidation of 2. Compound **2** (13 mg, 0.05 mmol) was dissolved in $CDCl_3$ (1.5 ml) in an NMR tube and *m*-chloroperoxobenzoic acid (40 mg, 0.23 mmol) was added. The reaction was monitored by NMR, and, on complete disappearance of the signals due to the cyclobutyl protons of **2**, the solution was extracted with $NHCO_3$ solution (3 × 10 ml) and water (10 ml) and dried ($MgSO_4$). Evaporation of the solvent gave a yellow solid which on crystallization (CCl_4) gave yellow crystals of the sulfone **3** (6 mg, 0.02 mmol, 40%): mass spectrum *m/e* 294.073 (calcd for $C_{18}H_{14}SO_2$, 294.072); ir (KBr) 1500, 1455, 1285, 1140, 1120, 765, 690 cm^{-1}; nmr (CCl_4) τ 2.50 (m, 10 H), 6.40 (s, 4 H); λ^{max} (Et_2O) 231 nm (ϵ 19,000), 383 (14,900).

Anal. Calcd for $C_{18}H_{14}SO_2$: C, 73.44; H, 4.79; S, 10.89; O, 10.87. Found: C, 73.32; H, 4.64; S, 10.95; O, 10.85.

Synthesis of Tetraphenyl-2,5-dithiabisnorbiphenylene (5). *cis,trans,cis*-1,2,3,4-Tetrabenzoylcyclobutane (460 mg, 0.975 mmol) was added to pyridine (25 ml) and the solution was heated to boiling. This solution was then added rapidly to a boiling mixture of phosphorus pentasulfide (400 mg, 1.79 mol) in pyridine (5 ml) under N_2. The mixture was heated under reflux for 2 hr, and the solvent was removed under reduced pressure. The black residue was chromatographed on silica (150 g) eluting with dichloromethane–pentane (1:4) to give **5** (13 mg, 0.028 mmol, 3%): mass spectrum *m/e* 468.102 (calcd for $C_{32}H_{20}S_2$, 468.101); ir (KBr) 1600, 1500, 1460, 1080, 1040, 920, 862, 764, 715, 700, 695 cm^{-1}; for nmr, see discussion; for electronic spectrum, see discussion.

Anal. Calcd for $C_{32}H_{20}S_2$: C, 82.01; H, 4.30. Found: C, 81.46; H, 4.65.

Acknowledgment. One of us (S.B.N.) thanks University College London for the award of a Thomas Witherden Batt Scholarship.

Registry No.—**1**, 54120-34-2; **2**, 54120-35-3; **3**, 54120-36-4; **4**, 54120-37-5; **5**, 54120-38-6.

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