was obtained, from 6 g of **13**, 5.82 g (93.5%) of **16**: mp 207–208°; ir (Nujol) 3500, 3450, 3300, 1740, 1695 cm^{-1}; nmr (CDCl$_3$) τ 7.55 (split s, 9 H), 2.80–2.50 (m, 6 H), 2.20–1.90 (m, 6 H), 0.16 (s, 1 H, exchanges very slowly with D$_2$O), −0.05 (S, 1 H, exchanges rapidly with D$_2$O); mass spectrum exhibits highest peak at *m/e* 334 (p$^+$ − CH$_3$C$_6$H$_4$CO).

Anal. Calcd for C$_{27}$H$_{23}$N$_3$O$_4$: C, 71.51; H, 5.11; N, 9.27. Found: C, 71.40; H, 4.88; N, 9.19.

2,5-Di-*p*-Tolyloxazolo[5,4-*d*]pyrimidin-7-one (18).—From 9.0 g of **13** was obtained, according to the procedure for compound **4**, 4.0 g (58%) of **17**: mp >320°: ir (Nujol) 3200, 1720, 1620 cm^{-1}; nmr (CF$_3$CO$_2$H) τ 7.43 (s), 7.37 (s), 2.60–2.30 (m), 1.96–1.68 (m) (the solution was too dilute for meaningful integration); mass spectrum *m/e* (rel intensty) 317 (47), 200 (52), 158.5 (7, p^{2+}), 119 (100).

Anal. Calcd for C$_{19}$H$_{15}$N$_3$O$_2$: C, 71.91; H, 4.76; N, 13.24. Found: C, 71.63; H, 4.52; N, 12.95.

Registry No.—**2,** 34905-95-8; **4,** 34905-96-9; **5,** 34905-97-0; **6,** 34905-98-1; **7,** 34905-99-2; **8,** 34906-00-8; **9,** 34906-01-9; **11,** 34906-02-0; **12,** 34906-03-1; **13,** 34906-04-2; **16,** 34906-05-3; **17,** 34906-06-4; **18,** 34906-07-5; 5-amino-4,6-dihydroxy-2-phenylpyridine, 34906-08-6.

Reaction between Tetrasulfur Tetranitride and Some Hydrocarbons[1]

VINCENZO BERTINI,* ANGELA DE MUNNO, AND ANTONIO MARRACCINI

Istituto di Chimica Organica, Facoltà di Scienze dell'Università Via Risorgimento, 35, 56100 Pisa, Italy

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9,10-Dihydrophenanthrene reacts with S$_4$N$_4$, by heating or uv radiation, to give a mixture of phenanthrene and phenanthro[9,10-*c*]-1,2,5-thiadiazole (**1**) in the ratio 7.6:1. Under analogous conditions, the tetrahydronaphthalene reacts to give a mixture of 3,4-dihydronaphtho[1,2-*c*]-1,2,5-thiadiazole (**2**), naphtho[1,2-*c*]-1,2,5-thiadiazole (**3**), and naphtho[1,2-*c*:3,4-*c'*]bis-1,2,5-thiadiazole (**4**) in the ratio 20:5:1. Compound **2** also reacts with S$_4$N$_4$ to give **3** and **4** in the ratio 5:1. Compound **1**, by reaction with Grignard reagents followed by hydrolysis, is transformed into 9,10-phenanthrenedione. Analogies between the reactions of S$_4$N$_4$ with hydrocarbons and autoxidation reactions have been pointed out and a free-radical initiation mechanism has been proposed for the former.

In a previous paper[2] we have shown that sulfur nitride, S$_4$N$_4$, reacts easily with unsaturated hydrocarbons such as acetylene and ethylene, displaying strong dehydrogenating power. Moreover, ethane is practically unreactive,[2] although its reactivity is substantially improved by the presence of aryl substituents; ethylbenzene, 2-ethylnaphthalene, and 1,2-diphenylethane all react with S$_4$N$_4$ in refluxing xylene to give the corresponding 1,2,5-thiadiazole derivatives, together with elemental sulfur and ammonia.[3]

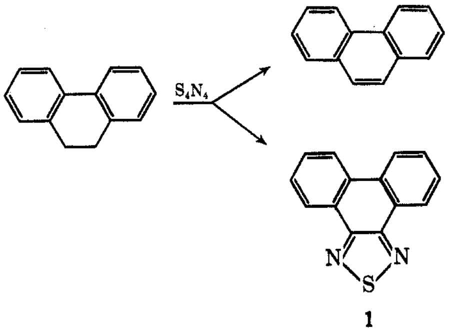
In order to obtain some preliminary information on the mechanism of the reaction between S$_4$N$_4$ and paraffins we have focused on the effects of the aryl substituents and examined the reactivity of S$_4$N$_4$ toward 9,10-dihydrophenanthrene and tetrahydronaphthalene. These reactions afforded complex mixtures of products, always containing ammonia and elemental sulfur.

The reaction of S$_4$N$_4$ with 9,10-dihydrophenanthrene, carried out in boiling xylene, gave a mixture of phenanthrene and phenanthro[9,10-*c*]-1,2,5-thiadiazole[4,5] (**1**) in the ratio 7.6:1 (Scheme I).

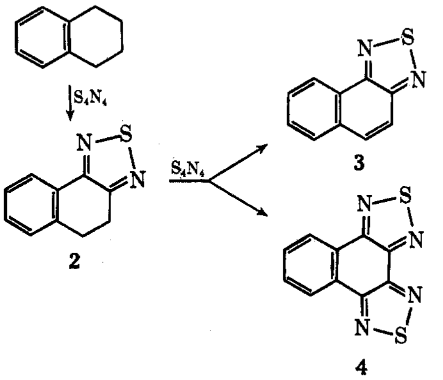
The reaction between S$_4$N$_4$ and tetrahydronaphthalene at about 140°, both with and without xylene, yielded a mixture of 3,4-dihydronaphtho[1,2-*c*]-1,2,5-thiadiazole (**2**), naphtho[1,2-*c*]-1,2,5-thiadiazole (**3**), and naphtho[1,2-*c*:3,4-*c'*]bis-1,2,5-thiadiazole (**4**) in the ratio 20:5:1 (Scheme II). Dehydrogenation derivatives of tetrahydronaphthalene were not found.

Compound **3** was obtained in good yields carrying out the aromatization of **2** by heating with sulfur. It was also synthesized, for the sake of comparison, by reaction of 1,2-diaminonaphthalene with thionyl chloride according to Michaelis, *et al.*[6]

SCHEME I



SCHEME II



Compound **1**, on reaction with Grignard reagent followed by hydrolysis, was transformed into 9,10-phenanthrenedione in good yield. This reaction shows that the sulfur atom of **1**, analogous to the behavior of

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[1] Preliminary communication: V. Bertini, IV Symposium on Organic Sulfur, Venezia, June 1970.

[2] V. Bertini and A. De Munno, *Gazz. Chim. Ital.*, **97**, 1614 (1967).

[3] V. Bertini and P. Pino, *Angew. Chem.*, **77**, 262 (1965).

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[5] K. Pilgram, *J. Org. Chem.*, **35**, 1165 (1970).

[6] A. Michaelis and G. Erdmann, *Chem. Ber.*, **28**, 2192 (1895).

other 1,2,5-thiadiazole derivatives,[7,8] easily undergoes attack by strong nucleophiles, consistent with the structure of the product. The assigned structures are also in full accord with the analytical, cryoscopic, and spectroscopic data (see Experimental Section).

The formation of phenanthrene in the reaction with 9,10-dihydrophenanthrene confirms the dehydrogenating character of S_4N_4, which was noted earlier in the reactions with acetylene and ethylene. However, S_4N_4 has no dehydrogenating effect on tetrahydronaphthalene, which could eliminate four hydrogen atoms to give an aromatic system. Instead the reaction between S_4N_4 and tetrahydronaphthalene involves the formation of compound **2**, which, upon further reaction with S_4N_4, is dehydrogenated to **3** or transformed into **4**. To confirm this, the reaction between S_4N_4 and compound **2** was carried out in boiling xylene; it gave a mixture of **3** and **4** in about the same ratio as the product originating from tetrahydronaphthalene.

Several observations, such as the multiplicity of products, changes of color, and the competition between the dehydrogenation and formation of 1,2,5-thiadiazole rings, are reminiscent of other reactions of the 9,10-dihydrophenanthrene and tetrahydronaphthalene which are of free-radical nature and resemble in this respect oxidation reactions.[9] Moreover, if the initiation of reaction between S_4N_4 and hydrocarbons originated with a free radical, the activating effect of aryl substituents on the ethane system could be understood on the basis of the high reactivity of the benzylic positions. This is also suggested by the observation that S_4N_4 easily gives under a variety of conditions several free-radical species which have been identified by their esr spectra.[10,11]

On this assumption the reaction of S_4N_4 with 9,10-dihydrophenanthrene and tetrahydronaphthalene was undertaken at room temperature in the presence of uv light as the source of the radical initiators. Both of these reactions took place readily and yielded a mixture of products whose composition in each case was similar to that obtained from the same reagents in the corresponding thermal reaction. These results support the suggestion that the initiator abstracts one hydrogen atom from a benzylic position, thus bringing about a sequence of reactions culminating in aromatization or cyclization.

Experimental Section

Melting points were determined with a Kofler apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 225 spectrophotometer. Ultraviolet spectra were determined with a Hilger-Watts "Uvispek" H-700 apparatus. Nmr spectra were run on a DA-60 IL Varian instrument.

Reaction of S_4N_4 with 9,10-Dihydrophenanthrene. A. Thermal.—A mixture of 6.00 g (32.56 mmol) of S_4N_4, 30 ml of xylene (mixture of the isomers), and 5.85 g (32.45 mmol) of 9,10-dihydrophenanthrene was refluxed under nitrogen with stirring. The heating was continued to the end of ammonia evolution (5–6 hr), the solvent was distilled and the residue was extracted with petroleum ether (bp 40–60°), and the extracts were chromatographed on a column of alumina (Merck Al_2O_3 according to Brockmann, 80 g; column diameter 21.5 mm, height 245 mm; eluent petroleum ether, bp 40–60°). This yielded 4.38 g (24.57 mmol) of phenanthrene and a sample of **1**, which after treatment with decolorizing carbon in benzene solution and crystallization from ligroin weighed 0.763 g (3.23 mmol): colorless needles; mp 169–170° (lit.[4] mp 167–168.5°); nmr ($CDCl_3$) δ 8.67 (m, 2, 4- and 5-H), 8.43 (m, 2, 1- and 8-H), 7.60 (m, 2, 2- and 7-H), 7.50 (m, 2, 3- and 6-H).

B. Uv Irradiation.—A homogeneous solution of 2.00 g (10.85 mmol) of S_4N_4, 250 ml of benzene, and 2.95 g (16.37 mmol) of 9,10-dihydrophenanthrene in a reactor equipped with a low-pressure mercury vapor immersion lamp was irradiated for 54 hr at room temperature under a slow stream of nitrogen. After removal of the solvent by evaporation at room temperature and reduced pressure, the residue was extracted with petroleum ether and the extracts were chromatographed on a column of alumina. After the unreacted 9,10-dihydrophenanthrene was collected, 0.124 g (0.70 mmol) of phenanthrene and 0.027 g (0.11 mmol) of **1** were isolated.

Reaction between 1 and Ethylmagnesium Bromide.—A solution of 0.113 g (0.48 mmol) of **1** in 10 ml of benzene was added dropwise to 3.5 ml (5 mmol) of a solution of ethylmagnesium bromide, prepared from 1.216 g of magnesium and 5.45 g of ethyl bromide in ether (final volume 35 ml). The mixture was refluxed for about 3 hr, hydrolyzed with iced water, acidified with HCl, and extracted with ether. The residue after removal of the solvent, as determined by tlc analysis on Merck GF$_{254}$ silica gel (eluent benzene–acetone, 98:2), appeared to be free from compound **1**. Purification of the residue by preparative layer chromatography yielded orange crystals (0.088 g, 0.42 mmol), mp 207–208°, ir spectrum superimposable on that of an authentic sample of 9,10-phenanthrenedione.

Reaction of S_4N_4 with Tetrahydronaphthalene. A. Thermal (Molar Ratio 1:7.6).—A 6.00-g (32.56 mmol) sample of S_4N_4 in 32.55 g (246 mmol) of tetrahydronaphthalene was heated to 140–145° under a nitrogen atmosphere with continuous stirring. Copious evolution of ammonia was observed while the color of the solution changed from red to green-brown. When the evolution of ammonia ceased (11–12 hr) the excess tetrahydronaphthalene was distilled at about 20 Torr and the residue was extracted with petroleum ether. The solution, after separation of the elemental sulfur, was chromatographed on a column of alumina (Merck Al_2O_3 according to Brockmann, 85 g; column diameter 21.5 mm, height 260 mm; eluent petroleum ether, bp 40–60°). The fractions collected yielded a mixture of **3** and **2** and 0.186 g (0.76 mmol) of **4**. The compound **4**, after treatment with decolorizing carbon in benzene solution, crystallization from petroleum ether (bp 60–80°), and sublimation at 150° (0.005 Torr), yielded white needles: mp 208–209°; molecular weight by cryoscopy in benzene 246; uv max (isooctane) 239 nm (log ϵ 4.83), 264 (4.41), 290 (4.43), 295 (4.46), 300 (4.47), 308 (4.46), 315 (4.54), 322 (4.45), 330 (4.69), fine structure in the region 230–260 nm; ir (KBr) 1406, 777, 523 cm^{-1}; nmr ($CDCl_3$) δ 8.59 (dd, 2, $J = 6$ and 3.2 Hz, 5- and 8-H), 7.73 (dd, 2, $J = 6$ and 3.2 Hz, 6- and 7-H).

Anal. Calcd for $C_{10}H_4N_4S_2$: C, 49.17; H, 1.65; N, 22.93; S, 26.25. Found: C, 49.10; H, 1.89; N, 22.79; S, 26.44.

The mixture of **2** and **3** was separated by preparative layer chromatography on Merck PF$_{254}$ silica gel (thickness 1.5 mm; eluent 35:65 benzene–petroleum ether, bp 40–60°), yielding 0.704 g (3.78 mmol) of **3** and 2.810 g (14.93 mmol) of **2**. The ir spectrum of **3** (mp after crystallization from methanol 80–81°) appeared to duplicate that of an authentic sample.[6,12] Compound **2**, on crystallization from methanol and sublimation at room temperature (0.1 Torr), gave white crystals: mp 29–30°; molecular weight by cryoscopy in benzene 185; uv max 226 nm (log ϵ 3.94), 287 (4.11), 304 (4.26); ir (liquid film) 1409, 787, 533 cm^{-1}; nmr (CCl_4) δ 7.91 (m, 1, 8-ArH), 7.16 (m, 3, 5-, 6-, and 7-ArH), 3.07 (s, 4, two CH_2).

Anal. Calcd for $C_{10}H_8N_2S$: C, 63.80; H, 4.28; N, 14.88; S, 17.03. Found: C, 63.66; H, 4.47; N, 15.10; S, 16.87.

B. Thermal (Molar Ratio 1:1).—A mixture consisting of 6.00 g (32.56 mmol) of S_4N_4, 24 ml of xylene (mixture of the isomers), and 4.36 g (32.98 mmol) of tetrahydronaphthalene was refluxed under a nitrogen atmosphere with continuous stirring until the end of ammonia evolution. The solvent was then

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(7) V. Bertini, A. De Munno, and P. Pino, *Chim. Ind. (Milan)*, **49**, 1384 (1967).

(8) V. Bertini, X Congresso Nazionale della Società Chimica Italiana, XIII-58, Padova, June 1968.

(9) C. E. Frank, *Chem. Rev.*, **46**, 155 (1950).

(10) D. Chapman and A. G. Massey, *Trans. Faraday Soc.*, **58**, 1291 (1962).

(11) D. A. C. McNeil, M. Murray, and M. C. R. Symons, *J. Chem. Soc. A*, 1019 (1967).

(12) H. Beecken, *Chem. Ber.*, **100**, 2164 (1967).

distilled and the residue was chromatographed as described for the preparation above, yielding 0.110 g (0.45 mmol) of **4**, 0.417 g (2.24 mmol) of **3**, and 1.796 g (9.54 mmol) of **2**.

C. **Uv Irradiation.**—A homogeneous solution of 1.35 g (7.33 mmol) of S_4N_4, 200 ml of benzene, and 4.15 g (31.39 mmol) of tetrahydronaphthalene was irradiated for 206 hr at room temperature. After removal of the solvent under vacuum at room temperature, the residue was chromatographed. In addition to the unreacted tetrahydronaphthalene, 0.256 g (1.36 mmol) of **2** and 0.067 g (0.36 mmol) of **3** were obtained. Compound **4** was recovered in traces and identified by tlc analysis.

Reaction of S_4N_4 with 2.—A 0.748-g (3.97 mmol) sample of **2** in 20 ml of xylene was treated with 1.10 g (5.97 mmol) of S_4N_4 and the mixture was refluxed for about 8 hr under nitrogen atmosphere with stirring. After removal of the solvent by distillation at 20 Torr, the residue was chromatographed, yielding 0.059 g (0.24 mmol) of **4**, 0.229 g (1.23 mmol) of **3**, and 0.469 g (2.49 mmol) of **2**.

Reaction of 2 with Sulfur.—A mixture of 0.109 g (0.58 mmol) of **2** and 0.022 g (0.69 mmol) of sulfur was heated at 250–270° for 2.5 hr. After cooling the residue gave after crystallization from methanol 0.078 g (0.42 mmol) of **3**.

Registry No.—**1**, 1143-73-3; **2**, 34910-55-9; **3**, 233-68-1; **4**, 34910-56-0; **5**, 28950-34-7; 9,10-dihydrophenanthrene, 776-35-2; tetrahydronaphthalene, 119-64-2.

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New Precursors for Arylcarbenes. Photocycloelimination Reactions of Cyclic Sulfites[1,2]

GARY W. GRIFFIN* AND AWINASH MANMADE[3]

Department of Chemistry, Louisiana State University in New Orleans, New Orleans, Louisiana 70122

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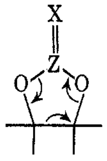
Cyclic arylpinacol sulfites are found to undergo [5 → 2 + 2 + 1] photocycloeliminations to give arylcarbenes in addition to other products. The sulfites studied include benzopinacol sulfite, fluorenopinacol sulfite, *meso*- and *dl*-hydrobenzoin sulfites, and methyl-substituted hydrobenzoin sulfites. With the exception of fluorenopinacol sulfite all fragment to give carbenes and have synthetic utility. Arylcarbenes formed by photolysis of these substrates when generated in methanol give methyl ethers and the transient obtained by photolysis of *meso*- and *dl*-hydrobenzoin sulfites is shown to be virtually identical in properties with that obtained from conventional precursors such as *trans*-2,3-diphenyloxirane and phenyldiazomethane; *i.e.*, the secondary to primary insertion selectivity in pentane and the high stereoselectivity of addition to *cis*-2-butene are the same for phenylcarbene generated from the hydrobenzoin sulfites, 2,3-diphenyloxirane and phenyldiazomethane. The observed lack of dependence of chemical behavior on precursor structure suggests that free phenylcarbene is involved in each case. [5 → 3 + 2] cycloelimination to sulfur trioxide and substituted stilbenes appears to be a competitive process. Under the reaction conditions the stilbenes undergo a secondary reaction, namely cyclization to phenanthrenes. In addition, 1,2-aryl migrations, preceded or accompanied by loss of sulfur dioxide, also compete with cycloelimination. The rearrangements are shown to occur with retention of the substitution patterns on the aryl groups. Thermal reactions of the cyclic sulfites have also been studied and a comparison of the sulfite photo- and thermochemistry made. Possible mechanisms are discussed.

An increasing number of photocycloelimination reactions leading to carbenes have appeared in the literature and these reactions have been surveyed recently.[4] Their thermal counterparts are also the subject of a recent review.[5] In continuing efforts to broaden the scope and synthetic utility of photocycloelimination reactions for the preparation of arylcarbenes, several precursors of the type shown in the general structures **1** and **2** have been investigated.[2,6,7] Substrates of the type **1** were selected for evaluation in cycloelimination studies because of their ready accessibility from the corresponding diols, which themselves may be prepared under reductive conditions. Consequently, such reagents would complement the existing oxirane



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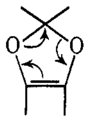

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carbene precursors which in general are formed oxidatively.[8]

In previous investigations we have established that many vicinal diaryl-substituted heterocyclic systems undergo photocycloelimination to give arylcarbenes.[6,7,8] *A priori*, one might expect that systems such as **1** and **2** undergo cycloelimination reactions in the [5 → 2 + 2 + 1] and [5 → 4 + 1] modes, respectively, and indeed members of these classes behave as anticipated.[9]

For example, *trans*-4,5-diphenyl-4,5-dicyano-1,3,2-dioxa-P^V-phospholane (**3**), a system structurally related to **1**, undergoes [5 → 2 + 2 + 1] cycloelimination as

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[1] We gratefully acknowledge financial support of this research from the National Science Foundation (Grants GP 9434 and GP 28171) and The Petroleum Research Fund (Grant PRF 5471).

[2] For preliminary communications on this and related work see (a) R. L. Smith, A. Manmade, and G. W. Griffin, *J. Heterocycl. Chem.*, **6**, 443 (1969); (b) R. L. Smith, A. Manmade, and G. W. Griffin, *Tetrahedron Lett.*, 663 (1970).

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[4] G. W. Griffin, *Angew. Chem.*, **83**, 604 (1971); *Angew. Chem., Int. Ed. Engl.*, **10**, 537 (1971).

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[6] P. Petrellis and G. W. Griffin, *Chem. Commun.*, 1099 (1968).

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[8] For the latest papers in the oxirane series see (a) R. S. Becker, R. O. Bost, J. Kolc, N. R. Bertoniere, R. L. Smith, and G. W. Griffin, *J. Amer. Chem. Soc.*, **92**, 1302 (1970); (b) N. R. Bertoniere, S. P. Rowland, and G. W. Griffin, *J. Org. Chem.*, **36**, 2956 (1971).

[9] We shall employ the convention suggested by R. Huisgen [*Angew. Chem.*, **80**, 329 (1968); *Angew. Chem., Int. Ed. Engl.*, **7**, 321 (1968)] in which cycloadditions and cycloeliminations are classified on the basis of the size of the ring formed or destroyed and the number of ring members contributed to each fragment.