centration of this solution left an orange-colored oil, 258 mg (74%), a portion of which was injected into the gas chromatograph (240°, UCW-98 column). The ratio of **11a** to **11b** varied among several such alkylations from 75–95% **11a** to 5–25% **11b** depending upon the amount of butyllithium and the care exercized in the work-up to exclude moisture. Since the products were very sensitive to base, equilibration conditions were difficult to circumvent. The highest proportion (<95%) of **11a** (Figure 2) was accomplished in the above described experiment: nmr ($CDCl_3$) $\delta$ 5.80 (1, d, $J$ = 10 Hz, =CH), 3.75 [1, d ($J$ = 10 Hz) of t ($J$ = 7 Hz), CHCN], 2.8–3.1 (m, 4, $CH_2S$), 2.1–2.4 (m, 2, $-CH_2CH_2S$), 1.75 (2, p, $J$ = 7 Hz, $CH_2CH_3$), 1.1 (3, t, $J$ = 7 Hz, $CH_3$); infrared (neat) 2239 $cm^{-1}$ (unconjugated C≡N); $m/e$ 199 (calcd 199). The gas chromatogram indicated a small amount of a second component poorly resolved from the main peak of **11a**.

Equilibration of **11a** in sodium ethoxide–ethanol at −20° for 30 hr gave after recovery (as described for equilibration of **1** to **6**) a product which exhibited two distinct peaks in the gas chromatogram (UCW-98 column, 240°) integrating at 23:77. The nmr ($CDCl_3$) for this equilibrated product is shown in Figure 2 (bottom). The infrared (neat) shows two clearly separated bands at 2240 (unconjugated C≡N) and 2219 $cm^{-1}$ (conjugated C≡N).

**Alkylation of 1 or 6 with Isopropyl Bromide.**—To 150 mg (0.88 mmol) of **6** or **1** in 2 ml of anhydrous tetrahydrofuran cooled to −78° under nitrogen was added 267 mg (0.88 mmol) of 21 wt % $n$-butyllithium in hexane. After 30 min 221 mg (1.8 mmol) of isopropyl bromide in 1 ml of tetrahydrofuran was added and the reaction was allowed to warm to room temperature. The solvents were evaporated and the residue was triturated several times with 15-ml portions of hot hexane. Filtration of the hexane solution followed by concentration left a yellow oil, 58 mg (31%). Vpc examination (UCW-98, 250°) revealed two distinct peaks (19 and 81%). Collection from the vpc gave $m/e$ 213 (calcd 213), **11a** and **11b** (R = $i$-Pr): infrared (neat) 2240, 2220 $cm^{-1}$ (unconjugated and conjugated CN); nmr ($CDCl_3$) $\delta$ 6.2 [d, $J$ = 11 Hz, 0.2 H, $CH{=}C(CN)C_3H_7$], 5.85 (d, $J$ = 9 Hz, 0.8 H, $-S_2C{=}CH$), 5.1 (d, $J$ = 11 Hz, 0.2 H, $-S_2CH-$), 3.7 [d ($J$ = 9 Hz) of d ($J$ = 9 Hz), 0.8 H, −CHCN], 2.9–3.1 (m, 4, $CH_2S$), 1.6–2.6 [m, 3, $CH_2CH_2S$, $CH(CH_3)_2$], 0.9–1.4 [m, 6, $(CH_3)_2C$].

Equilibration of this mixture with sodium ethoxide–ethanol at −20° for 30 hr gave no significant changes in the vpc, ir, and nmr analyses.

**Wittig Coupling of 2-Formyl-1,3-dithiane with the Phosphorane of Ethyl α-Bromobutyrate (14a and 14b). A. N-Propyltriphenylphosphonium Bromide.**—A solution of triphenylphosphine (48 g) and 1-bromopropane (22.4 g) in dry xylene was heated under reflux for 20 hr. Upon cooling, the solid was removed by filtration, washed with dry ether, and dried: yield 63 g (90%); nmr ($CDCl_3$) $\delta$ 7.6–8.2 (m, 15), 3.5–4.0 (m, 2, $-CH_2P^+Ph_3$), 1.1–2.1 (m, 5, $CH_3CH_2$).

**B. 1-Carboethoxy-n-propyltriphenylphosphonium Chloride.**[11]—$n$-Propyltriphenylphosphonium bromide (28.4 g, 73.6 mmol) as a suspension in dry benzene (50 ml) at 0° under nitrogen was treated with $n$-butyllithium (38 ml, 61 mmol) as a 15 wt % solution in hexane. The mixture was stirred for 1 hr, a solution of ethyl chloroformate (3.33 g, 30.5 mmol) in 5 ml of benzene was added, and stirring was continued for an additional 1 hr at room temperature. The phosphorane thus formed *in situ* was then treated with a benzene solution (5 ml) of 2-formyl-1,3-dithiane (5.0 g, 33 mmol). The mixture was stirred at room temperature for 16 hr and then poured into ice water. The benzene layer was separated and the aqueous solution was extracted with ether. Combination of the organic extracts, drying ($MgSO_4$), and concentration produced a residue, 6.4 g, which was distilled, bp 110–114°, (0.1 mm). The gas chromatogram (UCW-98, 240°) showed that two components in the ratio 82:18 were present: nmr ($CDCl_3$) $\delta$ 6.65 (d, $J$ = 10 Hz, 0.18 H, CH=C in **14b**), 5.82 (d, $J$ = 10 Hz, 0.82 H, $-S_2C{=}CH$ in **14a**), 4.82 (d, $J$ = 11 Hz, 0.18 H, $-S_2CH$ in **14b**), 4.15 (two overlapping quartets for $-OCH_2-CH_3$ in **14a**, **14b**), 3.40 [d ($J$ = 7 Hz) of t ($J$ = 10 Hz), 0.82 H, $-CH(C_2H_3)CO_2Et$ in **14a**], 2.8–3.1 (m, 4, $SCH_2$), 2.0–2.5 (m, 2, $CH_2CH_2S$), 0.85–1.9 (m, 8); $m/e$ 246 (calcd 246).

**Registry No.**—**1**, 34906-11-1; **3** (R = H), 34906-12-2; **6**, 34906-13-3; **11a**, 34906-14-4; **11b**, 34906-15-5; **14a**, 34906-16-6; **14b**, 34906-17-7.

**Acknowledgment.**—The authors are grateful to the Lithium Corporation of America for their continuing interest and contribution of generous quantities of organolithium reagents. Certain technical assistance by Dr. Eric W. Collington and Mr. G. Ray Malone is also gratefully acknowledged.

(11) H. J. Bestmann and H. Schulz, *Angew. Chem.*, **72**, 27 (1961), has described the *in situ* preparation of α-alkylcarboethoxy phosphoranes.

# The Structure of Aroyl Isocyanide Trimers[1]

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*Received February 23, 1972*

The structure of the trimer of benzoyl isocyanide prepared by the action of silver cyanide on benzoyl bromide is shown to be 7-benzoylimino-2,5-diphenyloxazolo[5,4-*d*]pyrimidin-7-one (**2**) on the basis of chemical and spectroscopic evidence. The scope and limitation of the trimerization reaction is discussed.

The trimer of benzoyl isocyanide was first reported in 1895 by Nef[2] who prepared it by treating benzoyl bromide with silver cyanide. Diels and Stein[3] repeated this work in 1907 and on the basis of chemical evidence proposed the azetine structure **1**. In a review of trimethylenimines,[4] Moore noted that structure **1** was quite unlikely for the trimer. The benzoyl isocyanide trimer is also formed[5] as a minor product (2%) in the thermolysis of 2-azido-5-phenyl-1,3,4-oxadiazole along with benzoyl cyanide (35%).

## Results

The benzoyl isocyanide trimer has been shown to be 7-benzoylimino-2,5-diphenyloxazolo[5,4-*d*][1,3]oxazine (**2**) on the basis of spectral and chemical evidence. The mass spectrum of the trimer afforded a molecular ion at $m/e$ 393 consistent with $(PhCONC)_3$. The nmr spectrum indicated the presence of aromatic hydrogens only. The ir spectrum was devoid of triple-bond absorption and exhibited maxima at 1718 (sh), 1700, 1660, and 1640 $cm^{-1}$. Considered in conjunction with the chemical evidence presented below only structures **2** and **3** are consistent with the data. Structure **2**, a primary adduct, is favored over Dimroth rearrangement

(1) Presented in part at the 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 12–17, 1971.

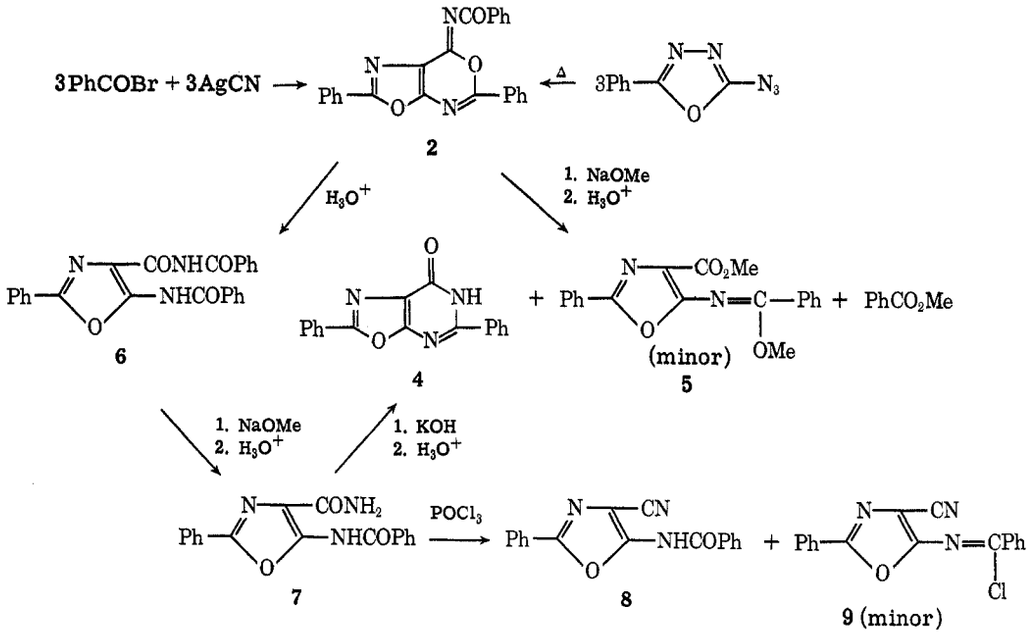
(2) J. U. Nef, *Ann.*, **287**, 303 (1895).

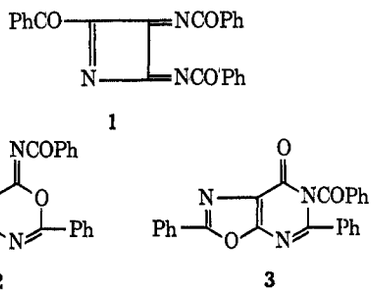
(3) O. Diels and H. Stein, *Ber.*, **40**, 1655 (1907).

(4) J. A. Moore in "Heterocyclic Compounds with Three and Four Membered Rings," Part II, R. Weissberger, Ed., Interscience, New York, N. Y., 1964, p 916.

(5) P. A. S. Smith in "Nitrenes," W. Lwowski, Ed., Interscience, New York, N. Y. 1970, p 149; H. Dounchis, Ph.D. Thesis, The University of Michigan, Ann Arbor, Mich, 1967.

SCHEME I





product **3** on the basis of the carbonyl frequency. Compound **3**, being an imide, would be expected[6] to display absorption above that observed.

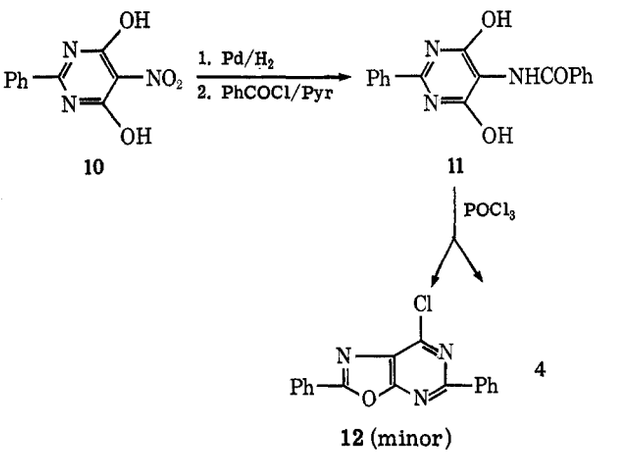
The chemical evidence which supports structure **2** is as follows. Treatment of the trimer with sodium methoxide[3] yielded a sodium salt and methyl benzoate. Protonation of this salt gave rise to a high melting solid which was shown to be 2,5-diphenyloxazolo[5,4-*d*]-pyrimidin-7-one (**4**) by comparison with authentic material which was independently synthesized. Traces of the imidate ester **5** were also isolated. The depicted sequence of transformations (Scheme I) supports the structural assignment.

The trimer underwent facile hydration in aqueous acetic acid to afford **6** which exhibited characteristic imide absorption at 1720 $cm^{-1}$ ($CHCl_3$). Sodium methylate smoothly debenzoylated **6** to give carboxamide **7**. Compound **7** was cyclized to **4** with hot aqueous potassium hydroxide. Dehydration of **7** to nitrile **8** was accomplished with phosphorus oxychloride. A small amount of imidoyl chloride **9** was also isolated. Compounds **4**, **6**, and **7** were characterized by Diels and Stein but were not assigned correct structures.

Structure **7** is also consistent with the chromic acid oxidation of this derivative which Diels and Stein reported gave dibenzoyloxamide.

2,5-Diphenyloxazolo[5,4-*d*]pyrimidin-7-one (**4**) was independently prepared by the synthetic sequence shown in Scheme II. Nitropyrimidine **10**[7] was catalyti-

SCHEME II



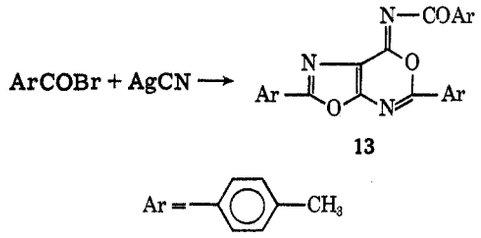
cally reduced to the corresponding amine which was acylated with benzoyl chloride in pyridine to give 5-benzamido-4,6-dihydroxy-2-phenylpyrimidine (**11**). Benzamide **11** was cyclized to oxazolopyrimidine **4** with phosphorus oxychloride. A small amount of 7-chloro-2,5-diphenyloxazolo[5,4-*d*]pyrimidine (**12**) was also formed.

Compound **4** prepared in the above sequence was identical with the product obtained from the debenzoylation of the benzoyl isocyanide trimer **2**.

Treatment of *p*-toluoyl bromide with silver cyanide afforded the oxazolo[5,4-*d*]oxazine **13** in 81% yield. Compound **13** reacted with sodium methoxide and with aqueous acetic acid to give analogs of **4** and **6**, respectively. Complex mixtures resulted when acetyl bro-

(6) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Wiley, New York, N. Y., 1962, p 221.

(7) J. A. Hendry and R. F. Homer, *J. Chem. Soc.*, 328 (1951).



13

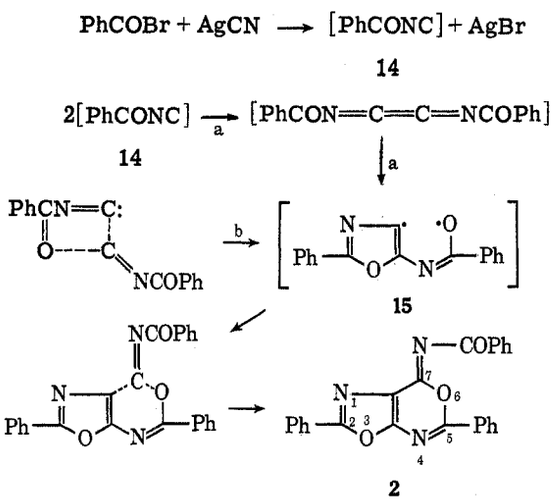


mide and *n*-butyl bromide were treated with silver cyanide.

## Discussion

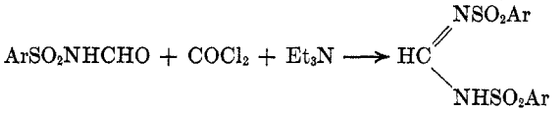
A detailed mechanism for the formation of trimer **2** must await further study. The formation of **2** can, however, be rationalized in general terms by the sequence shown in Scheme III.

SCHEME III



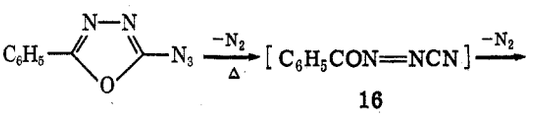
**2**

Benzoyl isocyanide **14** must be an intermediate in the formation of **2**. Isocyanide **14** would be expected to be highly reactive as stabilization of the electron deficient isocyanide carbon atom by the juxtaposed nitrogen lone pair is retarded by overlap of the nitrogen lone pair with the adjacent carbonyl group. This same destabilizing effect is observed[8] when N-formylsulfonamides are dehydrated with phosgene and triethylamine. The sulfonyl isocyanide is not isolated but reacts with starting material to ultimately give an *N,N'*-disulfonylformamidine. The formation of **2** from

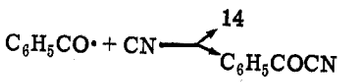


**14** can be rationalized by a head to head dimerization of two isocyanide molecules followed by isomerization to a diradical or carbenoid oxazole **15** (path a) or *via* a 1:1 cyclization to **15** (path b) followed by a novel[9] 1:5 cyclization with a third molecule of isocyanide Analogy to the 1:4 cyclization depicted in path b can be seen in the ring closure of acyl isocyanates and isocyanides to oxazole derivatives.[10] It is of interest to note that no evidence for the formation of the oxazolooxazole which would form by ring closure of **15** has been obtained.

A mechanism for the formation of **2** from isocyanide **14** *via* a complex with silver appears attractive, *a priori*, on several counts. Silver is known[11] to form stable complexes with isocyanides and such a complex might be expected to be a suitable intermediate for the highly specific trimerization observed. The fact that **2** is also formed in the thermolysis of 2-azido-5-phenyl-1,-3,4-oxadiazole, in which case there is no transition metal present, argues against such a mechanism although it does not rule it out. It is likely that **14** is an intermediate in the azide thermolysis. Its formation can be explained by decomposition of the azide to benzoyl azocyanide **16** which undergoes loss of nitrogen to afford



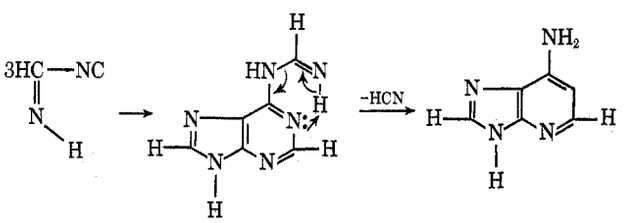
**16**



benzoyl radicals and ambident cyano radicals which couple to give either benzoyl cyanide or **14** which trimerizes.

Oxazolo[5,4-*d*]oxazine **2** undergoes facile addition of nucleophiles (*i.e.*, amines, CH acids) to give high yields of 1:1 adducts which arise predominately from $O_6$–$C_7$ bond cleavage although some $O_6$–$C_5$ cleavage is observed for nucleophiles with low steric requirements. These reactions will be discussed in a subsequent paper.

The formation of **2** may have implication for the biogenetic synthesis of adenine *via* the trimerization of dimeric hydrogen cyanide in the isonitrile form followed by loss of hydrogen cyanide.



## Experimental Section

Melting points were taken on a Thomas-Hoover melting point apparatus and are uncorrected. The nuclear magnetic resonance spectra were determined on a Varian Associates spectrophotometer, Model A-60A. Ir spectra were obtained with a Perkin-Elmer Model 421 ir spectrophotometer. Mass spectra were recorded on a Consolidated Electrodynamics Corporation Type 21-103C mass spectrometer. Elemental analyses were performed by the staff of the Analytical Laboratory of the Central Research Group, FMC Corporation.

**7-Benzoylimino-2,5-diphenyloxazolo[5,4-*d*][1,3]-oxazine (2).**[2,3] —This compound was prepared by a slight modification of the procedure of Diels and Stein. A solution of benzoyl bromide, 100 g, in 600 ml of anhydrous ether in which was suspended 100 g of silver cyanide, was vigorously stirred and refluxed for 21 hr. The solids were collected and washed with cold ether. Hot chloroform separated the yellow product from the silver salts. Concentration of the chloroform solution followed by recrystallization of the residue from benzene afforded 56.2 g

(8) I. Hajedorn, H. Etling, and K. E. Lichtel, *Ber.* **99**, 520 (1966).
(9) B. Zeeh *Syn.*, **2**, 65 (1969).
(10) R. Neidlein, *Ber.*, **97**, 3476 (1964).
(11) L. Malatesta and F. Bonati, "Isocyanide Complexes of Metals," Wiley, New York, N. Y., 1969, Chapter 3.

(79.6%) of a yellow solid, mp 190–193° (lit.[3] mp 191°). Subsequent recrystallization gave a product of mp 192–193°: uv max (EtOH) 282 nm (ε 19,000), 235 (23,800) and 205 (34,500); ir ($CHCl_3$) 1718 (sh), 1700, 1660, and 1640 $cm^{-1}$; nmr ($CDCl_3$) τ 2.80–2.60 (m, 9 H), 2.20–1.90 (m, 6 H); mass spectrum (70 eV) *m/e* (rel intensity) 393 (2.5), 137 (3), 129 (4), 125 (3), 123 (4), 112 (3), 111 (7).

*Anal.* Calcd for $C_{24}H_{15}N_3O_3$: C, 73.27; H, 3.82; N, 10.68. Found: C, 73.02; H, 4.10; N, 10.63.

**2,5-Diphenyloxazolo[5,4-d]pyrimidin-7-one[3] (4) and Methyl *N*-(4-Carbomethoxy-2-phenyloxazol-5-yl)benzimidate (5).**—Trimer **2**, 7.20 g, was stirred at ambient temperature for 16 hr in 70 ml of anhydrous methanol containing 2.0 g of sodium methoxide. The presence of methyl benzoate in the reaction mixture was shown by vpc analysis. The mixture was filtered and 4.28 g (75%) of the sodium salt of **4** was obtained after washing with methanol and drying. The sodium salt was converted to **4**, mp 376–379° (lit.[3] mp 365°), in quantitative yield by stirring in 50% aqueous acetic acid: **4** was too insoluble to obtain an nmr spectrum; ir (KBr) 3240, 3200 (NH) and 1685 $cm^{-1}$ (C=O); mass spectrum (70 eV) *m/e* (rel intensity) 289 (100), 187 (10), 186 (81), 115 (91), 105 (54), 104 (15).

*Anal.* Calcd for $C_{17}H_{11}N_3O_3$: C, 70.58; H, 3.83; N, 14.53. Found: C, 70.72; H, 3.89; N, 14.39.

The initial filtrate deposited 0.70 g (14.7%) of **5** as yellow crystals, mp 110–113°, upon standing, which were pure by tlc. Recrystallization from cyclohexane afforded an analytical sample: mp 113–114°; ir ($CHCl_3$) 1730 and 1650 $cm^{-1}$; nmr ($CDCl_3$) τ 6.30 (s, 3 H), 5.82 (s, 3 H), 2.70–2.50 (m, 8 H), and 2.10–1.85 (m, 2 H); mass spectrum *m/e* (rel intensity) 336 (100), 207 (15), 202 (8), 174 (2), 162 (6), 146 (3), 105 (21).

*Anal.* Calcd for $C_{19}H_{16}N_2O_4$: C, 67.84; H, 4.80; N, 8.33. Found: C, 68.16; H, 4.54; N, 8.29.

***N*-(4-*N*-Benzoylcarboxamido-2-phenyloxazol-5-yl)benzamide (6).**—This compound was prepared according to the procedure[8] of Diels and Stein. Thus, 20 g of **2** was heated 15 min at 80–90° in 300 ml of 50% aqueous acetic acid to afford a quantitative yield of pure **6** after collecting and drying: mp 186–188° (lit.[3] 187–188°); uv max (EtOH) 283 nm (ε 20,700), 238 (30,000), 206 (33,000); ir ($CHCl_3$) 3390, 3320, 1720, 1690, 1685, and 1660 $cm^{-1}$; nmr ($CDCl_3$) τ 2.70–2.30 (m, 9 H), 2.10–1.80 (m, 6 H), 0.00 (s, 1 H), and −0.04 (s, 1 H) (the latter two absorptions collapsed with $D_2O$); mass spectrum *m/e* (rel intensity) 411 (6.3), 292 (3.5), 291 (2.7), 290 (9.7), 188 (2.5), 121 (9.8), 115 (3.0), 105 (100), 104 (5).

***N*-(4-Carboxamido-2-phenyloxazol-5-yl)benzamide (7).**—Compound **6**, 18.0 g, was refluxed for 3 hr in a solution of methanolic sodium methoxide prepared from 2.80 g of sodium in 50 ml of methanol. The mixture was concentrated, acidified with 50% aqueous acetic acid, warmed to 80° for 5 min, and cooled to room temperature, and the resulting product was collected and recrystallized from ethanol affording 5.16 g (86.2%) of **7**: mp 210–211° (lit.[2] mp 208–210°); uv max (MeOH) 283 nm (ε 20,000) and 207 (26,300); ir (KBr) 3460, 3420, 3325, 3260, 1695, 1670 $cm^{-1}$; nmr (DMSO-$d_6$) τ 2.5–2.0 (m, 8 H), 2.0–1.8 (m, 4 H), and −1.0 (s, 1 H) (two H at 2.5–2.0 and that at −1.0 are exchangeable with $D_2O$); mass spectrum *m/e* (rel intensity) 307 (100), 105 (100), 89 (4), 77 (36).

*Anal.* Calcd for $C_{17}H_{13}N_3O_3$: C, 66.44; H, 4.26. Found: C, 66.64; H, 4.45.

**5-Benzamido-4-cyano-2-phenyloxazole (8) and *N*-(4-Cyano-2-phenyloxazol-5-yl)benzimidoyl Chloride (9).**—Carboxamide **7**, 6.51 g, was suspended in 50 ml of stirred phosphorus oxychloride and heated for 50 min at 48–53°. The mixture was cooled to room temperature affording 1.25 g (19.2%) of starting material **7**. Concentration of the filtrate gave 4.1 g (67%) of **8** after washing with water and drying: mp 215–216°; uv max (EtOH) 293 nm (ε 28,200) and 208 (27,600); ir ($CHCl_3$) 3420, 2240, and 1700 $cm^{-1}$; nmr (DMSO-$d_6$) τ 2.45–2.20 (m, 6 H), 2.10–1.80 (m, 4 H), and −1.8 to 2.2 (m, 1 H); mass spectrum *m/e* (rel intensity) 289 (10), 105 (100), and 77 (6).

*Anal.* Calcd for $C_{17}H_{11}N_3O_2$: C, 70.58; H, 3.83; N, 14.53. Found: C, 70.33; H, 3.78; N, 14.33.

Chromatography of the above filtrate on silica gel yielded ~0.50 g of **9**, mp 140–140.5°, upon elution with 9:1 chloroform–ethyl acetate, extraction with ether, and recrystallization from heptane: ir ($CHCl_3$) 2270 and 1640 $cm^{-1}$; mass spectrum *m/e* (rel intensity) 309 (34), 308 (20), 307 (100), 228 (31), 227 (15), 226 (95), 192 (18), 169 (52), 141 (36).

*Anal.* Calcd for $C_{17}H_{10}N_3OCl$: C, 66.30; H, 3.25; N, 13.65. Found: C, 66.58; H, 3.71; N, 13.33.

**5-Benzamido-4,6-dihydroxy-2-phenylpyrimidine (11).**—4,6-Dihydroxy-5-nitro-2-phenylpyrimidine,[7] 2.80 g, was suspended in 50 ml of acetic acid containing 300 mg of 10% palladium on charcoal and hydrogenated at 35 psi for 2 hr at ambient temperature. The mixture was treated with 75 ml of DMF to dissolve the white precipitate and filtered through Celite and the filtrate was concentrated at reduced pressure. The resulting solid was washed with ethanol and dried to give 1.1 g of a red-tinged solid. The product was dissolved in 25 ml of concentrated HCl and a small amount of insoluble solid was filtered off. The filtrate was diluted with 150 ml of water and carefully neutralized to pH 6.5 with sodium hydroxide at which point the off-white crystalline product precipitated. The product was collected, washed with water, and dried under vacuum over $P_2O_5$ at 80° for 1 hr. The amine weighed 0.65 g (37.2%) and melted at 245–248° dec. The amine became colored upon standing in the light at room temperature [ir (Nujol) 3450, 3325, 3225, 3100–2600, 1660 $cm^{-1}$].

The amine, 200 mg, was dissolved in 2 ml of pyridine and treated with 180 mg (20% excess) of benzoyl chloride. A voluminous precipitate formed after 2 min at ambient temperature. The mixture was poured into 25 ml of water after 20 min and collected. The solid was washed with water and then methanol and dried under vacuum over $P_2O_5$ giving 200 mg (66%) of **11**, mp 328–330° dec. An analytical sample, mp 329–330° dec, was prepared by recrystallization from aqueous DMF: ir (Nujol) 3350, 1645, and 1620 $cm^{-1}$; mass spectrum *m/e* (rel intensity) 307 (61), 289 (28), 203 (12), 188 (19), 122 (17), 105 (100), and 77 (21).

*Anal.* Calcd for $C_{17}H_{13}N_3O_3$: C, 66.44; H, 4.26; N, 13.68. Found: C, 66.50; H, 4.43; N, 13.40.

**2,5-Diphenyloxazolo(5,4-*d*]pyrimidin-7-one (4) by Cyclization of 5-Benzamido-4,6-dihydroxy-2-phenylpyrimidine (11).**—Benzamide **11**, 100 mg, was suspended in 5 ml of phosphorus oxychloride and heated at reflux for 1.5 hr. The reaction mixture was cooled and a white solid precipitated. It was collected and washed with ethanol and dried at 95° under vacuum giving 28 mg of pure **4**, mp 376–378° dec. Concentration of the filtrate gave a clear oil which yielded an additional 35 mg of **4** (combined crude yield 67%) which was contaminated by a trace of 7-chloro-2,5-diphenyloxazolo[5,4-*d*]pyrimidine (**12**) as indicated by tlc. Compound **4** thus obtained was identical (ir, mass spectrum, $R_f$ on tlc, and mixture melting point) with **4** obtained from treatment of **2** with sodium methoxide followed by acidification.

*Anal.* Calcd for $C_{17}H_{11}N_3O_2$: C, 70.58; H, 3.83; N, 14.53. Found: C, 70.55; H, 4.02; N, 14.58.

**7-Chloro-2,5-diphenyloxazolo[5,4-*d*]pyrimidine (12).**—2,5-Diphenyloxazolo[5,4-*d*]pyrimidin-7-one (**4**), 13.2 g, *N*,*N*-diethylaniline, 6.80 g, and phosphorus oxychloride, 50 ml, were refluxed for 16 hr. The phosphorus oxychloride was removed by distillation at reduced pressure and the residue was taken up in methylene chloride. The resulting solution was washed with 5% hydrochloric acid, water, 5% aqueous sodium bicarbonate, and water and dried ($Na_2SO_4$). Filtration and removal of the solvent gave an oil which solidified upon trituration with petroleum ether affording 14.90 g of crude **12**, mp 195–197°. Successive recrystallizations from cyclohexane and ethyl acetate yielded 8.60 g (61.5%) of pure **12**: mp 209–211°; uv max (EtOH) 399 nm (ε 14.000), 326 (22,000), 256 (5,400), and 209 (14,800); ir (Nujol) 1620, 1600 $cm^{-1}$; nmr ($CDCl_3$) τ 2.5–2.3 (m, 6 H), 1.7–1.5 (m, 4 H); mass spectrum, *m/e* (rel intensity) 309 (34), 307 (100), 168 (15), 141 (25), 105 (17), 103 (39), and 89 (48).

*Anal.* Calcd for $C_{17}H_{10}N_3OCl$: C, 66.40; H, 3.25; N, 13.65. Found: C, 66.29; H, 3.00; N, 13.34.

**7-*p*-Toluoylimino-2,5-di-*p*-tolyloxazolo[5,4-*d*][1,3]oxazine (13).**—According to the procedure for compound **2**, from *p*-toluoyl bromide (39.0 g), silver cyanide (41.0 g), and ether (400 ml) there was obtained 22.9 g (81%) of **13**: mp 216–216.5°: ir (Nujol) 1730, 1680, 1625 $cm^{-1}$; nmr ($CDCl_3$) τ 7.58 (s, 9 H), 2.90–2.60 (m, 6 H), 2.10–1.80 (m, 6 H); mass spectrum *m/e* (rel intensity) 435 (100), 310 (8), 129 (7), 119 (53).

*Anal.* Calcd for $C_{27}H_{21}N_3O_3$: C, 74.47; H, 4.86; N, 9.65. Found: C, 74.07; H, 4.61; N, 9.64.

***N*-(4-*N*-*p*-Toluoylcarboxamido-2-*p*-tolyloxazol-5-yl)-*p*-toluamide (17).**—By the procedure used to prepare compound **6**, there

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 ($CDCl_3$) $\tau$ 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 $D_2O$), −0.05 (S, 1 H, exchanges rapidly with $D_2O$); mass spectrum exhibits highest peak at *m/e* 334 ($p^+ - CH_3C_6H_4CO$).

*Anal.* Calcd for $C_{27}H_{23}N_3O_4$: 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 ($CF_3CO_2H$) $\tau$ 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 $C_{19}H_{15}N_3O_2$: 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]

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9,10-Dihydrophenanthrene reacts with $S_4N_4$, 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 $S_4N_4$ 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 $S_4N_4$ 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, $S_4N_4$, 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 $S_4N_4$ 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 $S_4N_4$ and paraffins we have focused on the effects of the aryl substituents and examined the reactivity of $S_4N_4$ toward 9,10-dihydrophenanthrene and tetrahydronaphthalene. These reactions afforded complex mixtures of products, always containing ammonia and elemental sulfur.

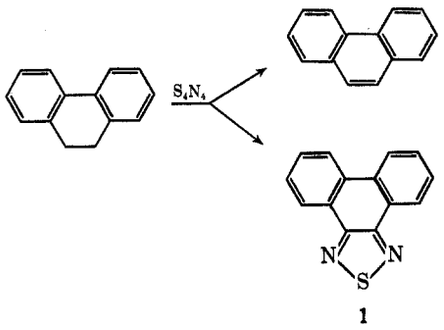
The reaction of $S_4N_4$ with 9,10-dihydrophenanthrene, carried out in boiling xylene, gave a mixture of phenanthrene and phenanthro[9,10-*c*]-1,2,5-thiadiazole[4,5] (**1**) in the ratio 7.6:1 (Scheme I).

The reaction between $S_4N_4$ 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]

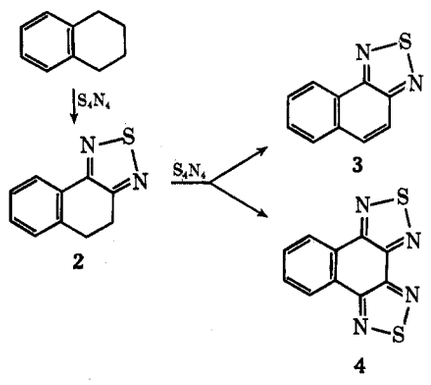
Compound **1**, on reaction with Grignard reagent followed by hydrolysis, was transformed into 9,10-phenanthrenedione in good yield. This reaction shows that the sulfur atom of **1**, analogous to the behavior of

SCHEME I




1

SCHEME II




2 3 4

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