# Ring Opening Reactions of 6*H*-Anthra[1,9-*cd*]isoxazol-6-ones and Related Compounds

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Nucleophilic attack of anthra[1,9-*cd*]isoxazol-6-ones, and of anthra[1,9-*cd*:5,10-*c'd'*]isoxazole by various sulfoxides, triphenyl phosphine, and aliphatic or aromatic phosphites proceeded with cleavage of the nitrogen-oxygen bond of the isoxazole ring. This method provided ready access to substituted anthraquinones bearing sulfoximido-, triphenylphosphazo-, and dialkyl(aryl)phosphoramidic groups attached to the 1- and the 1,5-positions of the anthraquinone system. The structures of the newly synthesized anthraquinone derivatives were supported by analytical and spectral data. 1-*S*,*S*-dimethyl-*N*-(5-benzamidoanthraquinon-1-yl)-sulfoximide yielded in 90% sulfuric acid the 1-amino-5-sulfoximido anthraquinone without hydrolyzing the sulfoximido group.

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## Introduction

During the course of an investigation of the reactivity of 6*H*-anthra[1,9-*cd*]isoxazol-6-ones towards nucleophiles, it became apparent that the predominant reaction occurring was ring opening of the isoxazole moiety, with concurrent formation of the anthraquinone system. The overall reaction preceeded to completion usually within a short period of time, furnishing new substituted anthraquinones in high yield.

We were interested in synthesizing derivatives bearing sulfoximido-, triphenylphosphinimino-, and dialkyl(aryl)-phosphoramidic groups attached to the 1- and the 1,5-positions of anthraquinone.

## 6*H*-Anthraisoxazolones and Anthrabisisoxazoles.

The synthesis of 6*H*-anthra[1,9-*cd*]isoxazol-6-ones was readily achieved by thermal nitrogen extrusion from 1-azidoanthraquinones, following generally the procedures reported earlier by several authors (1,2). The products obtained by these authors were presumed to possess the 6*H*-anthra[1,9-*cd*]isoxazol-6-one structure, the evidence resting largely on the isolated 1-aminoanthraquinones formed by the reductive cleavage of the isoxazole ring.

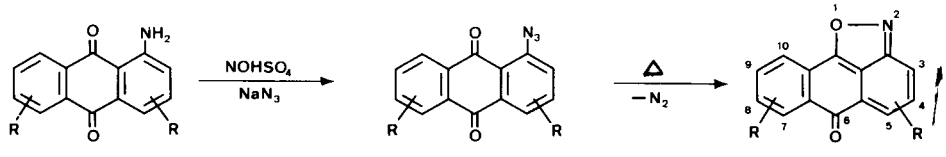
Recently this method was used again (3) to synthesize a large number of anthra[1,9-*cd*]isoxazol-6-ones substituted by phenylamino groups in the 3- or the 5-positions, respectively.

The 1-azidoanthraquinones required for our investigations were prepared by diazotation of the respective 1-aminoanthraquinones (**1-11**, Scheme 1) either by adding sodium nitrite to a solution of the amine in concentrated sulfuric acid or by addition of nitrosyl sulfuric acid to the amine solution, the latter method being used generally for diazotation of chloro- or nitro-substituted 1-aminoanthraquinones.

The respective 1-anthraquinonediazonium hydrogensulfates thus obtained precipitated upon dilution with water, were filtered from the solution and used moist for the subsequent reaction with an aqueous solution of sodium azide, furnishing 1-azidoanthraquinones.

The 1,5-bis(azidoanthraquinone) (**26**) was prepared essentially according to a known method (1), first by

Scheme 1



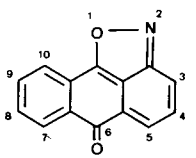

1−11

1 R = H
2 R = 2−$CH_3$
3 R = 2−Br
4 R = 4−Cl
5 R = 5−Cl
6 R = 2,4−$Cl_2$
7 R = 5,8−$Cl_2$
8 R = 4−$OCH_3$
9 R = 4−$NO_2$
10 R = 5−$NO_2$
11 R = 5−NH−CO−$C_6H_5$

14−24

14 R = H
15 R = 3−$CH_3$
16 R = 3−Br
17 R = 5−Cl
18 R = 7−Cl
19 R = 3,5−$Cl_2$
20 R = 7,10−$Cl_2$
21 R = 5−$OCH_3$
22 R = 5−$NO_2$
23 R = 7−$NO_2$
24 R = 7−NH−CO−$C_6H_5$

Table 1
Substituted Anthra[1,9-*cd*]isoxazoles



| Compound No. | R | Reaction Solvent | Reaction Temp °C | Reaction Time, Hours | MP °C (Solvent) | Yield % | Formula | Analysis, % | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **14** | H | Toluene | 80 | 3 | 300 (Xylene) (a) | 87 | $C_{14}H_7NO_2$ | Calcd. | C, 76.01 | H, 3.19 | — | N, 6.33 |
| | | | | | | | | Found | C, 76.22 | H, 3.42 | — | N, 6.40 |
| **15** | 3-$CH_3$ | Dichlorobenzene (e) | 155 | 0.5 | 199-200 (Toluene) | 67.8 | $C_{15}H_9NO_2$ | Calcd. | C, 76.59 | H, 3.86 | — | N, 5.96 |
| | | | | | | | | Found | C, 76.51 | H, 4.09 | — | N, 6.01 |
| **16** | 3-Br | Xylene | 130 | 1.5 | 261-263 (Xylene) | 51.3 | $C_{14}H_6BrNO_2$ | Calcd. | C, 56.03 | H, 2.02 | Br, 26.63 | N, 4.67 |
| | | | | | | | | Found | C, 56.28 | H, 2.09 | Br, 26.71 | N, 4.51 |
| **17** | 5-Cl | Dichlorobenzene | 150 | 1 | 216-217 (Xylene) (a) | 83 | $C_{14}H_6ClNO_2$ | Calcd. | C, 65.77 | H, 2.36 | Cl, 13.87 | N, 5.48 |
| | | | | | | | | Found | C, 65.68 | H, 2.53 | Cl, 13.86 | N, 5.54 |
| **18** | 7-Cl | Toluene | 80 | 1 | 246 (Xylene) (b) | 78.6 | $C_{14}H_6ClNO_2$ | Calcd. | C, 65.77 | H, 2.36 | Cl, 13.87 | N, 5.48 |
| | | | | | | | | Found | C, 65.91 | H, 2.57 | Cl, 13.91 | N, 5.56 |
| **19** | 3,5-$Cl_2$ | Toluene | 75 | 3.5 | 207-208 (Xylene) | 91 | $C_{14}H_5Cl_2NO_2$ | Calcd. | C, 57.96 | H, 1.74 | Cl, 24.44 | N, 4.83 |
| | | | | | | | | Found | C, 58,21 | H, 1.94 | Cl, 24.14 | N, 4.85 |
| **20** | 7,10-$Cl_2$ | Toluene | 95 | 2.5 | 257-258 (Toluene) | 40.2 (d) | $C_{14}H_5Cl_2NO_2$ | Calcd. | C, 57.96 | H, 1.74 | Cl, 24.44 | N, 4.83 |
| | | | | | | | | Found | C, 57.83 | H, 1.86 | Cl, 24.65 | N, 4.80 |
| **21** | 5-$OCH_3$ | Xylene | 135 | 1 | 226-228 (Xylene) (b) | 35.4 | $C_{15}H_9NO_3$ | Calcd. | C, 71.71 | H, 3.61 | — | N, 5.58 |
| | | | | | | | | Found | C, 71.62 | H, 3.72 | — | N, 5.62 |
| **22** | 5-$NO_2$ | Toluene | 75 | 5 | 250 (dec) (Dichlorobenzene) (c) | 74.4 | $C_{14}H_6N_2O_4$ | Calcd. | C, 63.17 | H, 2.27 | — | N, 10.52 |
| | | | | | | | | Found | C, 63.40 | H, 2.38 | — | N, 10.78 |
| **23** | 7-$NO_2$ | Toluene | 80 | 3 | 250 (Xylene) | 86 | $C_{14}H_6N_2O_4$ | Calcd. | C, 63.17 | H, 2.27 | — | N, 10.52 |
| | | | | | | | | Found | C, 62.98 | H, 2.51 | — | N, 10.39 |
| **24** | 7-NH-CO-$C_6H_5$ | Toluene | 82 | 4 | 249 (dec) (Xylene) | 71.7 | $C_{21}H_{12}N_2O_3$ | Calcd. | C, 74.11 | H, 3.56 | — | N, 8.23 |
| | | | | | | | | Found | C, 74.46 | H, 3.83 | — | N, 8.09 |

(a) Lit (1a). (b)) Lit (2b) No physical data are reported. (c) Lit (1b. (d) Yield after recrystallization. (e) Dimethyl sulfoxide was used alternatively.

diazotation of 1,5-diaminoanthraquinone (**12**) with nitrosyl sulfuric acid (2a,4), followed by reaction of the isolated anthraquinone bis(diazonium hydrogensulfate) (**13**) (4) with an aqueous solution of sodium azide (Scheme 2).

All the anthraquinone derivatives having azido groups in the 1- or the 1,5-positions, respectively, are rather unstable compounds, tending to release nitrogen either readily in solution during attempts to recrystallize them, or slowly in the crystalline state (1,2). Therefore, the solid cake of moist 1-azidoanthraquinones or of 1,5-bisazidoanthraquinone was slurried in toluene and subsequently heated to a temperature of 80-90° where upon nitrogen evolution commenced at a steady rate. The remaining water did not interfere with the reaction as far as the yields or the purity of the products were concerned, and it was finally azeotropically removed from the solution by distillation of a part of the toluene.

The reaction may be monitored by the evolution of nitrogen or by disappearance of the intense azide absorption at 2120 $cm^{-1}$ in the infrared spectrum. The time required for the complete decomposition of the various azidoanthraquinones varied between 1-4 hours at 80-150°.

A series of 6*H*-anthra[1,9-*cd*]isoxazol-6-ones (**14-24**) were prepared following this procedure (Scheme 1) and the physical and analytical data are compiled in Table 1.

The same reaction sequence and preparative technique was applied also to the preparation of anthra[1,9-*cd*:5,10-*c'd'*]bisisoxazole (**25**) (Scheme 2).

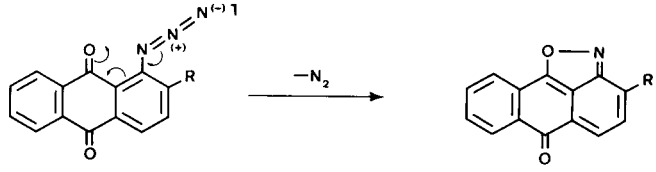
A convenient alternate procedure for the direct preparation of **25** utilized the nucleophilic displacement of the two nitro groups of 1,5-dinitroanthraquinone (**27**) by azide anion. Reaction with sodium azide in dimethylformamide at 40° and subsequent nitrogen extrusion performed in a "one pot reaction" gave **25** in a yield of 80%. In principle, this reaction is also amenable to the synthesis of 5-nitroanthraisoxazolone by reacting only one mole of sodium azide with 1,5-dinitroanthraquinone. However, the product always contained, beside **25**, various amounts of mono- and bis-azide and starting material, and separation of this mixture became rather unattractive for synthetic purposes.

Compounds **14** and **25**, respectively, have also been syntheized earlier by hypobromite oxidation of 1-amino- and 1,5-diaminoanthraquinones, respectively (2b).

Reaction temperatures and times have been listed in table 1, although they bear little significance to mechanistic considerations, since they are only indicative of convenient reaction times.

During the pyrolytic decomposition of the 1-azidoanthraquinones, we have not generally observed any products which could be associated with arylnitrene formation, *i.e.*, azo compounds, anilines, insertion products and polymers, indicating that the incipient nitrenes formed by the nitrogen extrusion may be bridged by the carbonyl group thus preventing the intrusion of other reaction mechanisms, as shown in Scheme 3 (6a-c).

**Scheme 3**



This view is consonant with previous suggestions postulating a concerted $\pi$-bond reorganization, which provides the driving force in this reaction, as pictured in Scheme 3. Such a pericyclic mechanism would become effective when the participating orbitals of the 1-azido and the keto-group lie essentially in the plane of the anthraquinone system.

The higher temperature of pyrolyis, or extended reaction times required for compounds **15, 16, 19** reflects the

**Scheme 2**

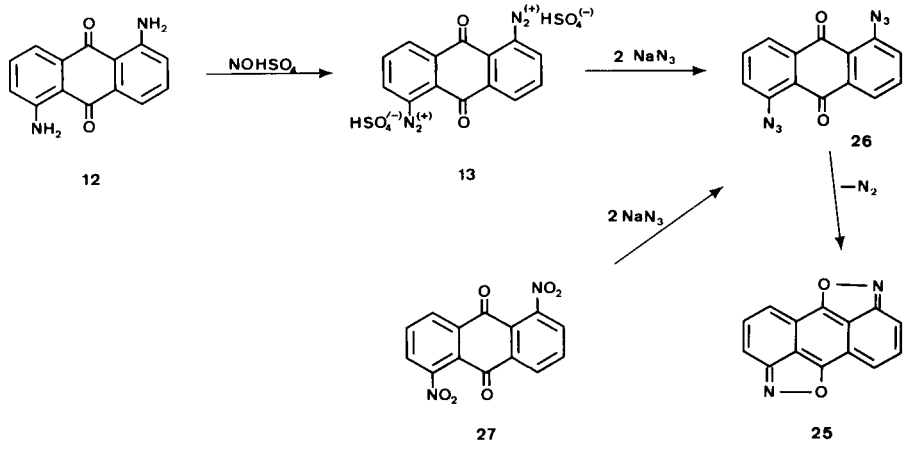
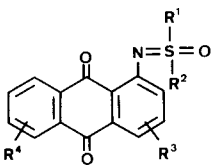


Table 2

Substituted 1-*S*,*S*-Dialkyl(aryl)*N*-(anthraquinon-1-yl)sulfoximides



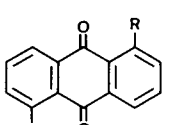
| Compound No. | $R^1$ | $R^2$ | $R^3$ | MP °C | Crytallization solvent | Yield % | Formula | Analysis, % | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **28** | $CH_3$ | $CH_3$ | H | 150-151 | Toluene | 81.2 (a) | $C_{16}H_{13}NO_3S$ | Calcd. | C, 64.20 | H, 4.38 | — | N, 4.68 S, 10.71 |
| | | | | | | | | Found | C, 64.52 | H, 4.45 | — | N, 4.75 S, 10.47 |
| **29** | $CH_3$ | $CH_3$ | 4-Cl | 185-187 | Xylene | 71.3 (a) | $C_{16}H_{12}ClNO_3S$ | Calcd. | C, 57.58 | H, 3.63 | Cl, 10.62 | N, 4.20 S, 9.61 |
| | | | | | | | | Found | C, 57.88 | H, 3.64 | Cl, 10.60 | N, 4.20 S, 9.56 |
| **30** | $CH_3$ | $CH_3$ | 5-Cl | 162.5-164 | Xylene | 72.8 (a) | $C_{16}H_{12}ClNO_3S$ | Calcd. | C, 57.58 | H, 3.63 | Cl, 10.62 | N, 4.20 S, 9.61 |
| | | | | | | | | Found | C, 57.79 | H, 3.78 | Cl, 10.71 | N, 4.31 S, 9.61 |
| **31** | $CH_3$ | $CH_3$ | 5,8-$Cl_2$ | 196-198 | Xylene | 85.6 | $C_{16}H_{11}Cl_2NO_3S$ | Calcd. | C, 52.19 | H, 3.01 | Cl, 19.26 | N, 3.81 S, 8.71 |
| | | | | | | | | Found | C, 52.31 | H, 2.98 | Cl, 19.53 | N, 3.61 S, 8.36 |
| **32** | $CH_3$ | $CH_3$ | 4-$OCH_3$ | 197-199 | Dichlorobenzene | 88.1 | $C_{17}H_{15}NO_4S$ | Calcd. | C, 62.00 | H, 4.59 | — | N, 4.25 S, 9.74 |
| | | | | | | | | Found | C, 62.00 | H, 4.29 | — | N, 4.32 S, 9.38 |
| **33** | $CH_3$ | $CH_3$ | 4-$NO_2$ | 261-262 | Dichlorobenzene | 94.8 | $C_{16}H_{12}N_2O_5S$ | Calcd. | C, 55.81 | H, 3.52 | — | N, 8.14 S, 9.31 |
| | | | | | | | | Found | C, 55.92 | H, 3.54 | — | N, 8.21 S, 9.29 |
| **34** | $CH_3$ | $CH_3$ | 5-$NO_2$ | 234-235 | Dichlorobenzene | 100 | $C_{16}H_{12}N_2O_5S$ | Calcd. | C, 55.81 | H, 3.52 | — | N, 8.14 S, 9.31 |
| | | | | | | | | Found | C, 55.76 | H, 3.59 | — | N, 8.22 S, 9.07 |
| **35** | $CH_3$ | $CH_3$ | 5-NH-C-$C_6H_5$ (O) | 217-220 | Dichlorobenzene | 89.7 | $C_{23}H_{18}N_2O_4S$ | Calcd. | C, 66.02 | H, 4.34 | — | N, 6.69 S, 7.66 |
| | | | | | | | | Found | C, 66.19 | H, 4.48 | — | N, 6.61 S, 7.32 |
| **36** | $C_4H_9$ | $C_4H_9$ | H | 78-79 | Petrolether | 35 | $C_{22}H_{25}NO_3S$ | Calcd. | C, 68.90 | H, 6.57 | — | N, 3.65 S, 8.36 |
| | | | | | | | | Found | C, 69.10 | H, 6.71 | — | N, 3.62 S, 8.12 |
| **37** | $C_4H_9$ | $C_4H_9$ | 4-$NO_2$ | 149-150.5 | Toluene | 79.4 | $C_{22}H_{24}N_2O_5S$ | Calcd | C, 61.67 | H, 5.65 | — | N, 6.54 S, 7.48 |
| | | | | | | | | Found | C, 61.82 | H, 5.71 | — | N, 6.43 S, 7.29 |
| **38** | $CH_3$ | $C_6H_5$ | H | 170-171 | Toluene | 64.4 (a) | $C_{21}H_{15}NO_3S$ | Calcd. | C, 69.79 | H, 4.18 | — | N, 3.88 S, 8.87 |
| | | | | | | | | Found | C, 69.61 | H, 4.21 | — | N, 3.91 S, 8.68 |
| **39** | $CH_3$ | $C_6H_5$ | 4-Cl | 202-204 | Dichlorobenzene | 69.5 (a) | $C_{21}H_{14}ClNO_3S$ | Calcd. | C, 63.75 | H, 3.56 | Cl, 8.96 | N, 3.54 S, 8.10 |
| | | | | | | | | Found | C, 63.62 | H, 3.69 | Cl, 9.32 | N, 3.41 S, 7.82 |
| **40** | $CH_3$ | $C_6H_5$ | 5-Cl | 193-193.5 | Dichorobenzene | 55.6 (a) | $C_{21}H_{14}ClNO_3S$ | Calcd. | C, 63.75 | H, 3.56 | Cl, 8.96 | N, 3.54 S, 8.10 |
| | | | | | | | | Found | C, 63.51 | H, 3.69 | Cl, 9.29 | N, 3.61 S, 8.31 |
| **41** | $CH_3$ | $C_6H_5$ | 5,8-$Cl_2$ | 155-157 | Dichlorobenzene | 53.5 (a) | $C_{21}H_{13}Cl_2NO_3S$ | Calcd. | C, 58.62 | H, 3.05 | Cl, 16.48 | N, 3.36 S, 7.45 |
| | | | | | | | | Found | C, 58.38 | H, 3.02 | Cl, 16.78 | N, 3.28 S, 7.17 |
| **42** | $CH_3$ | $C_6H_5$ | 4-$NO_2$ | 262.5-264 | Dichlorobenzene | 96.8 | $C_{21}H_{14}N_2O_5S$ | Calcd. | C, 62.06 | H, 3.47 | — | N, 6.89 S, 7.89 |
| | | | | | | | | Found | C, 61.87 | H, 3.53 | — | N, 6.89 S, 7.51 |
| **43** | $CH_3$ | $C_6H_5$ | 5-$NO_2$ | 238-239 | Dichlorobenzene | 54 (a) | $C_{21}H_{14}N_2O_5S$ | Calcd. | C, 62.06 | H, 3.47 | — | N, 6.89 S, 7.89 |
| | | | | | | | | Found | C, 62.28 | H, 3.58 | — | N, 6.91 S, 7.52 |
| **44** | $C_6H_5$ | $C_6H_5$ | H | 237-239 | Xylene | 82.7 | $C_{26}H_{17}NO_3S$ | Calcd. | C, 73.74 | H, 4.05 | — | N, 3.31 S, 7.57 |
| | | | | | | | | Found | C, 74.01 | H, 4.31 | — | N, 3.42 S, 7.61 |

| | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **45** | $C_6H_5$ | $C_6H_5$ | 4-Cl | 235-237 | Dichlorobenzene | 88.5 (a) | $C_{26}H_{16}ClNO_3S$ | Calcd. | C, 68.19 | H, 3.52 | Cl, 7.74 | N, 3.06 | S, 7.00 |
| | | | | | | | | Found | C, 68.20 | H, 3.59 | Cl, 8.02 | N, 3.12 | S, 7.10 |
| **46** | $C_6H_5$ | $C_6H_5$ | 5-Cl | 256-258 | Dichlorobenzene | 77.6 (a) | $C_{26}H_{16}ClNO_3S$ | Calcd. | C, 68.19 | H, 3.52 | Cl, 7.74 | N, 3.06 | S, 7.00 |
| | | | | | | | | Found | C, 68.01 | H, 3.69 | Cl, 8.06 | N, 3.04 | S, 6.82 |
| **47** | $C_6H_5$ | $C_6H_5$ | 5,8-$Cl_2$ | 204.5-206.5 | Xylene | 87.4 | $C_{26}H_{15}Cl_2NO_3S$ | Calcd. | C, 63.42 | H, 3.07 | Cl, 14.40 | N, 2.85 | S, 6.51 |
| | | | | | | | | Found | C, 63.15 | H, 3.17 | Cl, 14.78 | N, 2.80 | S, 6.37 |
| **48** | $C_6H_5$ | $C_6H_5$ | 4-$OCH_3$ | 237.5-239 | Dichlorobenzene | 64.5 (a) | $C_{27}H_{19}NO_4S$ | Calcd. | C, 71.51 | H, 4.22 | — | N, 3.09 | S, 7.07 |
| | | | | | | | | Found | C, 71.28 | H, 4.39 | — | N, 3.11 | S, 6.88 |
| **49** | $C_6H_5$ | $C_6H_5$ | 4-$NO_2$ | 249-251 | Dichlorobenzene | 85.5 | $C_{26}H_{16}N_2O_5S$ | Calcd. | C, 66.66 | H, 3.44 | — | N, 5.98 | S, 6.84 |
| | | | | | | | | Found | C, 66.52 | H, 3.52 | — | N, 6.12 | S, 6.71 |
| **50** | $C_6H_5$ | $C_6H_5$ | 5-$NO_2$ | 275-276 | Dichlorobenzene | 90.8 | $C_{26}H_{16}N_2O_5S$ | Calcd. | C, 66.66 | H, 3.44 | — | N, 5.98 | S, 6.84 |
| | | | | | | | | Found | C, 66.71 | H, 3.51 | — | N, 6.01 | S, 6.91 |

(a) Yield after recrystallization.

Table 3

1,5-Disubstituted Anthraquinones by Ring Opening of Anthra[1,9-cd:5,10-c'd']bisisoxazole



| Compound No. | R | Reaction Solvent | Reaction Temp °C | MP °C | Yield % | Crystallization Solvent | Formula | | Analysis, % | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **51** | $(CH_3)_2S(O)=N-$ | Dimethyl Sulfoxide | 150-160 | 243-246 | 98.2 (a) | Toluene (b) | $C_{18}H_{18}N_2O_4S_2$ | Calcd. | C, 55.37 | H, 4.65 | N, 7.17 | S, 16.42 |
| | | | | | | | | Found | C, 55.49 | H, 4.54 | N, 7.39 | S, 16.57 |
| **52** | $(C_6H_5)_2S(O)=N-$ | Dichloro-benzene | 175 | >300 | 69.3 | Dichlorobenzene | $C_{38}H_{26}N_2O_4S_2$ | Calcd. | C, 71.45 | H, 4.10 | N, 4.39 | S, 10.04 |
| | | | | | | | | Found | C, 71.19 | H, 4.13 | N, 4.39 | S, 10.31 |
| **53** | $(C_6H_5)(CH_3)S(O)=N-$ | Dichloro-benzene | 175 | 251-252 | 44 | Dichlorobenzene | $C_{28}H_{22}N_2O_4S_2$ | Calcd. | C, 65.35 | H, 4.31 | N, 5.44 | S, 12.46 |
| | | | | | | | | Found | C, 65.24 | H, 4.41 | N, 5.41 | S, 12.13 |
| **60** | $(C_6H_5)_3P=N-$ | Xylene | 135 | >300 | 98 | Dichlorobenzene | $C_{50}H_{36}N_2O_2P_2$ | Calcd. | C, 79.14 | H, 4.78 | N, 3.69 | S, 8.16 |
| | | | | | | | | Found | C, 79.29 | H, 4.81 | N, 3.87 | S, 7.98 |
| **78** | $(CH_3O)_2P(O)-NH-$ | Toluene | 105 | 221-224 | 83.7 | Xylene | $C_{18}H_{20}N_2O_6P_2$ | Calcd. | C, 47.59 | H, 4.44 | N, 6.17 | S, 13.64 |
| | | | | | | | | Found | C, 47.85 | H, 4.39 | N, 6.20 | S, 13.66 |

(a) Prepared according to method B). (b) Ethyl cellosolve was used alternatively.

steric hindrance to the attainment of the planar transition state in the decomposition of the 2-methyl- or 2-halogen-1-azidoanthraquinones, an effect which has also been noted during a study of the pyrolysis of 6-chloro- and 6-methyl-2-nitro-phenylazides, respectively, and been attributed to the need for coplanarity between the azido-group and the assisting keto-group (7a-d).

The infrared spectra of the 6*H*-anthraisoxazol-6-ones show characteristic absorption bands of medium intensity due to the ring stretching mode at 1535-1564 $cm^{-1}$, which may be assigned to the isoxazole ring. The absorption pattern of the anthrabisisoxazole, however, is more instructive since there is no interference of the absorption due to the aromatic stretching mode. The spectrum of **25** shows absorption at 1535 $cm^{-1}$ for the heterocycle and the absorption at 1605 $cm^{-1}$ is assigned to the C=C bond.

All of the anthraisoxazol-6-ones show two absorption bands for the carbonyl frequencies at 1682-1662 $cm^{-1}$, in potassium bromide discs, the frequency separation between the bands lying in the range of 20 $cm^{-1}$.

Cleavage of the Isoxazole Ring.

The nitrogen-oxygen bond of the isoxazole ring can be cleaved by a variety of nucleophiles. They are prone to attack the nitrogen of the heterocyclic ring with subsequent cleavage of the bond between the two hetero atoms and concomitant formation of the quinone system.

Apart from the reductive cleavage of the heterocyclic ring which has already been described in the early literature (1,2), only very recently a ring opening reaction of 2-phenoxyanthraisoxazol-6-one with concurrent bond reorganization and formation of phthalylphenoxazines has been reported (8a).

Furthermore the synthesis of 1-amino-4-arylamino-anthraquinones has been described, whereby ring opening of the heterocyclic moiety in 5-chloroanthra[1,9-*cd*]isoxazol-6-one was achieved by heating the compound with anilines in dimethylformamide (8b) under reflux.

We now report in this paper reactions of 6*H*-anthra[1,9-*cd*]isoxazol-6-ones with a) alkyl- or arylsulfoxides, b) with triphenylphosphine and c) with trialkyl- or triarylphosphites, yielding the corresponding 1-substituted anthraquinones. Those anthraisoxazolones bearing either a methyl (**15**) or a chloro substituent (**19**) in the 3-position failed to undergo those ring opening reactions, which may very likely be attributed to the steric hindrance of these substituents.

Similar reactions could be performed using **25** which furnished 1,5-disubstituted anthraquinone derivatives bearing sulfur or phosphorus organic substitutents.

1-*S,S*-Dialkyl(aryl)*N*-(anthraquinon-1-yl)sulfoximides.

We were interested in synthesizing anthraquinoyl derivatives of sulfoximides, since this class of compounds is little known in the aromatic series, and the biological and herbicidal activity of this family of nitrogen-sulfur derivatives made these substance attractive subjects for synthetic study.

The reaction of organic azides with sulfoxides is known to yield sulfoximides. A survey of this versatile class of compounds is provided by the article of Kennewell and Taylor (9). The general routes for their preparation were described by trapping, with various sulfoxides, the nitrenes generated by photolyis, thermolytic or α-elimination reactions from appropriate precursors (9,10). Most papers have dealt with the synthesis of sulfoximides and trapping the generated nitrenes by the solvent, mostly dimethyl sulfoxide, to give *N*-arylsulfonylsulfoximides (9).

The ready accessibility of sulfimides by a variety of methods, followed by their subsequent oxidation with potassium permangante or with peracids provided a practical route to sulfoximides. A more recently described method used to oxidation of arylamines with a complex formed from dimethyl sulfoxide and *t*-butyl hypochlorite (11,12).

There are only scant reports describing the reaction of alkyl- or arylsulfoxides with azides having the azido group attached directly to the aromatic ring. Pentafluorophenyl azide (13) and 4-azidotetrafluoropyridine (14), respectively, provide two examples of compounds which liberated nitrogen when heated in dimethyl sulfoxide at elevated temperature to furnish modest yields of the corresponding *S,S*-dimethyl-*N*-aryl(pyridyl)-sulfoximides. Low yields of sulfoximides were also obtained from the reaction of tetrazolo[1,5]pyridines with dimethyl sulfoxide (15).

Cleavage of the nitrogen-oxygen bond of the isoxazole ring of the anthraisoxazolones occurred readily on heating compounds **14, 17, 18, 20-24** for a short period of time with an alkyl- or an arylsulfoxide, whereby sulfoximides **28-50** were obtained (Scheme 4). The physical and the analytical data are compiled in Table 2.

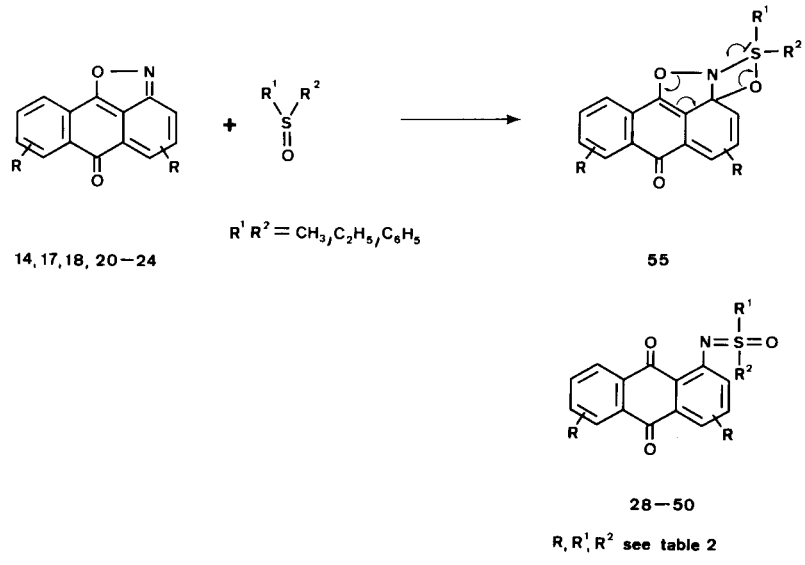
Two of the sulfoximides (**26, 51**) were also synthesized directly from the azides without isolating the anthraisoxazolones, by heating a suspension of the respective azide with dimethyl sulfoxide.

Only two compounds are recorded as example for higher aliphatic sulfoxides, in which dibutyl sulfoxide was used since extensive decompostion occurred on heating the isoxazolones with aliphatic sulfoxides having higher aliphatc substituents, to the required reaction temperature.

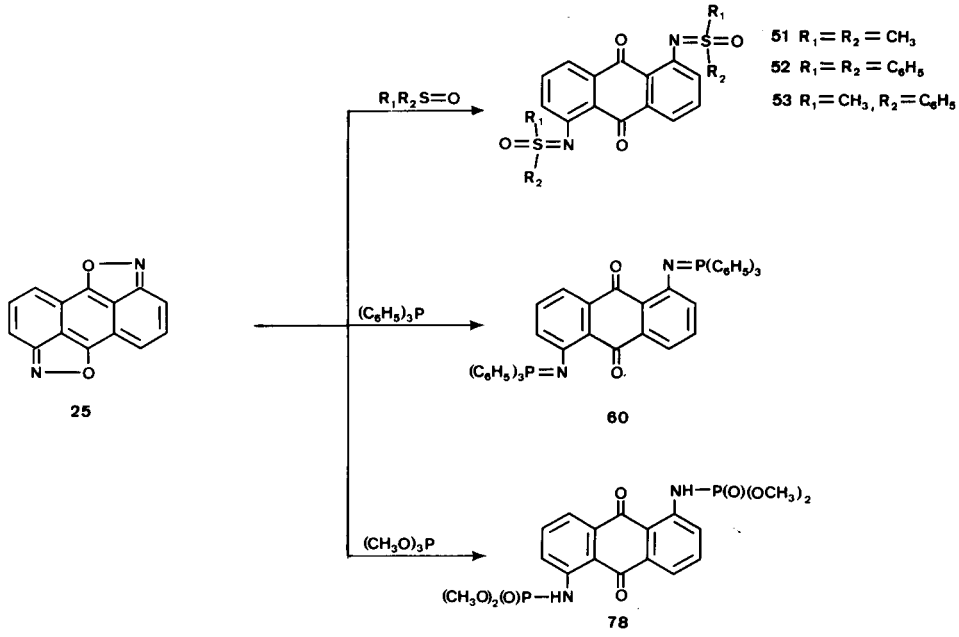
Diphenyl sulfoxide reacted with the anthraisoazolones much more slowly, and the reactions were preferably carried out in a solvent such as dichlorobenzene as otherwise considerable decomposition occured.

The anthrabisisoxazole (**25**) was reacted similarly with different substituted sulfoxides yielding the correspond-

Scheme 4




Scheme 5



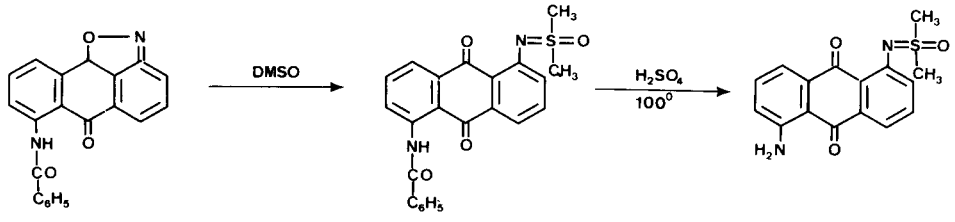

ing anthraquinon-1,5-diylsulfoximides (**51-53**) (Scheme 5). The physical and analytical data of these compounds are recorded in table 3.

Compounds **28-50** and **51-53**, respectively, formed dark yellow crystals which were recrystallized preferably from xylene or from dichlorobenzene.

The infrared spectra of the sulfoximides exhibited intense bands at 1250-1263 $cm^{-1}$ which were assigned to the stretching frequency of the N=S=O group, and in addition further characteristc bands were observed around 1170 $cm^{-1}$ and 1080-1100 $cm^{-1}$ (16) which are due to the sulfur-nitrogen stretching frequency (17).

The sulfur nitrogen bond of the anthraquinon-1-ylsulfoximides exhibited remarkable stability towards mineral acids or bases. For example, these compounds could be dissolved in 90% sulfuric acid and were reprecipitated unchanged by adding the acidic solution to water. This property of hydrolytic stability was successfully employed for the preparation of a 5-aminoanthraquinon-1-ylsulfoximide (**54**) (scheme 6). The reaction of 7-benzamido-anthraisoxazolone (**24**) with dimethyl sulfoxide furnished 1-*S*,*S*-dimethyl-*N*-(5-benzamidoanthraquinon-1-yl) sulfoximide (**35**), which underwent hydrolysis of the benzamido group on heating in 90% sulfuric acid, yielding **54**.

Scheme 6




24 35 54

Attempts to benzoylate the amino group of **54** with benzoylchloride in *N*-methylpyrrolidone failed, since 1,5-dibenzamidoanthraquinone was formed with extrusion of dimethyl sulfoxide.

Although the cleavage of the nitrogen-oxygen bond of the isoxazole ring in this particular structural type of a condensed aromatic system proved generally applicable, there were notable exceptions of anthraisoxazolones bearing substitutuents attached to the C-3 position of the molecule. Heating 1-azido-2-methyl- and 1-azido-2,4-dichloroanthraquinone in dimethyl sulfoxide yielded only the corresponding anthraisoxazole **15** and **19**, respectively, both of which proved stable under the conditions applied, and the reaction failed to proceed further with ring opening and formation of the corresponding sulfoximido compounds.

The ring cleavage reaction may be envisaged as proceeding *via* a four centered transition state or intermediate (**55**) (Scheme 4) which is formally analogous to that accepted for the Wittig-reaction. This mechanism would account for the failure of the 3-substituted anthraisoxazolones to undergo a ring opening reaction because the reagent cannot approach the isoxazole ring from a sterically favourable position to form the postulated intermediate **55**.

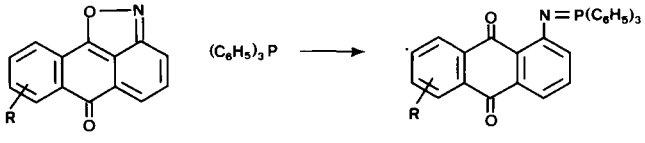
The exclusive formation of 1-sulfoximidoanthraquinones directly from 1-azidoanthraquinones is presumed to proceed via the isolable anthraisoxazolones, and may, therefore, represent a singular case of an azide decomposition with an entirely different mechanism compared with the one postulated for the formation of structural analogous in the benzene or in the pyridine series (13,14). This aspect is further supported by the failure of 2-azidoanthraquinone to react with either dimethyl sulfoxide, or with one of the organic phosphorus compounds under nitrogen extrusion on heating to 130° for a period of 18 hours. The only identifiable product was 2-aminoanthraquinone. Likewise, 1-azido-4-nitrobenzene proved unreactive towards dimethyl sulfoxide.

*N*-(Anthraquinon-1-yl)triphenylphosphazenes.

The similarity between the thermal reaction of aromatic nitrenes with nucleophiles and with that of anthraisoxazolones with such species is further demonstrated by their reactivity towards triphenylphosphine.

When a suspension of an anthraisoxazolone (**14, 18, 20, 23**) in toluene was heated with triphenylphosphine, the isoxazole ring was opened with formation of *N*-(anthraquinon-1-yl)triphenylphosphazenes (**56-59**), (Scheme 7, Table 4). The compounds were obtained as dark orange or red colored crystals. The anthrabisisoxazolone (**25**) reacted similarly forming the 1,5-disubstituted anthraquinone derivative (**60**) (Scheme 5, Table 3).

Scheme 7




| 14, 18, 20, 23 | | 56–59 | |
|---|---|---|---|
| 14 | R = H | 56 | R = H |
| 18 | R = 7–Cl | 57 | R = 5–Cl |
| 20 | R = 7,10–$Cl_2$ | 58 | R = 5,8–$Cl_2$ |
| 23 | R = 7–$NO_2$ | 59 | R = 5–$NO_2$ |

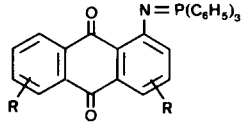
The structure of these derivatives as 1-mono- and 1,5-disubstituted anthraquinones were confirmed by the infrared spectral data (Table 6).

A related ring cleavage of the benzoisoxazoles (anthranils) with triphenylphosphines yielding (2-acylphenyl)triphenylphosphazenes has been reported earlier (18).

These ring opening reactions of isoxazoles extend the scope of methods for the synthesis of triphenyl-*N*-arylphosphazenes, the formation of which does not involve either an azido group (19), a phosphine dihalide (19) or a chloramine-T derivative (19). These methods are quite straightforward and sufficiently versatile, while the new

Table 4

*N*-(Anthraquinon-1-yl)triphenylphosphazene

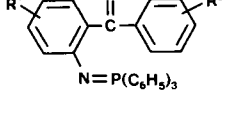



| Compound No. | R | MP °C | Crystallization Solvent | Yield % | Formula | | Analysis, % | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **56** | H | 229.5-230.5 | Toluene | 76 | $C_{32}H_{22}NO_2P$ | Calcd. | C, 79.49 | H, 4.59 | — | N, 2.90 | P, 6.41 |
| | | | | | | Found | C, 79.64 | H, 4.78 | — | N, 2.99 | P, 5.98 |
| **57** | 5-Cl | 216.5-218 | Toluene | 83 | $C_{32}H_{21}ClNO_2P$ | Calcd. | C, 74.21 | H, 4.09 | Cl, 6.84 | N, 2.70 | P, 5.98 |
| | | | | | | Found | C, 74.26 | H, 4.12 | Cl, 6.81 | N, 2.79 | P, 5.91 |
| **58** | 5,8-$Cl_2$ | 202-203 | Acetonitrile | 86 | $C_{32}H_{20}Cl_2NO_2P$ | Calcd. | C, 69.58 | H, 3.65 | Cl, 12.84 | N, 2.54 | P, 5.61 |
| | | | | | | Found | C, 69.61 | H, 3.81 | Cl, 13.12 | N, 2.55 | P, 5.42 |
| **59** | 5-$NO_2$ | 229.5-231 | Acetonitrile | 63.4 (a) | $C_{32}H_{21}N_2O_4P$ | Calcd. | C, 72.72 | H, 4.01 | — | N, 5.30 | P, 5.86 |
| | | | | | | Found | C, 72.90 | H, 4.19 | — | N, 5.48 | P, 5.92 |

(a) Yield after recrystallization.

Table 5

Substituted *N*-Triphenylphosphoranylidene-2-benzophenonamines

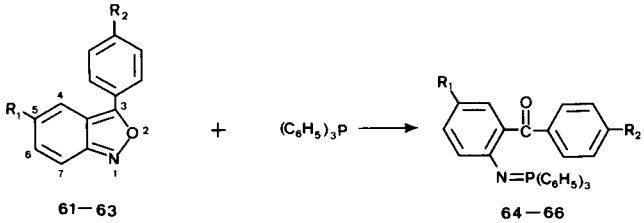



| Compound No. | $R^1$ | $R^2$ | MP °C | Yield % | Crystallization Solvent | Formula | | Analysis, % | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **64** | 5-Br | H | 207-208.5 | 79.5 | Toluene | $C_{31}H_{23}BrNOP$ | Calcd. | C, 69.41 | H, 4.32 | N, 2.61 | Br, 14.90 | P, 5.77 |
| | | | | | | | Found | C, 69.54 | H, 4.45 | N, 2.80 | Br, 14.91 | P, 5.81 |
| **65** | 5-Cl | H | 213-214.5 | 55 | Xylene | $C_{31}H_{23}ClNOP$ | Calcd. | C, 75.69 | H, 4.71 | N, 2.85 | Cl, 7.21 | P, 6.30 |
| | | | | | | | Found | C, 75.62 | H, 4.80 | N, 2.89 | Cl, 7.14 | P, 6.22 |
| **66** | 5-Cl | 4'-Cl | 156-157 | 68 | Cyclohexane | $C_{31}H_{22}Cl_2NOP$ | Calcd. | C, 70.73 | H, 4.21 | N, 2.66 | Cl, 13.47 | P, 5.88 |
| | | | | | | | Found | C, 70.85 | H, 4.30 | N, 2.71 | Cl, 13.42 | P, 5.92 |

method is an addition relying on the particular formation of an isoxazole ring as an intermediate.

It was attempted to apply this particular ring opening reaction of condensed isoxazoles with triphenylphosphine also to substituted 2,1-benzisoxazoles (anthranils). The 3-phenyl substituted 2,1-benzisoxazoles **(61-63)** were prepared according to known procedures (20). However, much longer reaction times were required to form the phosphoranes **64-66** from the substituted benzisoxazoles (anthranils) **(61-63)** as compared with the formation of phosphoranes from anthraisoxazoles (Scheme 8, Table 5). In xylene, of example, reaction times of approximately 100 hours were necessary while the reaction in refluxing dichlorobenzene (180°) was completed after 7 hours.

Scheme 8




61—63

$R_1$ = Br $R_2$ = H
$R_1$ = Cl $R_2$ = H
$R_1$ = Cl $R_2$ = Cl

64—66

$R_1$ = Br $R_2$ = H
$R_1$ = Cl $R_2$ = H
$R_1$ = Cl $R_2$ = Cl

Neither dimethyl sulfoxide nor an aliphatic or an aromatic phosphite could be induced to bring about cleavage of the nitrogen-oxygen bond of compounds **61-63**.

The mechanism of the reaction between triphenylphosphine and the isoxazole moiety probably involes nucleophilic attack by the phosphine on the nitrogen atom of the heterocyclic ring. Again, as in the aformentioned ring opening reaction with dimethyl sulfoxide, the reaction failed with an anthraisoxazolone having a substituent attached to the C-3 position, such as compounds **15, 16** or **19**.

Triphenylarsine proved to be unreactive, very likely because of the much lower basicity of the arsenic atom compared with the phosphorus atom in triphenylphosphine.

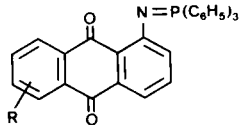
Aryltriphenylphosphazenes are susceptible to hydrolysis, the ease of hydrolysis being related to the basicity of the imine. The nitrogen atom of the P=N moiety can be readily protonated by strong acids, and for example, compound **60** can be reprecipited unchanged by adding a solution of **60** in sulfuric acid to water. Hydrolysis of **56-59** and of **60** required heating these compounds in 90% sulfuric acid to 50° yielding the respective aminoanthraquinones upon dilution with water.

Those anthraisoxazolones having substituents attached to the carbon atom C-3 or C-5 failed to undergo ring cleavage with triphenylphosphine.

The pertinent infrared frequencies of the keto-group, the phosphinimido- and of the nitrogen-phosphorus bonds are compiled in Table 6.

Table 6

Infrared Frequencies of Substituted *N*-Triphenylphosphoranylidene-1-anthraquinone Amines (1)




| Compound No. | R | C=O | N=P | C-P |
|---|---|---|---|---|
| **56** | H | 1675<br>1650 | 1365 | 1115 |
| **57** | 5-Cl | 1670<br>1650 | 1360 | 1112 |
| **58** | 5,8-$Cl_2$ | 1678 | 1380 | 1118 |
| **59** | 5-$NO_2$ | 1675<br>1660 | 1360 | 1115 |
| **60** | 5-N=$P(C_6H_5)_3$ | 1650 | 1360 | 1115 |

(1) In potassium bromide discs.

The carbonyl absorption frequencies show two bands with a frequency separation of 20-25 $cm^{-1}$, while compounds **60** exhibits, for reasons of symmetry only one frequency in the carbonyl region. The P=N stretching vibration was found to occur in the 1360-1380 $cm^{-1}$ region, which compares reasonably with the P=N frequency of known phosphazenes of similar structure, the substituent at the nitrogen being of aromatic nature (21-22).

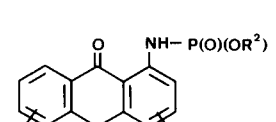
*N*-(Anthraquinon-1-yl)-*N*-dialkoxy(aryloxy)phosphoramidates.

When alkyl- or arylphosphites may attack at either oxygen or nitrogen, as the reactive sites of the isoxazole ring, the latter was found to be favoured. Heating anthraisoxazolones **(14, 17, 18, 20-23)** with trimethylphosphite in a solution of toluene yielded dark red oily products which upon dilution with hydrochloric acid formed yellow crystals of the phosphoramidates **(67-73)**. Triphenylphosphite reacted similarly yielding compounds **74** and **75**. The physical and analytical data are complied in Table 7. The anthrabis-isoxazole **25** yielded analogously the 1,5-disubstituted product (**78** Scheme 5, Table 3).

Ring opening of the isoxazole moiety of these compounds was indicated by the disappearance of the typical absorption bands due to the isoxazole ring frequency occurring at 1539-1555 $cm^{-1}$.

The mechanism of the ring opening reaction probably occurs *via* attack at the nitrogen atom of the isoxazole ring

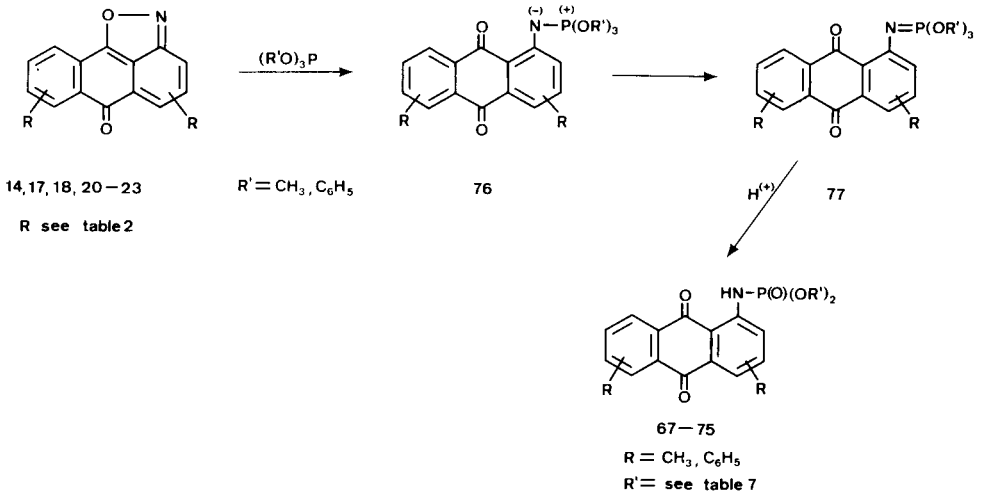
Table 7
Dimethyl (phenyl) (1′-anthraquinon-1-yl)phosphoramidates




| Compound No. | R¹ | R² | MP °C | Crystallization Solvent | Yield | Formula | | Analysis, % | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **67** | H | $CH_3$ | 165-165.5 | Toluene | 78.6 (a) | $C_{16}H_{14}NO_5P$ | Calcd. | C, 58.01 | H, 4.26 | — | N, 4.23 | P, 9.35 |
| | | | | | | | Found | C, 58.31 | H, 4.32 | — | N, 4.31 | P, 9.21 |
| **68** | 4-Cl | $CH_3$ | 173-173.5 | Toluene | 76.6 | $C_{16}H_{13}ClNO_5P$ | Calcd. | C, 52.55 | H, 3.58 | Cl, 9.69 | N, 3.83 | P, 8.47 |
| | | | | | | | Found | C, 52.28 | H, 3.61 | Cl, 9.71 | N, 3.74 | P, 8.36 |
| **69** | 5-Cl | $CH_3$ | 194.5-195 | Toluene | 99.8 | $C_{16}H_{13}ClNO_5P$ | Calcd. | C, 52.55 | H, 3.58 | Cl, 9.69 | N, 3.83 | P, 8.47 |
| | | | | | | | Found | C, 52.72 | H, 3.62 | Cl, 9.71 | N, 3.91 | P, 8.41 |
| **70** | 5,8-$Cl_2$ | $CH_3$ | 139-140 | Toluene | 37.5 (b) | $C_{16}H_{12}Cl_2NO_5P$ | Calcd. | C, 48.03 | H, 3.02 | Cl, 17.72 | N, 3.50 | P, 7.74 |
| | | | | | | | Found | C, 47.99 | H, 3.20 | Cl, 17.56 | N, 3.33 | P, 7.69 |
| **71** | 4-$OCH_3$ | $CH_3$ | 148-150 | Toluene | 63.9 | $C_{17}H_{16}NO_6P$ | Calcd. | C, 56.52 | H, 4.47 | — | N, 3.88 | P, 8.57 |
| | | | | | | | Found | C, 56.70 | H, 4.41 | — | N, 3.91 | P, 8.26 |
| **72** | 4-$NO_2$ | $CH_3$ | 189-190 | Xylene | 65 | $C_{16}H_{13}N_2O_7P$ | Calcd. | C, 51.08 | H, 3.48 | — | N, 7.45 | P, 8.23 |
| | | | | | | | Found | C, 51.41 | H, 3.54 | — | N, 7.65 | P, 7.98 |
| **73** | 5-$NO_2$ | $CH_3$ | 195.5-197 | Xylene | 93 | $C_{16}H_{13}N_2O_7P$ | Calcd. | C, 51.08 | H, 3.48 | — | N, 7.45 | P, 8.23 |
| | | | | | | | Found | C, 51.20 | H, 3.51 | — | N, 7.31 | P, 8.03 |
| **74** | H | $C_6H_5$ | 145-146 | Ethyl acetate | 84.4 | $C_{26}H_{18}NO_5P$ | Calcd. | C, 68.57 | H, 3.98 | — | N, 3.08 | P, 6.80 |
| | | | | | | | Found | C, 68.32 | H, 4.11 | — | N, 3.22 | P, 6.92 |
| **75** | 5-$NO_2$ | $C_6H_5$ | 179-181 | Ethyl acetate | 42 | $C_{26}H_{17}N_2O_7P$ | Calcd. | C, 62.41 | H, 3.42 | — | N, 5.60 | P, 6.19 |
| | | | | | | | Found | C, 62.62 | H, 3.51 | — | N, 5.70 | P, 6.21 |

(a) Yield obtained from 1-azidoanthraquinone 79%. (b) After recrystallization.

Scheme 9




by the phosphite (**76**) (Scheme 9). The first formed phosphorimidate (**77**), which is presumed to be an intermediate, is subsequently hydrolyzed in the presence of dilute hydrochloric acid (23), yielding anthraquinon-1-yl phosphoramidates (**67-75**).

The infrared absorption spectra of the phosphoramidates showed characteristic bands for NH at 3150 $cm^{-1}$, for P=O at 1270 $cm^{-1}$ and for P-O-C at 1030 $cm^{-1}$ and 1045 $cm^{-1}$, respectively, which were in general agreement with the values previously reported for these stretching vibrations (24, 25). The absorption bands which can be assigned to the P-N frequency were observed at 940-970 $cm^{-1}$, which agrees with values found by other authors (26, 27). The carbonyl frequencies showed two absorption bands centered at 1670-1680 $cm^{-1}$ and 1648-1660 $cm^{-1}$, respectively.

Those anthraisoxazolones having substitutents such as methyl- (**15**), chloro- (**19**) or bromo- (**16**) attached to the carbon atom C-3 failed to react with trimethylphosphite, which may be attributed to steric hindrance as pointed out before.

The phosphoramidates may also be prepared directly from the azides with the corresponding phosphorus compound without having to isolate the isoxazole derivative, an example of which is given for the preparation of **67**.

Reactions of aromatic azides with phosphites are reported to give, in general, very low yields of products (28), however, since formation of the anthraquinon-1-yl amidates is assisted by regeneration of the anthraquinone system, yields are much improved which is explained in more detail in Scheme 9.

Several groups have studied the chemistry of iminotrialkoxyphosphoranes and have proffered three different methods of preparation (29), which are now complemented by the above method for anthraisoxazolones and anthrabisisoxazoles, respectively.

The anthraquinon-1-yl phosphoramidates, like the related triphenylphosphinimino compounds, were readily converted to 1-aminoanthraquinones on heating to 50° in sulfuric aicd. This procedure offers the advantage of converting an anthraisoxazole *via* its phosphoramidate to a 1-aminoanthraquinone without having to go through the stage of a 1-hydroxylamino derivative as an intermediate which is prone to form a mixture of 1-amino-2(or 4-)hydroxyanthraquinones, depending on reaction conditions.

## EXPERIMENTAL

Melting points were determined in open capillary tubes and are uncorrected. Samples for the infrared spectra were prepared in potassium bromide discs.

The anthraquinone compounds used were either prepared according to known procedures reported in the literature, or were commercially available products which were purified.

The preparation of substituted 2,1-benzisoxazoles was performed according to the literature procedures (20), *e.g.* 3-phenyl-5-bromo-2,1-benzisoxazole (**61**), 3-phenyl-5-chloro-2,1-benzisoxazole (**62**), and 5-chloro(4-chlorophenyl)-2,1-benzisoxazole (**63**).

6*H*-Anthra[1,9-*cd*]isoxazol-6-one (**14**).

Sodium nitrite (57 g, 0.83 mole) was added with stirring to 525 ml of concentrated sulfuric acid at a temperature of 30-40° over a period of 20 minutes and stirring continued for an additional one half hour. Then 170.6 (0.75 mole) of 1-aminoanthraquinone was added during 30 minutes and the solution stirred for an additional 4 hours at 50-55°. The resulting solution was added to 1150 g of ice, the yellow precipitate filtered washed with 200 ml of ice-water, followed by 500 ml of a 1:1 mixture of ethanol-ether. The moist filter cake of 1-anthraquinonediazonium hydrogensulfate was then added to a solution of sodium azide (78 g, 1.2 moles) in 1 l of water and stirred for 30 minutes, after which time nitrogen evolution had subsided. The product was filtered, washed on the filter with 700 ml of water, followed by 350 ml of a mixture (9:1) of acetone and water. The moist azide was suspended in 2 l of toluene, heated to a temperature of 70° and stirred. Nitrogen evolution commenced and a mixture of water and acetone was slowly distilled from the

suspension over a descending condensor during a period of 8 hours. The yellow crystalline suspension was filtered, washed on the filter with 500 ml of methanol and dried at 80°, yielding 144 g of **14**.

5-Chloro-6*H*-anthra[1,9-*cd*]isoxazol-6-one (**17**).

1-Amino-4-chloroanthraquinone (25.75 g, 0.1 mole) was dissolved in 100 ml of concentrated sulfuric acid at 60°. Then 9 ml of water were added, followed by the dropwise addition of nitrosyl sulfuric acid (33.4 g, of a 40% solution in sulfuric acid) over a period of 40 minutes. After the addition had been completed, stirring was continued for 10 hours. Slow addition of 400 ml of ice-water yielded a suspension of crystals which were filtered, washed with 70 ml of ice-water and subsequently with 150 ml of a mixture of ethanol-ether (1:1). The moist diazonium salt was added in small portions to a solution of 13 g (0.2 mole) of sodium azide in 300 ml of water. After the nitrogen evolution had ceased, the crystals were filtered from the solution and washed with 150 ml of water followed by 100 ml of a mixture of acetone-water (9:1) yielding the crude azide. The azide obtained was slurried in 350 ml of dichlorobenzene and heated to 150° over a period of 45 minutes. Decolorizing carbon was added to the hot solution and, after filtration, the solvent was distilled from the solution at reduced pressure. The crystalline residue was washed with 150 ml of methanol yielding **17**. A sample of 10.5 g of **17** was recrystallized from 100 ml of xylene furnishing 9.2 g.

Anthra[1,9-*cd*:5,10-*c'd'*]bis(isoxazole) (**25**).

Method A.

A solution of sodium azide (2.8 g, 0.043 mole) in 30 ml of water was added dropwise to a stirred suspension of 1,5-anthraquinone bis(diazonium hydrogensulfate) (**13**) (9.12 g, 0.22 mole) (4). A yellow suspension of the bis-azide (**26**) was formed which was stirred for 20 minutes, then collected by filtration and washed on the filter with 70 ml of water, followed by 50 ml of a mixture of acetone-water (9:1). The moist filter cake of **26** was suspended in 100 ml of toluene, heated to 90° and maintained at this temperature until the nitrogen evolution ceased. The dark orange-colored crystals were collected by filtration and washed on the filter with 100 ml of methanol, yielding 4.62 g (98.7%) of **25**. Recrystallization of 1 g from 300 ml of xylene furnished 0.85 g of pure **25**, mp >320° dec; ir: $cm^{-1}$ 1603 (C=C), 1535 (isoxazole).

*Anal.* Calcd. for $C_{14}H_6N_2O_2$: C, 71.80; H, 2.59; N, 11.96. Found: C, 71.65; H, 2.69; N, 11.97%.

Method B.

Sodium azide (7.8 g, 0.12 mole) was added to a suspension of 1,5-dinitroanthraquinone (8.94 g, 0.03 mole) in 90 ml of dimethylformamide and stirred for 7 hours at 40°. The suspension was then added to 500 ml of water, the precipitate filtered and washed on the filter with 200 ml of water. The moist diazide was suspended in 150 ml of toluene and heated under reflux for 3 hours. Crystals were filtered from the cold solution and washed with 60 ml of methanol yielding 5.6 g (80%) of **25**. The infrared spectra of the two specimens prepared according to these two methods were superimposable.

1-*S*,*S*-Dimethyl-*N*-(anthraquinon-1-yl)sulfoximide (**28**).

Method A.

A suspension of 2.21 g (0.01 mole) of **14** in 150 ml of dimethyl sulfoxide was heated under reflux for 20 minutes. The solvent was distilled from the reaction mixture under reduced pressure on a rotary evaporator, and the residue crystallized from toluene.

Method B.

A suspension of 13.2 g (approximately 0.03 mole) of moist 1-azidoanthraquinone in 180 ml of dimethyl sulfoxide was heated at 130° for 45 minutes, after which time nitrogen evolution had ceased. Decolorizing carbon (1 g) was added and the solution filtered. The filtrate was added to 1200 ml of water and the suspension stirred for 1 hour, the crystals filtered, washed with water, and dried at 80°/1 torr, yielding 7.3 g (81%) of product.

1-*S*,*S*-Dimethyl *N*-(5,8-Dichloroanthraquinon-1-yl)sulfoximide (**31**).

A suspension of 5.8 g (0.02 mole) of **20** in 100 ml of dimethyl sulfoxide was heated to 100° and the temperature then increased to 160° within a period of 15 minutes. The resulting red solution was allowed to cool to 120° and 0.1 g of decolorizing carbon was added. The filtered solution was then added to 1 l of water and stirred for 30 minutes. The yellow crystals were filtered and successively washed with 200 ml of water, 50 ml of methanol, and 70 ml of ether. A sample of 0.5 g was recrystallized from 7 ml of xylene yielding 0.42 g of product.

1-*S*,*S*-Dimethyl *N*-(4-Methoxyanthraquinon-1-yl)sulfoximide (**32**).

A suspension of 2.51 g (0.01 mole) of **21** in 50 ml of dimethyl sulfoxide was heated at 160° for 2 hours and then cooled to room temperature. The solution was then added to 140 ml of water and stirred for 1 hour. Crystals were filtered and washed successively with 40 ml of water and 40 ml of ether. A sample of 3.1 g was recrystallized from 40 ml of dichlorobenzene, filtered and washed with 10 ml of ether yielding 2.4 g of product.

1-*S*,*S*-Dimethyl *N*-(5-Benzamidoanthraquinon-1-yl)sulfoximide (**35**).

A suspension of 6.8 g (0.02 mole) of **24** in 100 ml of dimethyl sulfoxide was heated at 160° for 20 minutes. The orange colored suspension was added to 500 ml of water and stirred for 20 minutes. Crystals were filtered and washed with 150 ml of water, followed by 100 ml of a mixture of ethanol and ether (1:1). An analytical sample was recrystallized from dichlorobenzene.

1-*S*-Methyl-1-*S*-phenyl-*N*-(anthraquinon-1-yl)sulfoximide (**39**).

A suspension of 0.511 g (0.002 mole) of **17** in 0.56 g (0.004 mole) of methyl phenylsulfoxide in 2.5 ml of dichlorobenzene was heated under reflux for 2 hours. The solution was filtered hot and the filtrate cooled to 0°. Crystals were collected by filtration and washed with 5 ml of toluene followed by 20 ml of ether yielding 0.55 g of product.

Bis(*S*,*S*-dimethyl)-*N*,*N*-(anthraquinon-1,5-diyl)disulfoximide (**51**).

Method A. Synthesis from 1,5-Diazidoanthraquinone.

A solution of 14.3 g (0.22 mole) of sodium azide in 600 ml of water was added to a stirred suspension of 45.6 g (0.1 mole) of **13** (4) in 600 ml of water over a period of 20 minutes. The product formed was filtered from the suspension and washed successively with 250 ml of water and 150 ml of a mixture (9:1) of acetone-water, yielding 64 g of slightly moist 1,5-diazidoanthraquinone.

A stirred suspension of 32 g of the above prepared diazidoanthraquinone in 300 ml of dimethyl sulfoxide was heated to 80°, whereupon nitrogen evolution proceeded at a steady rate. After the nitrogen evolution had subsided the temperature was increased to 154° and stirring continued for 1 hour. Decolorizing carbon (0.1 g) was added and the orange colored solution filtered. The filtrate was reduced to about one third of its volume on a rotary evaporator and 19.2 g of crystals were filtered from the solution. Crystallization from 420 ml of ethyl cellosolve in presence of decolorizing carbon yielded 11.5 g (59%) of crystals, mp 240.5-241°; ir: $cm^{-1}$ 2998, 2992 ($CH_3$), 1668 (CO), 1580, 1250 (NSO), 1171, 1110, 1082.

*Anal.* Calcd. for $C_{18}H_{18}N_2O_4S_2$: C, 55.37; H, 4.65; N, 7.17; S, 16.42. Found: C, 55.49; H, 4.54; N, 7.39; S, 16.57.

Method B. Synthesis from **25**.

A suspension of 0.1 g of **25** in 20 ml of dimethyl sulfoxide was heated under reflux for 20 minutes. The solvent was evaporated on a rotary evaporator and the residue 0.095 g recrystallized from 2.7 ml of toluene yielding red crystals, mp 243-245°. The infrared spectra of the specimens prepared according to A) and B) were superimposable.

Bis-(*S*,*S*-diphenyl)-*N*,*N*-(anthraquinon-1,5-diyl)disulfoximide (**52**).

A suspension of 0.932 g (0.004 mole) of **25** and 2.42 g (0.012 mole) of diphenyl sulfoxide in 5 ml of dichlorobenzene was heated under reflux

for 1 hour. The dark brown suspension was filtered, washed with 5 ml of toluene followed by 20 ml of ether yielding 1.77 g of product which was recrystallized from 16 ml of dichlorobenzene.

1-*S*,*S*-Dimethyl *N*-(5-Aminoanthraquinon-1-yl)sulfoximide (**54**).

To 565 ml of 90% sulfuric acid 189 g (0.452 mole) of **35** was added with stirring at 45-55° within a period of 15 minutes. After addition was complete the temperature was increased to 90° and maintained for 1 hour. The brown-colored suspension was cooled to 25° and poured onto 4 l of ice-water. Then 225 g of sodium chloride were added, the mixture stirred for 15 minutes, and the precipitate filtered. The product was washed on the filter with 1 l of a 15% solution of sodium chloride in water and suspended in a solution of 70 g of sodium carbonate in 1.5 l of ice-water. After having been stirred for 1.5 hours, it was filtered and washed with 2 l of water yielding 131 g (91.6%) of product. Recrystallization of 131 g from 845 ml of dichlorobenzene furnished 113 g of product, mp 176.5-179°, ir: $cm^{-1}$ 3420, 3300 ($NH_2$), 1673 (CO), 1635, 1612 (CO, chelate).

*Anal.* Calcd. for $C_{16}H_{14}N_2O_3S$: C, 61.13; H, 4.49; N, 8.91; S, 10.20. Found: C, 61.20; H, 4.43; N, 8.94; S, 9.97.

*N*-(Anthraquinon-1-yl)triphenylphosphazene (**56**).

A solution of 0.551 g (0.002 mole) of **18** and 0.92 g (0.0035 mole) of triphenylphosphine in 3 ml of toluene was heated under reflux for 2 minutes. The solvent was then evaporated on a rotary evaporator, ether (20 ml) added to the residue and the crystals filtered. An analytical sample was prepared by recrystallization of 0.86 g from 4 ml of toluene.

*N*,*N*-(Anthraquinon-1,5-diyl)-bis(triphenylphosphazene) (**60**).

A suspension of 0.936 g (0.004 mole) of **25** and 2.8 g (0.01 mole) of triphenylphosphine in 7 ml of xylene was heated under reflux for 1.5 hours. The solvent was then distilled from the solution and 15 ml of ether added to the residue. The red crystals were filtered and washed with 10 ml of ether yielding 3.0 g of product which, after recrystallization from dichlorobenzene, furnished 1.75 g.

1,5-Diaminoanthraquinone by Hydrolysis of **60**.

A sample (1 g, 0.0013 mole) of **60** was heated with stirring in 15 ml of 85% sulfuric acid to a temperature of 140° for 10 minutes. The red solution was added to ice, the crystals filtered, then slurried in 30 ml of ether and again filtered. Evaporation of the etheral solution yielded 0.63 g (87%) of triphenylphosphine oxide. The ether insoluble residue gave 0.2 g (69%) of 1,5-diaminoanthraquinone. Both compounds were identified by comparison of their infrared spectra with those of authentic specimens.

5-Bromo-(*N*-triphenylphosphoranylidene)-2-benzophenonamin (**64**).

A solution of 3-phenyl-5-bromo-2,1-benzisoxazole (**61**) (2.74 g, 0.01 mole) and triphenylphosphine (5.24 g, 0.02 mole) in 50 ml of dichlorobenzene was heated under reflux for a period of 7 hours. The solvent was evaporated and 20 ml of toluene added to the residue. Crystals were filtered from the solution and washed with 15 ml of toluene, followed by 20 ml of ether, yielding 4.2 g of product. Recrystallization of 4.2 g from 30 ml of toluene yielded 3.3 g of **64**; ir: $cm^{-1}$ 1655 (CO), 1338 (N=P), 1115 (C-P).

Dimethyl *N*-(Anthraquinon-1-yl)phosphoramidate (**67**).

Method A. Synthesis from **14**.

A suspension of 2.21 g (0.01 mole) of **14** in 3.1 g (0.025 mole) of trimethylphosphite and 15 ml of toluene was heated under reflux for 10 minutes. The solution was then added to 80 ml of a mixture of concentrated hydrochloric acid and water (1:1 by volume) and stirred for 15 minutes. The crystals that separated were collected by filtration, washed with water and dried at 80°/1 torr. An analytical sample was obtained by crystallization from toluene.

Method B. Synthesis from 1-Azidoanthraquinone.

Trimethylphosphite (9.3 g, 0.075 mole) was added to a suspension of 7.5 g (0.03 mole) of slightly moist azidoanthraquinone in 50 ml of toluene. Nitrogen evolution commenced immediately. The solution was heated to 70° for 10 minutes and then worked up as described under A), yielding 7.9 g (79.7%), mp 164-165.

1-Aminoanthraquinone by Hydrolysis of **67**.

A sample of 7.9 g (0.03 mole) of **67** in 100 ml of sulfuric acid (90%) was heated at 40° for 1 hour. The solution was added to 1 l of water, and the crystalline suspension filtered. Crystals were washed on the filter with water and dried, yielding 4.85 g (73%) of 1-aminoanthraquinone, which was identified by comparison of its infrared spectrum with that of an authentic specimen.

*N*,*N*-(Anthraquinon-1,5-diyl)-bis(*N*-dimethoxyphosphoramidate) (**78**).

A suspension of 0.936 g (0.004 mole) of **25** in 2.0 g (0.016 mole) of trimethylphosphite and 7 ml of toluene was heated under reflux for 2.5 hours. The resulting solution was added to a mixture of 20 ml of concentrated hydrochloric acid and 20 ml of water and stirred for 10 minutes. Crystals were filtered from the solution, washed with 100 ml of water and subsequently with 30 ml of ether, yielding 1.52 g of product.

Diphenyl *N*-(5-nitroanthraquinon-1-yl)phosphoramidate (**75**).

A solution of 1.33 g (0.005 mole) of **23** and 3.1 g (0.01 mole) of triphenylphosphite in 7.5 ml of xylene was heated under reflux for 15 minutes. The volatile products were evaporated on a rotary evaporator under reduced pressure and 10 ml of ligroin added to the residual oil. Crystallization occured after a few minutes, and filtration yielded 2.8 g of crystals. These were suspended in 50 ml of a mixture of hydrochloric acid and water (3:1), stirred for 15 minutes and filtered. Crystallization from ethyl acetate furnished 1.0 g of product.

## REFERENCES AND NOTES

(1a) A. Schaarschmidt, *Chem. Ber.*, **49**, 1636 (1916); (b) Gattermann and Rolfes, *Ann. Chem.*, **425**, 135 (1921).

(2a) K. Brass and F. Albrecht, *Chem. Ber.*, **61**, 988 (1928), pertinent earlier references are listed there; (b) German Patent 335,160, Farbenfabriken, vorm. Bayer and Co.; *Chem. Zentr. II. 937 (1921); (c) K. H. Wuensch and A. J. Boulton in "Indoxazenes and Anthranils", in "Advances in Heterocyclic Chemistry"*, **8**, 277 (1966); A. R. Katritzky and A. J. Boulton, eds, Academic Press, New York, N.Y., 1967, p 311.

(3a) I. M. Gornostaev, G. F. Zeibert and G. I. Zolotareva, *J. Heterocyclic Compounds*, 912 (1980); (b) A. M. Galushko and N. S. Dokuniklin, *Zh. Org. Khim.*, 575 (1979); *Chem. Abstr.*, **91**, 39377g (1979).

(4) H. Fritz, G. Rihs, P. Sutter and C. D. Weis, *J. Heterocyclic Chem.*, **18**, 1571 (1981).

(5) German Patent 580,647 (1931), I. G. Farben, Methoden der Organischen Chemie, Vol. 7, Part 3C, O. Bayer, ed., G. Thieme Verleg, Stuttgart 1979, p 223.

(6) A. J. Boulton, A. C. G. Gray and A. R. Katritzky, *J. Chem. Soc.*, 5958 (1965); (b) A. J. Boulton, A. C. G. Gray and A. R. Katritzky, *J. Chem. Soc. (B)*, 909 (1967).

(7a) L. K. Dyall, *Aust. J. Chem.*, **30**, 2669 (1977); (b) L. K. Dyall and J. E. Kemp, *J. Chem. Soc. (B)*, 976 (1968); (c) L. K. Dyall, *Aust. J. Chem.* **28**, 2147 (1975); (d) a comprehensive treatise is given by B. Iddon, O. Meth-Cohn, E. F. V. Scriven, H. Sushitzky and P. T. Gallagher, *Angew. Chem.*, **91**, 965, (1979).

(8a) L. M. Gornostaev and V. A. Levdanskii, *Zh. Org. Khim.*, **16**, 2209 (1980); (b) USSR Patent SU 722,903 (1978).

(9a) P. D. Kennewell and J. B. Taylor, Chem. Soc. Rev., **4**, 189 (1975); (b) P. D. Kennewell, and J. B. Taylor, *ibid.*, **9**, 477 (1980).

(10) A. Nudelman, *Phosphorus Sulfur*, **9**, 66 (1980).

(11) R. W. Heintzelman, R. B. Bailey and D. Swern, *J. Org. Chem.*, **41**, 2207 (1976).

(12) A. J. Manusco and D. Swern, *Synthesis*, 168 (1981).

(13) R. E. Banks and A. Prakash, *J. Chem. Soc., Perkin Trans, I*, 1365 (1974).

(14) R. E. Banks and G. R. Sparkes, *J. Chem. Soc., Perkin Trans. I,* 2964 (1972).

(15) A. Pollak, S. Polanc, B. Stanovic and M. Tishler, *Monatsh. Chem.*, **103**, 1591 (1972).

(16) S. Oae, K. Harada, K. Tsujihara and N. Furukawa, *J. Int. Sulfur Chem.*, Part A, **2**, 49 (1972).

(17) J. A. Franz and J. C. Martin, *J. Am. Chem. Soc.*, **97**, 583 (1975).

(18) Y. Nomura, Y. Kikuchi and Y. Takeuchi, *Chem. Letters*, 575 (1974).

(19a) W. A. Johnson, "Ylid Chemistry, Organic Chemistry", A. T. Blomquist, ed, Academic Press, New York, N.Y., 1966 p 233; (b) Y. G. Gololobov, I. N, Zhmurova and L. F. Kasukhin, *Tetrahedron*, **37**, 437 (1981).

(20) R. B. Davis and L. C. Pizzini, *J. Org. Chem.*, **25**, 1884, (1960).

(21) W. Wilgrabe and H. Bock, *Chem. Ber.*, **101**, 1414 (1968).

(22) H. Bock, M. Schmoller and H. T. Diek, *ibid.*, **102**, 1363 (1969).

(23) J. I. Cadogan and H. N. Mouldon, *J. Chem. Soc.*, 3079 (1961).

(24) R. Cremlyn and N. Akhtar, *Phosphorus Sulfur*, **7**, 247 (1979).

(25) L. C. Thomas, "Interpretation of the Infrared Spectra of Organic Compounds", Heyden, London, 1974.

(26) B. Homstead and L. Larsson, *Acta Chem. Scand.*, 1179 (1951).

(27) R. B. Harvey and J. E. Mayhood, *Can. J. Chem.*, **33**, 1552 (1955).

(28) N. L. Mosby and M. L. Silva, *J. Chem. Soc.*, 2727 (1965).

(29a) M. I. Kabachnik and V. A. Gilyarov, *Bull. Acad. Sci. USSR.*, 809 (1956); (b) I. M. Zhmurova and A. V. Kirsanov, *Zh. Obshch. Khim.*, **29**, 1687 (1959); (c) A. V. Kirsanov and V. I. Shevchenko, *J. Gen. Chem.*, **24**, 483 (1954); (d) W. S. Wadsworth and W. D. Emmons, *J. Am. Chem. Soc.*, **84**, 1316 (1962); (e) W. S. Wadsworth and W. D. Emmons, *J. Org. Chem.*, **29**, 2816 (1964).