

The oxime (6.5 g) and polyphosphoric acid (150 g) were heated to 130° for 10 min with stirring. After cooling the reaction mixture was diluted and subsequently extracted several times with ether. (Ether solution=A). Reesterification of the partially hydrolyzed reaction product was effected with diazomethane. Examination by TLC now indicated the presence of two main constituents. The reaction product was submitted to column chromatography on silica gel. The crude base 3 (R=H, R'=COOCH<sub>3</sub>) (about 1 g) was eluted with light petroleum:ether (9:1). It was recrystallized twice from dilute methanol and sublimed at 95° under reduced pressure. Yield 0.5 g. M.p. 108–109°,  $[\alpha]_D$  3.3° (CHCl<sub>3</sub>, c=1.3). (Found: C 76.2; H 9.2; N 4.4; m.w. 315, determined by MS. Calc. for C<sub>20</sub>H<sub>29</sub>NO<sub>2</sub>: C 76.15; H 9.3; N 4.4; m.w. 315). IR 3390 cm<sup>-1</sup> (NH) and 1720 cm<sup>-1</sup>. No peak at about 1700 cm<sup>-1</sup>.  $\lambda_{\max}$ (EtOH) 253, 305 nm ( $\epsilon$  12 600, 3900). NMR: signals at ( $\delta$  ppm from internal standard TMS in CDCl<sub>3</sub>)  $\delta$  1.18 (6 H, doublet, *J* 7 cps), C(16) H<sub>3</sub> and C(17) H<sub>3</sub>;  $\delta$  1.11 and 1.32 (singlets, each 3 H), C(20) H<sub>3</sub> and C(19) H<sub>3</sub>; complex unresolved multiplet centered at  $\delta$  1.52 (7 H), C(1) H<sub>2</sub>, C(2) H<sub>2</sub>, C(3) H<sub>2</sub> and C(5) H;  $\delta$  2.18 (2 H, multiplet), C(6) H<sub>2</sub>;  $\delta$  2.75 (1 H, septet, *J* 7 cps), C(15) H;  $\delta$  3.60 (3 H, singlet), C(18) COOCH<sub>3</sub>;  $\delta$  6.24 (1 H, doublet, *J* 2 cps), C(14) H;  $\delta$  6.43 (1 H, quartet, *J* 8 and 2 cps), C(12) H;  $\delta$  6.92 (1 H, doublet, *J* 8 cps), C(11) H. On TLC plates sprayed with SbCl<sub>5</sub> in CHCl<sub>3</sub> this base gave a characteristic, initially weak reddish violet spot which gradually became intense.

For complete extraction of the base from ether solutions strong acids were required (20 % H<sub>2</sub>SO<sub>4</sub> or HCl) and for complete *N*-acetylation heating with acetic anhydride and pyridine for ca. 10 h at 100° was needed. The acetyl derivative melted at 112–113.5°.  $[\alpha]_D$  154° (CHCl<sub>3</sub>, c=1.0).  $\lambda_{\max}$ (EtOH) 258 nm ( $\epsilon$  11 400). (Found: C 74.2; H 8.8; N 3.8. Calc. for C<sub>22</sub>H<sub>31</sub>NO<sub>3</sub>: C 73.9; H 8.7; N 3.9).

At room temperature the base readily gave a dinitro derivative, formulated as 3 (R=NO<sub>2</sub>, R'=COOCH<sub>3</sub>) with nitric acid in acetic acid. Crystals, m.p. 100–101.5°,  $[\alpha]_D$  -53.9° (CHCl<sub>3</sub>, c=0.7).  $\lambda_{\max}$ (EtOH) 243, 375 nm ( $\epsilon$  8800, 8300). (Found: C 59.0; H 6.7; N 10.1. Calc. for C<sub>20</sub>H<sub>27</sub>N<sub>3</sub>O<sub>6</sub>: C 59.2; H 6.7; N 10.4).

A second fraction was eluted with ether to give lactam 2 (R=O, R'=COOCH<sub>3</sub>), which crystallized on trituration with light petroleum. Recrystallization from isooctane and sublimation under reduced pressure gave pure lactam, melting at 150–151°,  $[\alpha]_D$  -191° (CHCl<sub>3</sub>, c=0.8).  $\lambda_{\max}$ (EtOH) 245 nm ( $\epsilon$  12 200).

(Compare acetanilide: 240 and benzamide: 285 nm). (Found: C 73.5; H 8.5; N 3.9; m.w. 343 [MS]. Calc. for C<sub>21</sub>H<sub>29</sub>NO<sub>3</sub>: C 73.4; H 8.5; N 4.1; m.w. 343).

When the lactam 2 (R=O, R'=COOCH<sub>3</sub>) was treated in the same way as the oxime of methyl 7-ketodehydroabietate with polyphosphoric acid or, less advantageously, with conc. sulphuric acid, the presence of base 3 (R=H, R'=COOCH<sub>3</sub>) in the reaction mixture could be demonstrated by spraying the TLC plates with SbCl<sub>5</sub>.

The lactam 2 (R=O, R'=COOCH<sub>3</sub>) was reduced with LiAlH<sub>4</sub> in the usual way to the aminoalcohol 2 (R=H, R'=CH<sub>2</sub>OH). This compound was chromatographed on silica gel and recrystallized from light petroleum. M.p. 104–109°.  $[\alpha]_D$  -30° (CHCl<sub>3</sub>, c=0.8).  $\lambda_{\max}$ (EtOH) 245, 287 nm ( $\epsilon$  7100, 2200). (Found: C 79.8; H 10.6; N 4.3. Calc. for C<sub>20</sub>H<sub>31</sub>NO: C 79.7; H 10.4; N 4.65).

From the above ether fraction A, alkali removed the amino acid 3 (R=H, R'=COOH). It was sublimed under reduced pressure at 150° to give crystals, melting at 194–195°. (Found: C 75.7; H 9.0. Calc. for C<sub>19</sub>H<sub>27</sub>NO<sub>2</sub>: C 75.7; H 9.0).

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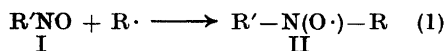
## Spin Trapping of the Radicals Formed by $\gamma$ -Irradiation of Sodium Phosphite in the Solid State

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The nitroxide method for trapping short-lived free radicals has now been applied to a large number of reactions.<sup>1-11</sup> The es-

sential features of this method involve the addition to the reaction system of a nitroso scavenger such as *t*-nitrosobutane or 2-methyl-2-nitrosobutanone-3 (I), which reacts with the short-lived radicals, R·, to give nitroxide radicals (II) stable enough to be detected by ESR spectroscopy (eqn. (1)).



In addition to the main triplet splitting caused by the  $^{14}\text{N}$  nucleus of the nitroxide group, the ESR spectra of the unsymmetric nitroxide radicals (II) exhibited secondary splittings which originated exclusively from magnetic nuclei in the part of the nitroxide radicals derived from R·. From these splittings it was in many cases possible to determine the structure of the trapped radicals.

The majority of the reaction systems so far investigated by the nitroxide method involve radicals formed in liquid solutions. However, radicals formed in solid state samples can also be trapped as nitroxide radicals upon dissolving the sample in a solution of the nitroso scavenger. In this way the radical species were trapped from  $\gamma$ -irradiated solid samples of substances such as sodium acetate, glycine, DL- $\alpha$ -alanine, and succinic acid.<sup>4</sup>

This note describes the trapping of the radical ion  $\cdot\text{PO}_3^{2-}$ , formed by  $\gamma$ -irradiation of a solid state sample of sodium phosphite,  $\text{Na}_2\text{HPO}_3 \cdot 5\text{H}_2\text{O}$ . The same radical ion was previously investigated in the solid state by Horsfield *et al.*<sup>12</sup> The radical was formed

in a  $\gamma$ -irradiated single crystal of  $\text{Na}_2\text{HPO}_3 \cdot 5\text{H}_2\text{O}$  after ejection of the hydrogen atom bonded to the phosphorus atom.

Polycrystalline samples of sodium phosphite were dried at  $+60^\circ\text{C}$  at reduced pressure. The samples were irradiated at room temperature by  $\gamma$ -rays from a  $^{60}\text{Co}$  source, and were given about 3 Mrad each. They were then dissolved in an aqueous solution of the nitroso scavenger *t*-nitrosobutane. In this way, the  $\gamma$ -induced radicals of the solid state samples were trapped as nitroxide radicals, the ESR spectrum of which is shown in Fig. 1. An identical spectrum was obtained when  $\text{H}_2\text{O}$  was replaced by  $\text{D}_2\text{O}$  as the solvent. The spectrum exhibited 6 lines of equal intensity, and was consistent with the interaction of the unpaired electron with one  $^{14}\text{N}$  and one  $^{31}\text{P}$  nucleus ( $a^{\text{N}}=13.4$  gauss,  $a^{\text{P}}=12.0$  gauss), and the formation of the nitroxide radical,  $\text{O}_3\text{P}-\text{N}(\text{O}\cdot)-\text{C}(\text{CH}_3)_2$  after the trapping of  $\cdot\text{PO}_3^{2-}$  radicals. No radicals could be trapped with non-irradiated samples of sodium phosphite.

A completely different interpretation might involve the formation of mono-*t*-butyl nitroxide radicals,  $\text{H}-\text{N}(\text{O}\cdot)-\text{C}(\text{CH}_3)_2$ , by trapping of the hydrogen atom produced in the irradiation process. Such a radical species was also expected to give rise to a 6-line spectrum with all lines of equal intensity. However, this alternative was ruled out by the following reasons. No hydrogen atoms could be detected at room temperature in the ESR spectra of the  $\gamma$ -irradiated solid state samples of sodium phosphite. Spin trapping of hydrogen

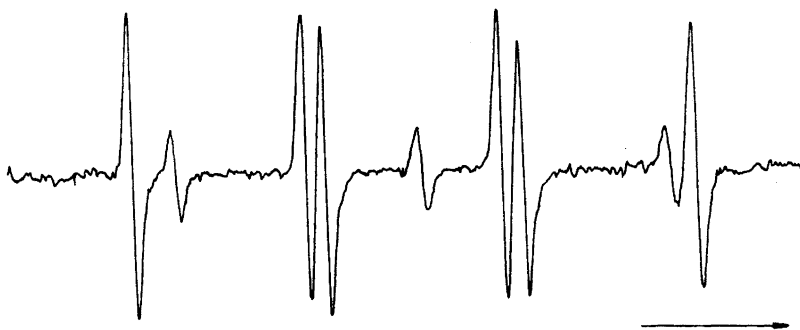


Fig. 1. ESR spectrum of the nitroxide radicals formed on dissolving a  $\gamma$ -irradiated solid sample of sodium phosphite in a water solution of *t*-nitrosobutane. The secondary doublet splitting indicates the trapping of the radical ion,  $\cdot\text{PO}_3^{2-}$ . A small amount of di-*t*-butyl nitroxide radicals derived exclusively from the scavenger is also present and gives rise to a 3-line system

atoms seems to be a reaction of low probability, and has not been described so far as we know. The spectrum of the mono-*t*-butyl nitroxide radical has recently been studied ( $a^N=13.8$ ,  $a_{NH}^H=13.8$  gauss, in  $H_2O$ ),<sup>13</sup> and is completely different from that of Fig. 1. Phosphorus-centered radical species have recently been produced by irradiation with UV light of liquid solutions of a number of phosphorus compounds, including  $Na_2HPO_3$ , and trapped as nitroxide radicals.<sup>11</sup> The results obtained are wholly consistent with the interpretation which involves the trapping of  $\cdot PO_3^{2-}$  radicals upon dissolution of  $\gamma$ -irradiated solid state samples of sodium phosphite.

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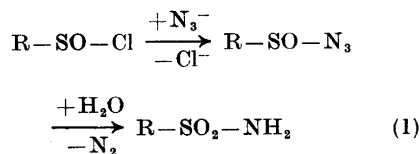
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## Die Darstellung neuer Sulfonamide nach der Sulfinylazidmethode

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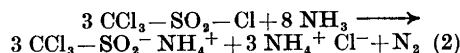
Maricich beschrieb vor kurzem die interessanten Reaktionen der bei tiefen Temperaturen darstellbaren Sulfinylazide.<sup>1</sup> Unter anderem besteht hier die Möglichkeit der Reaktionsfolge (1):



Der präparative Wert dieser Methode geht aus Maricichs Arbeit nicht hervor, da das nach (1) ( $R=C_6H_5$ ) erhaltene Benzolsulfonamid anders einfacher darzustellen ist.

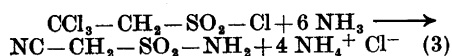
Wir haben mit Hilfe der Sulfinylazidmethode zwei Sulfonamide darstellen können, die auf anderem Wege nicht zugänglich sind und auf diese Weise ihren präparativen Wert gezeigt.

Trichlormethansulfonamid lässt sich nicht über das Trichlormethansulfonylchlorid darstellen, weil dieses positives Chlor enthält und Ammoniak oxydiert:<sup>2</sup>



Andere geeignete Acylierungsmittel, wie z.B.  $CCl_3-SO_2-F$  oder  $CCl_3-SO_2-O-SO_2-CCl_3$ , sind nicht bekannt. Nach (1) konnten wir das Trichlormethansulfonamid in 85% Ausbeute aus Trichlormethansulfinylchlorid<sup>3</sup> darstellen. Trichlormethansulfonamid ist erwartungsgemäss eine mittelstarke Säure ( $pK_s=6,43$ ), lässt sich *N*-methylieren und *N*-acylieren und bildet mit Dimethylsulfoxid einen stabilen 1:1-Komplex. Das *N*-Sulfinylderivat liefert mit Dimethylsulfoxid das entsprechende Sulfoximid.

2,2,2-Trichloräthansulfonylchlorid<sup>4</sup> reagiert mit Ammoniak nach (3)



\* Zuschriften an A.S.