References

1. E. Cotsaris and M. N. Paddon-Row, *J. Chem. Soc., Chem. Commun.*, 1984, **2**, 95.
2. R. G. Bulgakov, G. Ya. Maistrenko, and B. A. Tishin, *Dokl. Akad. Nauk SSSR*, 1989, **304**, 1166 [*Dokl. Chem.*, 1989, **304** (Engl. Transl.)].
3. V. A. Belyakov and R. F. Vasil'ev, in *Molekulamaya fotonika* [*The Molecular Photonics*], Nauka, Leningrad, 1970, 70 (in Russian).

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Reaction of PCl_5 with 1-hydroxy-10-anthrone

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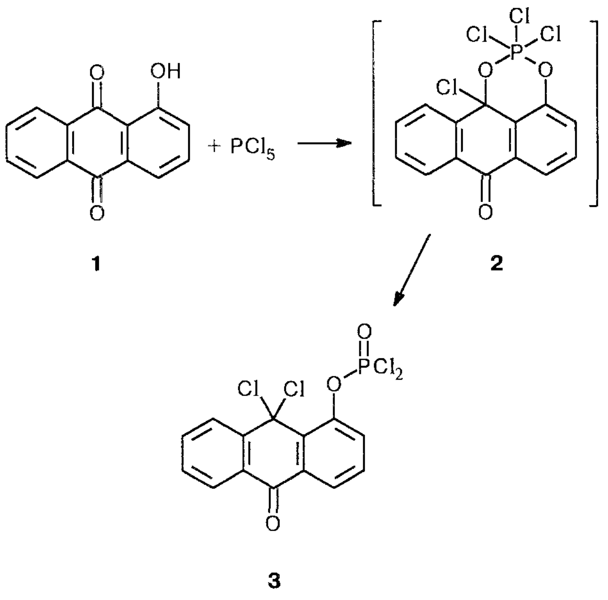
Previously,[1] it has been shown that the interaction between 1-hydroxy-9,10-anthraquinone (**1**) and PCl_5 (Scheme 1) affords 4-dichlorophosphoryloxy-10,10-dichloroanthrone (**3**). It was assumed that the reaction proceeds *via* cyclophosphorane **2** formation, however, the latter was not identified in the reaction mixture.

Scheme 1



We have studied the reaction of 1-hydroxy-10-anthrone (**1a**) with PCl_5 resulting in the products of the chlorination of the carbonyl group in the α-position, like in the case of compound **1**. In contrast to the reaction described previously, chlorination of the C atom in position 9 of the anthrone ring system also takes place. A study of the reaction by ^{31}P NMR and mass spectrometry demonstrated that 1-tetrachlorophosphoryloxy-10-anthrone (**4**) forms at the first stage, and subsequently undergoes intramolecular cyclization with the formation of trichlorocyclophosphorane **5** (Scheme 2).

Then phosphorane **5** either eliminates an HCl molecule and is transformed into cyclophosphorane **6**, or is oxidized by phosphorus pentachloride to form cyclophosphorane **8**. Compounds **6** and **8** subsequently isomerize into the corresponding dichlorophosphoryloxy-9-chloro-(9,10-dichloro)anthracenes (**7** and **9**). One cannot exclude the possibility of the chlorination of phosphoranes **6** and **7** by phosphorus pentachloride to afford compounds **8** and **9**, respectively. The combination of these data allows us to propose the reaction scheme (see Scheme 2).

PCl_5 (5.43 g, 0.013 mol) was added with stirring to a solution of 1-hydroxy-10-anthrone (2.74 g, 0.013 mol) in anhydrous benzene (50 mL) at *ca.* 20 °C. Five min after the beginning of the reaction a signal at −47 ppm corresponding to 1-tetrachlorophosphoryloxy-10-anthrone (**4**) was observed in the ^{31}P NMR spectrum of the reaction mixture. The mixture was heated at reflux for 1 h until HCl evolution ceased. In the ^{31}P NMR spectrum of the reaction mixture signals at 219.32 (PCl_3), 2.1 (1-dichlorophosphoryloxy-9-chloro-(9,10-dichloro)anthracene (**7** and **9**)), and −26.19 (compounds **5**, **6**, and **8** of the cyclophosphorane type) were observed. In the mass spectrum of the reaction mixture peaks at *m/z* 378 $[M]^+$, 380 $[M+2]^+$, 382 $[M+4]^+$, 384 $[M+6]^+$ (compounds **8** and **9**);

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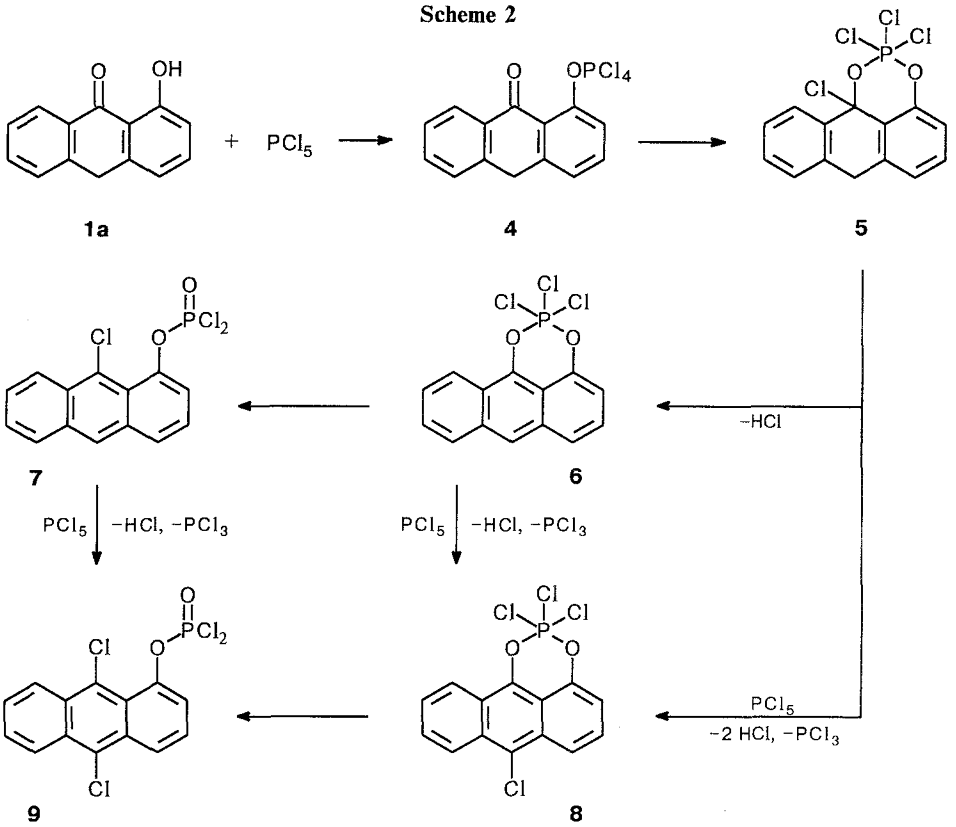
1066-5285/95/4401-0185 $12.50

Scheme 2



344 $[M]^+$, 346 $[M+2]^+$,and 348 $[M+4]^+$ (compound **7**) were present. During removal of the solvent the organic compounds were resinified, and only the signal at δ 219.32 (PCl_3) was present in the ^{31}P NMR spectrum of the distillate.

References

1. A. A. Kutyrev, V. V. Biryukov, I. F. Litvinov, O. N. Kataeva, R. Z. Musin, K. M. Enikeyev, V. A. Naumov, A. V. Ilyasov, and V. V. Moskva, *Tetrahedron*, 1990, 4333.

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3-Aza-Cope rearrangement as a route to higher branched aliphatic aldehydes from telomers of isoprene with secondary amines

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Higher branched aliphatic aldehydes and the C_8—C_{14} alcohols derived from them are valuable fragrant substances.[1] In order to synthesize such aldehydes we used the 3-aza-Cope rearrangement of telomers of isoprene with secondary amines, which can be easily prepared on palladium,[2] nickel,[3] or lithium[4] catalysts. The reaction of allyl bromide with *N,N*-diethylnerylamine (**1**), synthesized from isoprene and diethylamine on a

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