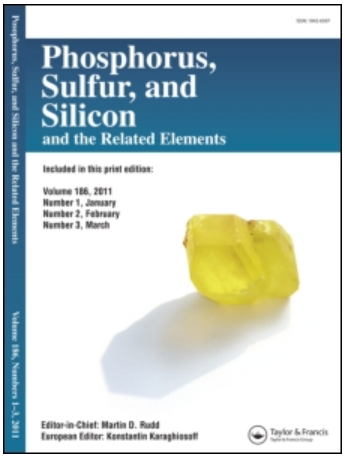

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COMMENT ON THE ARTICLE OF J. S. PIZEY AND K. SYMEONIDES (THIS JOURNAL, 8, 1 (1980)) ABOUT THE REACTION BETWEEN KETONES AND THIONYL CHLORIDE

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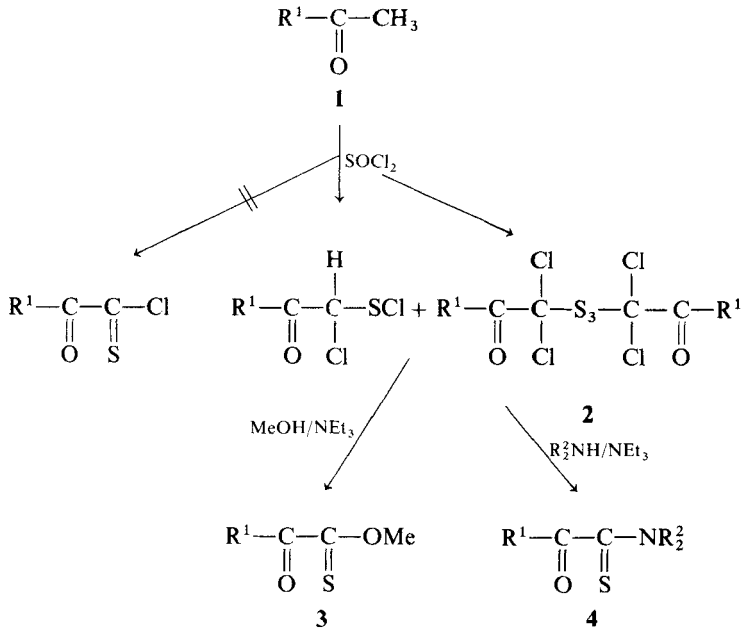
The structures of the intermediate 1,4-diaryl-2-chloro-1,4-dioxo-butane-2,3-disulphenyl chloride formed in the reaction of an acetophenone derivative with thionyl chloride and of the follow-up products, 1,4-diaryl-1,4-dioxo-butene-2,3-disulphenic acid diethyl ester and anilide **7** and **8** are called in question. More reliable structure for the compounds are proposed.

The reaction of certain methyl ketones with thionyl chloride has been studied by Oka and Hara in 1977.[1] However, recently we have shown,[2] that the α-oxo-thioacyl chlorides, claimed by these authors, are not formed in this reaction, α-chloro-sulphenyl chlorides and trisulphanes (**2**) being instead the primary products. The structure of the trisulphane (**2**, R^1 = tBu) has been confirmed by X-ray structure analysis.

On the other hand, α-oxo-thiono esters (**3**) and α-oxo-thioamides (**5**) are easily obtained from the reaction mixture by follow-up reaction with methanol or amines.

Our investigation included pinacolone (**1**, R^1 = tBu) as well as acetophenones (**1**, R^1 = Aryl). Surprisingly, Pizey and Symeonides[3] reported, that only trimethylacetyl chloride or its reaction

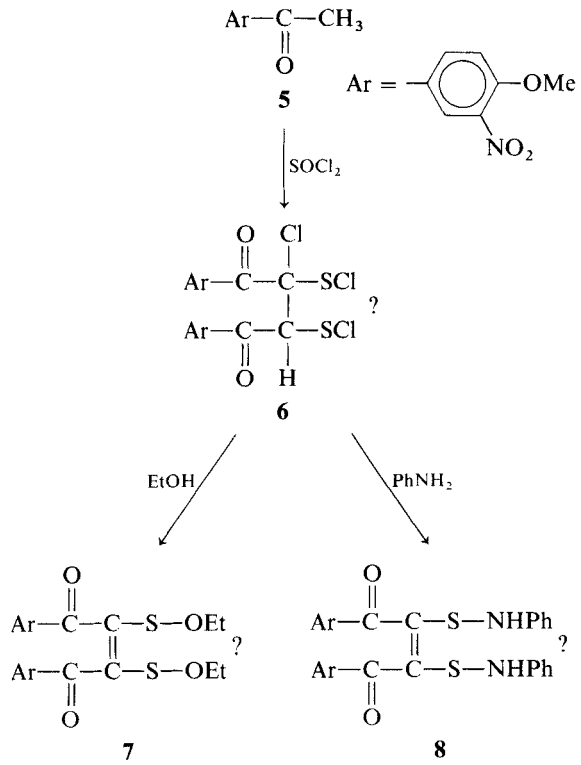


1 **2** **3** **4**

product with aniline, trimethylacetanilide, could be isolated from the reaction of pinacolone with thionyl chloride. In our experience[2] this should be due to the work-up procedure (distillation at 98°C at which temperature degradation of the labile reaction products occurs).[2]

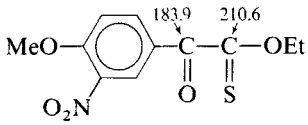
Furthermore, according to Pizey and Symeonides[3] 4-methoxy-3-nitro-acetophenone (**5**) should yield the 1,4-diaryl-2-chloro-1,4-dioxo-butane-2,3-disulphenyl chloride (**6**). This seems rather unlikely, since C—C coupling should not easily occur under the reaction conditions applied. In fact, the analytical and spectroscopic data given by the authors do not exclude isomeric structures without a newly formed C—C-bond, e.g. **13**.

The structures of the alcoholysis and aminolysis products (**7**) and (**8**) appear even more doubtful and have not at all been proved by convincing spectroscopic or chemical evidence.



We have therefore reproduced the preparations and have obtained the colourless crystals of $C_{18}H_{13}Cl_3N_2O_8S$, mp. 159°C (lit.:[3] mp. 159°C). Unfortunately the substance turned out to be too sparingly soluble in any solvent as to obtain a ^{13}C-NMR spectrum. Reaction of this material with ethanol and with aniline in the reported manner yielded yellow plates, mp. 68–70°C (lit.:[3] mp. 69–70°C) and yellow crystals, mp. 146°C (lit.:[3] 143°C), respectively. The elemental analyses of both compounds agreed with the literature data[3] and therefore with the reported stoichiometric formulas. However, evidently this is true for the "monomeric" formulas $C_{11}H_{11}NO_5S$ and $C_{15}H_{12}N_2O_4S$ as well! Determination of the molecular weight of the ethanolysis product by the osmometric method in our laboratory yielded MW = 271 in excellent agreement with MW = 269 calcalculated for $C_{11}H_{11}NO_5S$. Furthermore, the ^{13}C-NMR spectra unequivocally reveal the presence of a thiocarbonyl group in either compound: the chemical shifts of 210.6 and 187.9 ppm[4] respectively (cf. the formulas) agree well with those of reference compounds (**11**) and (**12**)[2] and with literature data,[5] whereas the olefinic carbon atom signals should not appear beyond 155 ppm.[6]

There is, therefore, no doubt, that these compounds exhibit the structure of an α-oxo-thiono ester (**9**) and anilide (**10**). Accordingly, the structure **6** can be also replaced by the more obvious one **13**.[7]



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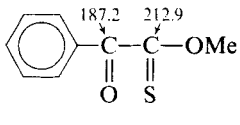

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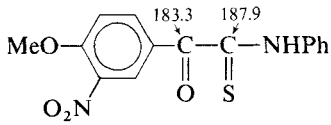

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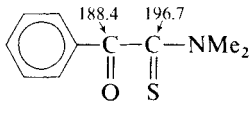

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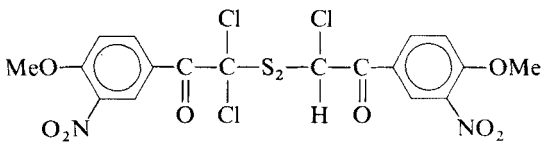

13

This result is in agreement with our findings on acetophenone derivatives[2,7] and seems to be much more probable, because the need of C—C-bond formation in the first step is dropped and the quite unusual vinyl bissulphenyl derivatives **7** and **8** have not to be taken into consideration.

EXPERIMENTAL

The melting points, determined on a Leitz-Heiztischmikroskop, are uncorrected. ^{13}C-NMR spectra were recorded on a Bruker WP 60 spectrometer (standard TMS, $\delta = 0.00$ ppm). The molecular weight of **9** was determined by means of the vapor pressure osmometer MECHROLAB osmometer 301a in $CHCl_3$ as solvent.

All preparations were performed as described by Pizey and Symeonides.[3]

4-Methoxy-3-nitroacetophenone (**5**)[8] 90 g *p*-Methoxyacetophenone were slowly added to a cooled mixture of 600 ml conc. H_2SO_4 and 600 ml conc. HNO_3 at 5°C. The reaction mixture was then stirred at room temperature for 30 min and poured on ice. The crystal cake was filtered off, washed with $NaHCO_3$-solution until the filtrate showed pH 7. The precipitate was recrystallized from ethanol to give yellow crystals of (**5**) mp. 98°C (lit.[8] mp. 99°C) yield 82%.

1,6-Bis(4-methoxy-3-nitrophenyl)-1,6-dioxo-2,2,5-trichloro-3,4-dithia-hexane (**13**) was obtained as colourless solid from **5** and $SOCl_2$. Mp 159°C (lit.:[3] mp. 159°C). (Calculated for $C_{18}H_{13}Cl_3N_2O_8S_2$: C, 38.90; H, 2.36; Cl, 19.14; N, 5.04; S, 11.54; Found: C, 39.30; H, 2.29; Cl, 18.24; N, 5.17; S, 11.38).

O-Ethyl 2-(4-methoxy-3-nitrophenyl)-2-oxoethanethioate (**9**) yellow plates, from **13** and EtOH. Mp. 68–70°C (lit.:[3] mp. 69–70°C). ^{13}C-NMR ($CDCl_3$): δ = 183.9 (C=O); 210.6 ppm (C=S). (Calculated for $C_{11}H_{11}NO_5S$: C, 49.07; H, 4.12; N, 5.20; S, 11.91; MW 269.3; Found: C, 48.95; H, 4.08; N, 5.12; S, 11.75; MW 271).

N-Phenyl-2-(4-methoxy-3-nitrophenyl)-2-oxoethanethioamide (**10**) yellow crystals, from **13** and aniline. Mp. 146°C (lit.[3]: mp 143°C). ^{13}C-NMR ($CDCl_3$): δ = 183.3 (C=O); 187.9 ppm (C=S). (Calculated for $C_{15}H_{12}N_2O_4S$: C, 56.95; H, 3.82; N, 8.86; S, 10.14; Found: C, 57.34; H, 3.81; N 8.87; S, 10.08).

ACKNOWLEDGMENTS

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3. J. S. Pizey and K. Symeonides, *Phosphorus Sulfur*, **8**, 1 (1980).
4. The signal of the thiocarbonyl carbon atom of **10** is shifted upfield by 9 ppm with respect to its counterpart in **12**. This effect is due to the N-phenyl group in **10**.
5. J. Voss in *The Chemistry of Functional Groups, Supplement B, The Chemistry of Acid Derivatives* (Ed. S. Patai), John Wiley & Sons, Chichester, New York, Brisbane, Toronto, 1979, p. 1021 ff.
6. E. Pretsch, T. Clerc, J. Seibl, and W. Simon, *Tabellen zur Strukturaufklärung organischer Verbidungen mit spektroskopischen Methoden*, Springer-Verlag, Berlin, Heidelberg, New York, 1976, p. C 90.
7. Interestingly the disulphane **13** is formed from **5**, whereas acetophenone yields the trisulphane **2**. This may be due to the extremely low solubility of **13** which causes its precipitation from the reaction mixture.
8. F. G. Pope, *Proc. Chem. Soc.* (*London*), **28**, 331 (1912); V. J. Harding, *J. Chem. Soc.* (*London*), **105**, 2790 (1914); O. Behaghel and H. Ratz, *Ber. Dtsch. Chem. Ges.*, **72**, 1257 (1939).