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INTERMEDIACY OF 1,2,4,5-DIOXADITHIANES IN THE CONVERSION OF THIOBENZOPHENONES INTO BENZOPHENONES. A NEW RING SYSTEM FORMATION

Janusz BARAN, Yvette HOUBRECHTS, and Pierre LASZLO*
Institut de Chimie Organique,
Université de Liège au Sart-Tilman,
4000 Liège, Belgium

3,3,6,6-tetraaryl-1,2,4,5-dioxadithianes, containing a new heterocycle, are isolated and characterized as reaction intermediates in thiocarbonyls to carbonyls transformations using clay supported metal nitrates. We propose a plausible mechanism, explaining the nitrosating behaviour of the reagent in this process.

Transient intermediates were observed during some of the earlier reported conversions of thiobenzophenones into benzophenones,[1)] using clay supported ferric nitrate. We report here isolation and characterization of two of these intermediates, 3,3,6,6-tetraphenyl- and 3,3,6,6-tetra(4-fluorophenyl)-1,2,4,5-dioxadithianes. Instead of the trithiolanes which had been postulated in the earlier literature,[2-4)] these intermediates are the six-membered title compounds. Trithiolanes themselves can be obtained in good yields by oxidation of thiones with tetrachloro-o-benzoquinone[5)] or with chloramine T.[6)] They differ from the actual intermediates in the transformation of thiobenzophenones into benzophenones. Our findings also rule out the intermediacy of sulfines. These are formed in the oxidation of thiones by oxygen with[7-9)] or without photoexcitation,[10)] by ozone [11)] or by peracid.[12)]

The following facts support our conclusions :

1. The ^{13}C NMR spectra (Table 1) of the two intermediates show non-equivalent phenyl rings at probe temperature (ca. 295 K) : this observation is hard to reconcile with a trithiolane structure, but is entirely consistent with a 1,2,4,5-dioxadithia- structure : the six-membered ring is in a chair conformation with non-equivalent axial and equatorial phenyl rings.

2. Mass spectroscopic determination of the elemental composition provides formulas $C_{26}H_{20}O_2S_2$ and $C_{26}H_{16}F_4O_2S_2$.[13)]

3. An authentic sample of the tetraphenyltrithiolane, prepared using secure methods from the literature[5)] is different (TLC, NMR, IR) from intermediate isolated from the reaction mixture.

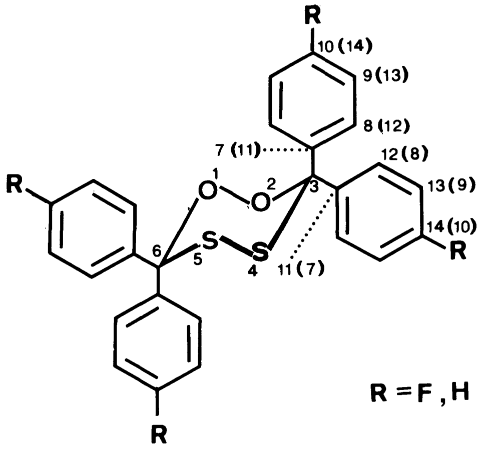


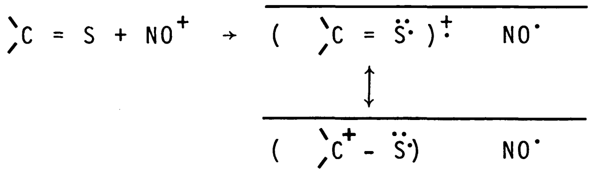
Table 1. Carbon-13 chemical shifts (ppm), at 75.432 MHz. ($CDCl_3$ solution)

Carbon[a]	R = F	R = H
3	185.75	188.40
7	130.90 (3.58)[b]	134.45
11	127.08 (2.70)[b]	134.45
8	131.63 (10.12)[b]	129.52
12	131.51 (8.60)[b]	129.33
9	116.32 (22.56)[b]	128.88
13	115.92 (22.56)[b]	128.58
10	164.56 (252.07)[b]	131.28
14	164.13 (256.14)[b]	130.72

a) Identification to either the axial or equatorial phenyl was not attempted.
b) C-F coupling in Hz.

From these results, we postulate a plausible reaction mechanism for the thiobenzophenone → benzophenone conversion, in the presence of clay-supported ferric nitrate :[1)]

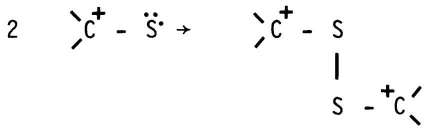
A. the nitrosonium cation NO^+ (E.A. = 9.26 eV [14)]) attaches to a lone pair on sulfur (I.P. = 8.60 - 9.38 eV [15)]), and generates a radical pair :



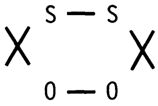
$$>C = S + NO^+ \rightarrow \overline{(\ >C = \ddot{S}\cdot\ )^{+\cdot}\quad NO^\cdot} \updownarrow \overline{(\ >C^+ - \ddot{S}\cdot)\quad NO^\cdot}$$

(we have shown in our numerous earlier publications, in ref. 1 for instance, that "clayfen" and "claycop" function as sources of nitrosonium NO^+ ions, from reaction of the metallic nitrate with dinitrogen tetroxide and from dismutation of N_2O_4 into NO_3^- and NO^+; the anhydrous metallic nitrates release spontaneously NO_2 radicals).

B. a radical coupling ensues :

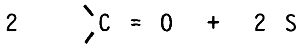


C. and is followed by addition of dioxygen :



The nitrate group or air serve as the source for the two atoms of oxygen and a reduced state of the metal could be involved at this stage.

D. cleavage and desulfurization then happen, again taking advantage of the strong affinity for sulfur of the soft Lewis acid NO^+ [14)]



The experimental procedure used was to a 2 mM solution of thiobenzophenone[16)] or 4,4'-difluorothiobenzophenone in 20 ml of dichloromethane under nitrogen, at 0 °C, 1.2 g of "claycop"[17)] was added in one portion, with stirring. After one hour the mixture was filtered, the solvent was evaporated as fast as possible under reduced pressure and the residue was dissolved in a small volume of dry dichloromethane. It was chromatographed twice on preparative silica-gel TLC plates (solvent - pentane : dichloromethane 1 : 2). The yields of title compounds ($R_f \cong 0.2$) were 11 - 23% (depending on work-up time). During the next few days slow decomposition took place (even under nitrogen and in the dark) and ketones formed (GC, TLC, IR).

3,3,6,6-tetraphenyl-1,2,4,5-dioxadithiane : oil; IR (KBr) : 1440, 1105, 1000, 750, 685 cm^{-1} (strong bands); MS (CI) : M^+ - m/z 446, M+1 31.0% M, M+2 14.3% M, Calcd for $C_{26}H_{20}O_2S_2 . NH_4$ m/z 446, M+1 30.6% M, M+2 13.8% M; Found : C 72.6%, H 4.85%, Calcd : C 72.87%, H 4.70%.

3,3,6,6-tetra(4-fluorophenyl)-1,2,4,5-dioxadithiane : mp 63-65 °C; IR(KBr) : 1590 (br.), 1490, 1225 (br.), 1155, 1110, 1090, 1005, 825, 800 cm^{-1}; MS (CI) : M^+ - m/z 518, M+1 28.7% M, M+2 13.8% M, Calcd for $C_{26}H_{16}F_4O_2S_2 . NH_4$ m/z 518, M+1 30.6% M, M+2 13.8% M; Found : C 63.13%, H 3.27%, Calcd : C 62.39%, H 3.22%.

3,3,5,5-tetraphenyl-1,2,4-trithiolane : mp 123-124 °C, lit,[3)] 124 °C,[5)] 128 °C;

IR (KBr) : 1480 (br.), 1440, 1220, 1180, 1080, 1030, 730, 690 cm^{-1}, lit.6) 1490, 1080, 1025, 920 cm^{-1}.

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References

1) S. Chalais, A. Cornélis, P. Laszlo, and A. Mathy, Tetrahedron Lett., 26, 2327 (1985).

2) H. Staudinger and H. Freudenberger, Chem. Ber., 61, 1836 (1928).

3) A. Schönberg, O. Schütz, and S. Nickel, Chem. Ber., 61, 2175 (1928).

4) E. Campaigne, Chem. Rev., 39, 1 (1946).

5) A. Schönberg and B. König, Chem. Ber., 101, 725 (1968).

6) M.M. Campbell and D.M. Evgenios, J. Chem. Soc., Chem. Commun., 1971, 179.

7) N. Ramnath, V. Ramesh, and V. Ramamurthy, J. Org. Chem., 48, 214 (1983).

8) N. Ramnath, V. Jayatherta Rao, V. Ramesh, and V. Ramamurthy, Chem. Lett., 1982, 89.

9) N. Ramnath, V. Ramesh, and V. Ramamurthy, J. Chem. Soc., Chem. Commun., 1981, 112.

10) L. Carlsen, J. Org. Chem., 41, 2971 (1976).

11) L. Carlsen, Tetrahedron Lett., 47, 4103 (1977).

12) B. Zwanenburg, L. Thijs, and J. Strating, Rec. Trav. Chim., 86, 577 (1967).

13) Values calculated for the alternate trithiolanes with the same M^+ were M+1 31.4% M, M+2 18.1% M.

14) W.D. Reents, Jr., and B.S. Freiser, J. Am. Chem. Soc., 103, 2791 (1981).

15) Sulfur lone pair ionization occurs at (eV) 9.38 for $H_2C=S$, 8.98 for $H_3CHC=S$ and 8.60 for $(H_3C)_2C=S$.

16) B.S. Pedersen, S. Scheibye, N.H. Nilsson, and S.-O. Lawesson, Bull. Soc. Chim. Belg., 87, 223 (1978).

17) "Claycop" - copper nitrate on K10 clay was used because reactions of thiones with this reagent run slower than with "clayfen" (ferric nitrate on K10 clay).

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