LITERATURE CITED

1. O. M. Nefedov and S. P. Kolesnikov, Izv. Akad. Nauk SSSR, Ser. Khim., 773 (1964).
2. F. Glockling, J. R. C. Light, and R. G. Strafford, J. Chem. Soc. A, 426 (1970).
3. E. Kováts, Helv. Chim. Acta, 41, 1915 (1958).
4. F. Glockling, J. R. C. Light, J. Walkner, and K. M. Mackay, J. Chem. Soc. A, 432 (1970).
5. F. Glockling and J. R. C. Light, J. Chem. Soc. A, 717 (1968).
6. A. Carrick and F. Glockling, J. Chem. Soc. A, 623 (1966).
7. S. P. Kolesnikov, I. S. Rogozhin, and O. M. Nefedov, Izv. Akad. Nauk SSSR, Ser. Khim., 2379 (1974).
8. M. S. Kharasch and O. Reinmuth, Grignard Reactions of Nonmetallic Substances, Prentice-Hall, New York (1954), p. 1055.

SYNTHESIS OF TETRABENZOYLTHIIRANE AND ITS REACTION WITH DERIVATIVES OF ACIDS OF TRIVALENT PHOSPHORUS

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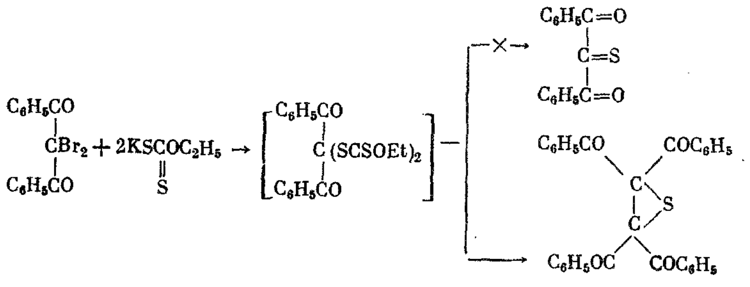
On reaction with trimethyl phosphite (TMP) and with dimethyl phenylphosphonite (DMPP), monothiobenzil forms 1,3,2-oxathiaphospholenes with a pentacoordinated phosphorus atom [1], and 2-oxo-1,3-dithioxo-1,3-diphenylpropane on reaction with derivatives of P(III) acids undergoes desulfuration and deoxidation [2]. It seemed of interest to synthesize 1,3-dioxo-2-thioxo-1,3-diphenylpropane and to study its reaction with trialkyl phosphites (TAPs) and phosphines. An attempt was made to synthesize the monothiotriketone mentioned by the reaction of dibromodibenzoylmethane with potassium xanthate by analogy with the reported preparation of 2-oxo-1,3-dithioxo-1,3-diphenylpropane [3,4].



(I)

The reaction actually gave a light yellow crystalline product with mp 192°C (yield 45%) corresponding, according to elementary analysis, to the formula $C_{30}H_{20}O_4S$. The individuality of the substance was confirmed by thin-layer chromatography. The PMR spectrum of the product contained only the signal of aromatic protons, and the IR spectrum had the bands of a benzoyl group at 1635 and 1680 cm^{-1}.

On the basis of all the facts given, the compound obtained was assigned the structure of the tetrabenzoylthiirane (I).

We have studied the reaction of (I) with tris(dimethylamino)phosphine (TDMAP), triphenylphosphine (TPP) and TMP at a ratio of the reactants of 1:2. It was found that in all cases the desulfuration and deoxidation of (I) took place with the formation of β,β'-dibenzoyl-α,α'-diphenylfuran (IV). The reaction took place at ~20°C. TDMAP reacted most readily, and the completion of the reaction with TMP required keeping the reaction mixture for several days.

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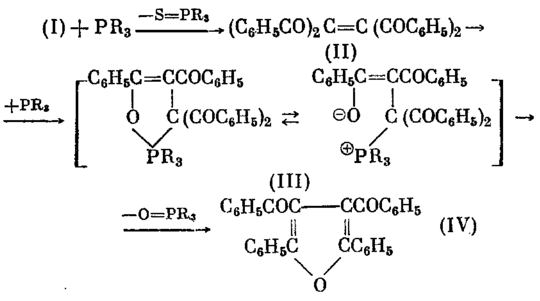
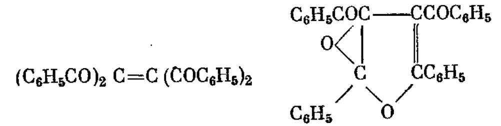
It is known that episulfides undergo desulfuration in reactions with TAPs and phosphines [5-7]. The tetrabenzoylethylene (II) formed in the course of the reaction reacts further with the P(III) compound giving the 1:1 adduct (III), which forms an equilibrium mixture of a phosphorane and a bipolar ion. The intermediate product (III) readily decomposes with the liberation of a phosphine oxide (or a phosphate) and the formation of β,β'-dibenzoyl-α,α'-diphenylfuran (IV). The analogous formation of oxides from 1,3,2-dioxaphospholanes has been reported previously [8]



R = OCH_3 (a), C_6H_5 (b), $N(CH_3)_2$ (c)

The formation of the bipolar ion (III) was shown by the ^{31}P NMR spectra in the reaction of (I) with TDMAP (δ_{31P}—60 ppm).

The course of the reactions that have been described was confirmed by a study of the reaction of (II) [9, 10] with TDMAP, TPP, and TMP. It has been shown [11-13] that (II) exists in two forms — α and β — that have the same melting point (184°C) and may change into one another in solution



(IIα) (IIβ)

The tetrabenzoylethylene synthesized in the form of light yellow crystals with mp 184°C has an IR spectrum identical with that of the α form [13]. In CH_2Cl_2 solution the substance has the same spectrum and it does not change on prolonged standing (2-3 weeks). We made an attempt to oxidize (II) to tetrabenzoyloxirane in order then to convert this into the tetrabenzoylthiirane (I). It was found, however, that on reaction with monoperphthalic acid tetrabenzoylethylene is recovered unchanged, and alkaline H_2O_2 cleaves (II) to benzoic acid. It has been shown [10] that the double bond in compound (II) is inactive and does not add bromine.

The reactions of (II) with TMP, TDMAP, and TPP were performed in CH_2Cl_2 solution at ~20°C and the reactions were complete in 10-15 days. In all cases the formation of the corresponding phosphine oxide (or phosphate) was shown by IR and ^{31}P NMR spectroscopy, and β,β'-dibenzoyl-α,α'-diphenylfuran (IV) was isolated.

EXPERIMENTAL

Tetrabenzoylthiirane (I). With stirring, 7.6 g of dibenzoyldibromomethane [14] was sprinkled into a solution of 6.4 g of potassium xanthate in 30 ml of DMF. The reaction mixture was stirred for 30 min, and then 50 ml of ethanol was added and it was left overnight in the refrigerator. The precipitate that had deposited was filtered off and was treated with hot water to eliminate KBr. The residual precipitate — 2.25 g (45%) — was recrystallized from a mixture of benzene and petroleum ether. Light yellow crystals with mp 192°C were obtained. Found: C 75.98; H 4.26; S 5.93%. $C_{30}H_{20}O_4S$. Calculated: C 76.05; H 4.20; S 6.73%. IR-spectrum (ν, cm^{-1}): 1680, 1635, 1595, 1580 s, 1495 w, 1455, 1335 s, 1315 m, 1270, 1235 s, 1185 m, 1140 s, 1100 s, 1080 m, 1045 w, 1025, 1005 m, 985 w, 905 s, 890, 840 m, 790 w, 765 m, 720, 700 s. When ethanol was used as the solvent for performing the experiments, the yield of (I) amounted to 1.9 g (38%).

Reaction of Tetrabenzoylthiirane (I) with Tris(dimethylamino)phosphine. In an atmosphere of dry nitrogen, a solution of 0.35 g of TDMAP in 5 ml of CH_2Cl_2 was added dropwise to a solution of 0.5 g of (I) in 15 ml of absolute CH_2Cl_2. The temperature rose slightly and the mixture almost immediately acquired an intense orange coloration which after a day had changed to straw yellow. The following signals were present in the

^{31}P NMR spectrum of the reaction mixture: —82 (S = P [NMe$_2$]$_3$), —25 (O = P(NMe$_2$)$_3$ and —60 ppm (III). After a few days the signal at —60 ppm had disappeared and the intensity of the signal at —25 ppm had increased. The solution was washed several times with water and was dried, and the solvent was distilled off in vacuum. The residue was recrystallized from ethanol. After several recrystallizations, yellow crystals with mp 124-126°C of (IV) were obtained. A mixture with authentic β,β'-dibenzoyl-α,α'-diphenylfuran had mp 124°C.

The reaction of (I) with triphenylphosphine was performed similarly. IR and NMR spectra showed the formation of S =P(C$_6$H$_5$)$_3$ (—42 ppm), O=P(C$_6$H$_5$)$_3$ (—27 ppm), and β,β'-dibenzoyl-α,α'-diphenylfuran. It was impossible to separate the products mentioned by fractional recrystallization.

Tetrabenzoylethylene (II) [9, 15].* A current of Cl$_2$ was passed into a boiling solution of 2.5 g of tetrabenzoylethane [15, 16] in 70 ml of glacial CH$_3$COOH until the solution had acquired a faint yellow coloration. It was then poured into water, neutralized with sodium carbonate and repeatedly extracted with ether, and the extract was dried over MgSO$_4$. After the solvent had been driven off, the residue was recrystallized from ethanol giving 1.6 g of (II) (64%) with mp 184°C. Found: 81.00; H 4.43%. C$_{30}$H$_{20}$O$_4$. Calculated: C 81.08; H 4.50%.

β,β'-Dibenzoyl-α,α'-diphenylfuran (IV) [10, 15].† A current of dry HCl was passed for several hours into a boiling solution of tetrabenzoylethane in glacial acetic acid. The resulting solution was poured into water, and the precipitate that deposited was recrystallized from ethanol. This gave yellow needles with mp 127.5-128°C. Found: C 84.39; H 5.00%. C$_{30}$H$_{20}$O$_3$. Calculated: C 84.10; H 4.67%. IR spectrum (ν, cm^{-1}): 1660 s, 1660, 1580, 1550 m, 1495, 1450, 1380 s, 1335 m, 1325, 1295 w, 1242 v. s, 1185, 1150, 1080, 1032 w, 915 s, 895 m, 780, 760, 750, 720, 705 m, 695 s.

Reaction of (II) with Tris(dimethylamino)phosphine. A mixture of 0.5 g of (II) and 0.2 g of P(NMe$_2$)$_3$ in 10 ml of CH$_2$Cl$_2$ was kept at ~20°C for 10 days. The formation of O=P(NMe$_2$)$_3$ was shown by IR and ^{31}P NMR spectroscopy (—24 ppm). The reaction mixture was washed several times with water and was dried over CaCl$_2$. After the solvent had been driven off, the residue was recrystallized from ethanol. Crystals with mp 124°C were obtained. A mixture with β,β'-dibenzoyl-α,α'-diphenylfuran gave no depression of the melting point. The IR spectrum was similar to that of (IV).

The reactions of (II) with trimethyl phosphite and with triphenylphosphine were performed similarly to that described above. The formation of, respectively, trimethyl phosphate (0 ppm) and of triphenylphosphine oxide (—28 ppm) was recorded by IR and ^{31}P NMR spectroscopy. In both cases, β,β'-dibenzoyl-α,α'-diphenylfuran with mp 125-126°C was isolated. A mixed melting point showed no depression.

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SUMMARY

1. Tetrabenzoylthiirane has been obtained by reaction of dibenzoyldibromomethane with potassium xanthate and its reactions with trimethyl phosphite, triphenylphosphine, and tris(dimethylamino)phosphine has been studied.

2. On reaction with the P(III) derivatives mentioned, tetrabenzoylthiirane undergoes desulfuration and deoxidation with the formation of β,β'-dibenzoyl-α,α'-diphenylfuran.

3. Tetrabenzoylethylene reacts with tris(dimethylamino)phosphine, with triphenylphosphine, and with trimethyl phosphite to form the corresponding oxide (or phosphate) and β,β'-dibenzoyl-α,α'-diphenylfuran.

LITERATURE CITED

1. B. A. Arbuzov, N. A. Polezhaeva, V. V. Smirnov, and A. A. Musina, Izv. Akad. Nauk SSSR, Ser. Khim., 1658 (1975).
2. B. A. Arbuzov, N. A. Polezhaeva, and M. N. Agafonov, Izv. Akad. Nauk, SSSR, Ser. Khim., 2101 (1976).
3. A. Schönberg and E. Frese, Tetrahedron Lett., 4063 (1969).

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* The syntheses of the compounds mentioned are not given in the citations, but the authors refer to A. Andres, Dissertation, Strasburg (1911).

†[This refers back to the same footnote as the previous asterisk].

4. A. Schönberg and E. Frese, Chem. Ber., 103, 3885 (1970).
5. C. C. J. Challenor, W. Davis, and N. S. Heath, J. Chem. Soc., 282 (1949).
6. N. P. Neureiter and F. C. Bordwell, J. Am. Chem. Soc., 81, 578 (1959).
7. J. I. G. Cadogan and R. N. Mockil, Chem. Soc. Revs., 3, 87 (1974).
8. B. A. Arbuzov and N. A. Polezhaeva, Usp. Khim., 43, 933 (1974).
9. H. V. Halban and H. Geigel, Z. Phys. Chem., 96, 233 (1920).
10. H. Keller and H. V. Halban, Helv. Chim. Acta, 27, 1253 (1944).
11. H. Keller and H. V. Halban, Helv. Chim. Acta, 28, 542 (1945).
12. H. Keller, E. Brandenberger, and H. V. Halban, Helv. Chim. Acta, 29, 1466 (1946)
13. H. Schmid, M. Hochweber, and H. V. Halban, Helv. Chim. Acta, 31, 1899 (1948).
14. Organic Syntheses [Russian translation], IL, Moscow, Coll. 2 (1949), p. 242.
15. H. Kleifeller and H. Trommsdorf, Chem. Ber., 71, 2448 (1938).
16. R. D. Abell, J. Chem. Soc., 101, 989 (1912).