The Reaction of Cyclopropenethione with Carbonyl-stabilized Phosphonium Methylides to Yield 2*H*-Pyran-2-thione

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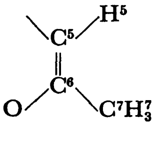
Synopsis. The reaction of diphenylcyclopropenethione with carbonyl-stabilized triphenylphosphonium methylides (**2**) to yield 2*H*-pyran-2-thiones was studied. It was clarified that electron-releasing substituents increased the reactivity of **2**.

The reactions of carbonyl-stabilized pyridinium and sulfonium methylides with cyclopropenone or cyclopropenethione to yield 2-pyrone derivatives[1,2] are well known. On the other hand the reaction of diphenylcyclopropenone with acyl- or alkoxycarbonyl-stabilized phosphonium methylides yields either 2-pyrone or methylenecyclopropene *via* (3+3)-cycloaddition or Wittig reaction.[1,2] However to our knowledge none of the reaction of diphenylcyclopropenethione (**1**) with carbonyl-stabilized phosphonium methylides (**2**) has been investigated.

In the continuation of our studies on the reaction of cyclopropenone with S-, N-, and P-ylides and imides,[3] we extended our attention to the use of carbonyl-stabilized phosphonium methylides (**2**) which are stable to air and moisture.

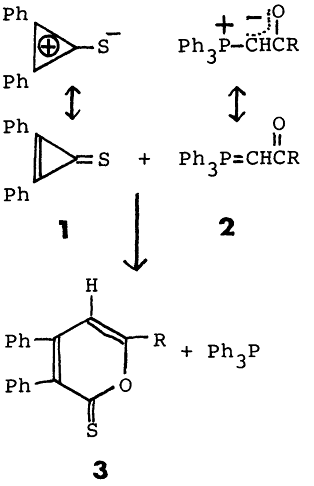
Methylides **2** were prepared according to the known methods.[4] Since **1** dimerizes on irradiation,[5] it was treated in the dark. Although a benzene solution of **1** and 1-(triphenylphosphoranylidene)-2-propanone **2a** at reflux gave only a tarry mixture, the reaction at room temperature for 3 d yielded a brown crystalline mass (51%) together with triphenylphosphine in 84% yield after TLC purification. The structure of the product was confirmed to be 3,4-diphenyl-6-methyl-2*H*-pyran-2-thione **3a** on the basis of IR ($\nu_{C=S}$ 1130 cm^{-1}) and NMR spectroscopic studies. The ^{13}C-NMR spectrum of **3a** gave a doublet at δ=111.1 (C^5, $J_{C^5H^5}$=170 Hz) and a quartet at δ=20.2 (C^7, $J_{C^7H^7}$=140 Hz) with long range couplings $J_{C^7H^5}$=3, $J_{C^5H^7}$=4, and $J_{C^6H^5 \text{ and } H^7}$=6 Hz), indicating the presence of the framework:



A similar treatment of the carbonyl-stabilized methylides **2b**—**d** with **1** afforded 2*H*-pyran-2-thiones **3b**—**d**. The methylides substituted with aroyl groups **2e**—**i** were less reactive toward **1** than **2a**—**d**. Thus, the ylides **2e**—**i** reacted with **1** at toluene reflux to give **3e**—**i** in moderate yields (Table 1 and 2). The known 2*H*-pyron-2-thione **3f** was obtained in a higher yield than the previously reported (71%).[2] Physical properties are collected in Table 2.

As is evident from the Table 1, increasing the electron releasing power of the substituent R increases the reactivity of **2**. The result correlates well with the reported mechanism for the reaction of cyclopropenone with S- and P-ylides.[1] Thus, the formation of 2*H*-pyran-2-thiones can be explained either by an initial attack on the thiocarbonyl group of **1** by the betaine oxygen atom of **2** or a Michael type addition of the methine of **2** to the C=C bond of **1** followed by isomerization to yield the product.

In conclusion, phosphonium methylides **2** have proven to be convenient reagents for the preparation of 2*H*-pyran-2-thiones in moderate yields.



2 3	R
a	Me
b	H
c	NMe$_2$
d	SMe
e	C$_6$H$_4$Me-4
f	C$_6$H$_5$
g	C$_6$H$_4$Br-4
h	C$_6$H$_4$NO$_2$-3
i	C$_6$H$_4$NO$_2$-4

Scheme 1.

Experimental

General. Melting points are uncorrected. ^{1}H-NMR spectra were recorded on a Hitachi R-24B (60 MHz) spectrometer using TMS as an internal standard and ^{13}C-NMR spectra on a JEOL JNM FX-60 spectrometer (15.04 MHz).

Materials. Diphenylcyclopropenethione **1** was prepared according to the literature.[6] Phosphonium methylides

Table 1. The reaction of **1** with **2**.

2	Reaction Temp/°C	Conditions Time	Yield 3/%
2a	25	3d	51
2b	25	4d	39
2c	25	1d	72
2d	25	1d	46
2e	110	6h	74
2f	110	8h	87
2g	110	4d	70
2h	110	6d	39
2i	110	6d	37

Table 2. Physical properties of **3**.

3	Mp θ_m/°C	^{1}H-NMR($CDCl_3$)	MS(M^+)	Found/% (Calcd/%) C	H	N
3a	135—137	2.43(3H, s, Me), 6.43(1H, s, C_6H), 6.8—7.6(10H, m, Ar)	278	77.92	4.87	
				(77.66	5.06	)
3b	148	6.57(1H, d, J=5Hz, C_5H), 6.8—7.4(10H, m, Ar), 7.78(1H, d, C_6H)	264	77.05	4.47	
				(77.24	4.57	)
3c	151—152	3.05(6H, s, 2Me), 5.44(1H, s, C_6H), 6.6—7.2(10H, m, Ar)	307	74.42	5.51	4.37
				(74.24	5.57	4.56)
3d	96—103	2.70(3H, s, Me), 6.70(1H, s, C_6H), 7.0—7.9(10H, m, Ar)	310	69.71	4.65	4.94
				(69.64	4.54	5.15)
3e	194—196	2.28(3H, s, Me), 6.7—7.9(14H, m, Ar)	354	81.16	5.32	
				(81.32	5.11	)
3f	169—170[a]	6.9—7.8(m, Ar)	340			
3g	210—211	6.6—7.9(m, Ar)	419	65.71	3.92	
				(65.87	3.60	)
3h	213—214	6.9—8.1(m, Ar)	385	71.73	3.84	3.52
				(71.67	3.92	3.63)
3i	194—196	6.5—8.4(m, Ar)	385	71.85	3.74	3.90
				(71.67	3.92	3.63)

a) Ref. mp 165—166 °C.[2)]

2 were obtained by the known methods.[4)]

Reaction of **1** *with* **2**. An equimolar mixture of **1** and **2** (**2a—d** in benzene at room temperature and **2e—i** in toluene at reflux temperature) was allowed to react in the dark. The disappearance of **1** was checked by TLC at suitable time intervals. Then, the solvent was removed *in vacuo* to give a crystalline mass. TLC separation over silica gel afforded **3** and triphenylphosphine. Yields and physical properties of **3a—i** are summarized in Tables 1 and 2.

^{13}C-NMR spectroscopic data. **3a**($CDCl_3$) δ=20.2 (q, Me), 111.1 (d, C^5), 127.5 (d), 127.9 (d), 128.0 (d), 128.4 (d), 128.7 (d), 130.6 (d), 136.1 (s), 136.8 (s), 137.0 (s), 147.9 (s), 165.8 (s, C^6), and 198.0 (s, C^2). **3f** ($CDCl_3$) δ=108.5 (d, C^5), 125.7 (d), 127.5 (d), 127.9 (d), 128.1 (s), 128.4 (d), 128.7 (d), 129.0 (d), 130.4 (s), 130.6 (d), 131.3 (d), 136.8 (s), 137.0 (s), 137.4 (s), 147.7 (s), 164.4 (s, C^6), and 196.9 (s, C^2).

References

1) K. T. Potts and J. S. Baum, *Chem. Rev.*, **74**, 189 (1974); K. Matsumoto and Y. Ikemi, *Heterocycles*, **14**, 1445 (1980) and references cited therein.

2) T. Eicher, E. Angerer, and A. Hansen, *Justus Liebigs Ann. Chem.*, **746**, 102 (1971); T. Eicher, U. Sebold, and U. Stegmann, *Tetrahedron Lett.*, **24**, 2977 (1983) and references cited therein.

3) H. Yoshida, S. Sogame, Y. Takishita, and T. Ogata, *Bull. Chem. Soc. Jpn.*, **56**, 2438 (1983).

4) H. J. Bestmann and R. Zimmermann, "Organic Phosphorus Compounds," ed by G. M. Kosolapoff and L. Maier, Wiley-Interscience, New York (1972) Vol. 3.

5) A. Schoenberg and M. Mamluk, *Tetrahedron Lett.*, **1971**, 4993.

6) H. Yoshida, M. Nakajima, and T. Ogata, *Synthesis*, **1981**, 36.