

THIONE STUDIES. REACTIONS OF STABLE ALICYCLIC THIONES  
WITH METHYLENETRIPHENYLPHOSPHORANE.

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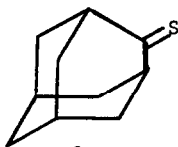
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One of the most extensively utilized reactions involving phosphorus ylides is the Wittig reaction with carbonyl compounds to produce olefins and a phosphine oxide. Numerous mechanistic and synthetic investigations have appeared on the Wittig reaction and the gross mechanistic features are reasonably well understood (1). Despite the extensive volume of literature concerning reactions of phosphorus ylides with carbonyl compounds, no research appears to have been reported on reactions of aliphatic or alicyclic thiones with ylides of this type. The aromatic thione, thiobenzophenone, has been reported to yield 1,1-diphenylethylene (76%) and triphenylphosphine sulfide (82%) on treatment with methylenetriphenylphosphorane (1) (2). As part of a continuing program of study of reactions of stable aliphatic thiones (3), we wish to report several novel reactions of thiones with methylenetriphenylphosphorane (1).

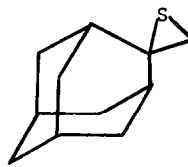
Adamantanethione (2) on treatment with 1 (all reactions were performed in ether and the ylide was generated by treatment of the phosphonium salt with a n-butyllithium solution in hexane; equimolar amounts of the ylide and the substrate were used in all reactions except where noted) leads to episulfide 3 and triphenylphosphine (both isolated in 80% yields). In contrasting behavior, treatment of adamantanone (2, S = O) with 1 leads to methyleneadamantane in an 80% yield (4).



1

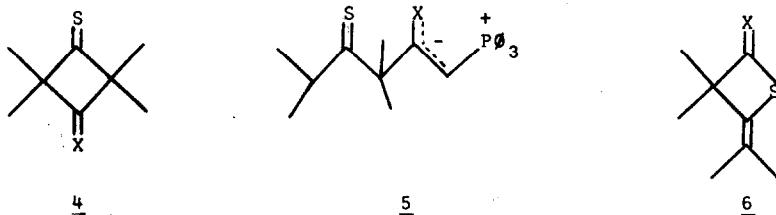


2



3

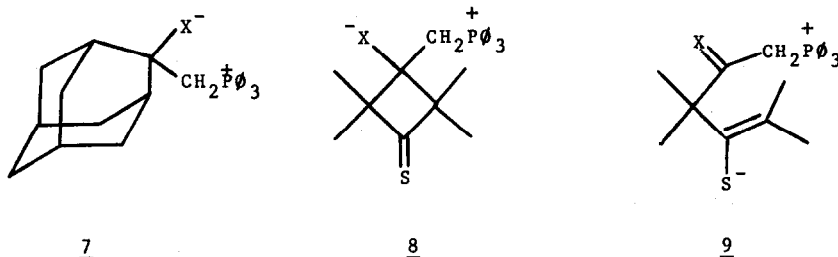
Treatment of the dithione 4 ( $X = S$ ) with 1 leads to the novel thiocarbonyl stabilized ylide 5 ( $X = S$ ) (20%) along with dithiolactone 6 ( $X = S$ ) (75%). Ylide 5 ( $X = S$ ) crystallizes from benzene-ligroin in orange clusters, melts at  $140^{\circ}$ - $142^{\circ}$ , and exhibits the following nmr pattern ( $CDCl_3$ ):  $\delta$  1.2 (d,  $J = 7$  Hz, 6H), 1.6 (s, 6H), 3.6 (septuplet,  $J = 7$  Hz, 1H), 4.7 (d,  $J = 29$  Hz [P-H], 1H), and 7.2 ppm (m, 15H). The carbonyl ylide 5 ( $S = O$ ,  $X = O$ ) exhibits a doublet at 3.7 ppm ( $J_{P-H} = 25$  Hz) (5). Dithiolactone 6 ( $X = S$ ) can be obtained by treatment of 4 ( $X = S$ ) with various bases (6). Treatment of dithiolactone 6 ( $X = S$ ) with 1 also leads to ylide 5 ( $X = S$ ) (15%) along with recovered starting material.



Treatment of the thioketone 4 ( $X = O$ ) with 1 leads to the carbonyl stabilized ylide 5 ( $X = O$ ) (38%) along with the thiolactone 6 ( $X = O$ ) (47%). When 4 ( $X = O$ ) is treated with 4 equivalents of 1 a 60% yield of 5 ( $X = O$ ) is obtained. Ylide 5 ( $X = O$ ) forms orange clusters from ligroin, melts at  $109^{\circ}$ - $112^{\circ}$ , and exhibits the following nmr pattern ( $CDCl_3$ ):  $\delta$  1.2 (d,  $J = 7$  Hz, 6H), 1.4 (s, 6H), 3.5 (d,  $J = 25$  Hz [P-H], 1H), 3.7 (m, 1H), and 7.3 ppm (m, 15H). In addition the ir spectrum shows strong absorption at  $1535\text{ cm}^{-1}$  ( $\delta_3^+ PCH=C=O$ ) (5). Thiolactone 6 ( $X = O$ ) on treatment with 1 leads to 5 ( $X = O$ ) (35%) and recovered starting material (42%).

Ylides 5 ( $X = S$ ) and 5 ( $X = O$ ) on being heated under reduced pressure (about 0.05 mm) lead to volatile products (30%-40%) which were identified as mixtures of diisopropylthione (40%) and the corresponding enethiol (60%) by nmr comparisons with reported literature values for these compounds (7).

The contrasting products which are obtained when ketone 2 ( $S = O$ ) and thione 2 are treated with 1 might be rationalized by considering the betaine intermediates 7 which might be formed on addition of 1 to these substrates. Betaine 7 ( $X = S$ ) could undergo a nucleophilic displacement of  $\phi_3P$  by  $S^-$ . Since  $S^-$  is expected to be more reactive towards saturated carbon than  $O^-$ , and since  $O^-$  is a better nucleophile for  $P^+$  than  $S^-$ , the formation of episulfide 3 from 7 ( $X = S$ ) and methyleneadamantane from 7 ( $X = O$ ) can be rationalized (8). One of the most powerful driving forces for



the success of the Wittig reaction with carbonyl substrates would appear to be the formation of the strong P-O bond in the decomposition step leading to the phosphine oxide and the olefin (8a). The formation of a P-S bond is a much less exothermic process (9). The recent mechanistic suggestion that the Wittig reaction is a  $\pi^2_s + \pi^2_a$  cycloaddition process must also be considered (1d). The cycloadduct formed from 1 and 2 might undergo a rapid ring-opening to yield betaine 7 (X = S) while cycloaddition of 1 and 2 (S = O) might lead to an oxaphosphetane which decomposes to methyleneadamantane. A mechanism involving thiophilic attack of ylide 1 on the C=S bond of thione 2 followed by displacement of  $\phi_3P$  must also be considered (10).

The formation of ylide 5 (X = S) and dithiolactone 6 (X = S) from thione 4 (X = S) suggests that both might arise from a common ring-opened intermediate. Attack of ylide 1 on 4 (X = S) could lead to 8 (X = S) which on ring-opening could lead to 9 (X = S). Intermediate 9 (X = S) could be the direct precursor of 5 (X = S) [via proton transfer] and 6 (X = S) [via nucleophilic displacement of 1]. Dithiolactone 6 (X = S), on treatment with 1, would also produce intermediate 9 (X = S). The formation of 5 (X = O) and 6 (X = O) from 4 (X = O) can be rationalized in a similar manner. Formation of 8 (X = O) would appear to be most favorable in this case and ring-opening of this intermediate would lead to 9 (X = O). Ylide 5 (X = O) and thiolactone 6 (X = O) could arise from intermediate 9 (X = O). Thiolactone 6 (X = O) would also yield 9 (X = O) on treatment with 1.

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