(1973); (g) R. Viau and T. Durst, *J. Amer. Chem. Soc.*, **95**, 1346 (1973); (h) K. Nishihata and M. Nishio, *Tetrahedron Lett.*, 4839 (1972).
(16) (a) B. J. Hutchinson, K. K. Anderson, and A. R. Katritsky, *J. Amer. Chem. Soc.*, **91**, 3839 (1969); (b) R. R. Fraser, F. J. Schuber, and Y. Y. Wigfield, *ibid.*, **94**, 8785 (1972).
(17) The ratios presented in Table I are quite reproducible and were shown not to vary in the presence or absence of triethylamine. The product sulfoxides **3a** and **3b** also were shown not to undergo appreciable epimerization under the reaction conditions.
(18) J. R. Hanson and E. Premuzic, *Angew. Chem., Int. Ed. Engl.*, **7**, 247 (1968).
(19) R. E. Erickson and R. K. Holmquist, *Tetrahedron Lett.*, 4209 (1969).
(20) J. K. Kochi and D. D. Davis, *J. Amer. Chem. Soc.*, **86**, 5264 (1964).
(21) J. K. Kochi and P. E. Mocaldo, *J. Org. Chem.*, **30**, 1134 (1965).
(22) D. G. Holah and J. P. Fackler, Jr., *Inorg. Syn.*, **20**, 26 (1967).
(23) The α,α-dichloro sulfoxides have S–O stretching frequencies near 1100 cm^{-1}, which is *ca.* 50 cm^{-1} higher than normal: K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, San Francisco; California, 1962, p 54.
(24) Our results here closely parallel those reported elsewhere.[10]
(25) W. R. Waldron and E. E. Reid, *J. Amer. Chem. Soc.*, **45**, 2399 (1923).
(26) I. Heilbron, "Dictionary of Organic Compounds," Vol. 4, Oxford University Press, New York, N. Y., 1965, p 2436.
(27) M. D. Wolfinger, Ph.D. Thesis, Northwestern University, 1968.

Desulfurization of β-Keto Sulfides and Thiocyanates with Tris(dialkylamino)phosphines[1a]

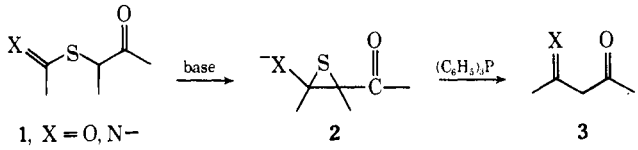
David N. Harpp* and S. Martin Vines[1b]

Department of Chemistry, McGill University, Montreal, Canada

Received August 10, 1973

Tris(dimethylamino)phosphine (**4a**) desulfurizes β-keto sulfides to afford a variety of products including ketones and enol ethers. The mechanism probably involves a phosphonium salt. Benzyl thiocyanate was readily desulfurized by **4a** in a complex reaction to afford benzyl cyanide and dibenzyl sulfide as the main products.

The reaction of trivalent phosphorus compounds with a wide variety of sulfur-containing molecules has received considerable attention in recent years, particularly as a technique for modifying the substrate by extrusion of the divalent sulfur atom.[2] While simple sulfides are inert to phosphines and phosphites, activated sulfides of type **1** are desulfurized in the presence of triphenylphosphine and base.[3] The reaction is widely applicable to the preparation of secondary vinylogous amides or enolizable β-diketones **3**. It has been suggested that **1** is first converted to an episulfide **2** which is then desulfurized.[4]

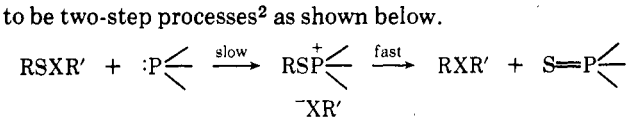


1, X = O, N– **2** **3**

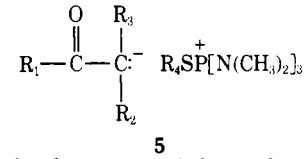
Related work has shown that tris(dialkylamino)phosphines (**4**) are particularly useful reagents for smoothly extruding sulfur from a variety of molecules. These include disulfides,[2] thiosulfonates ($RSSO_2R$),[5] sulfenyl thiosulfonates ($RSSSO_2R$),[5b] thiosulfinate esters [RS(=O)-SR],[6] trisulfides,[7] sulfenimides [$RSN(C(=O)R)_2$],[8] and sulfenate esters (RSOR).[9]

$(R_2N)_3P$
4a, R = CH_3
b, R = CH_2CH_3

The desulfurization reactions are in some cases known to be two-step processes[2] as shown below.



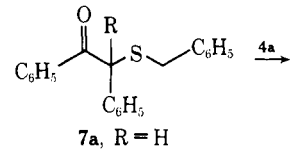
Reactions of β-Keto Sulfides. If the above pathway could be used to generate carbanions which fulfilled the dual role of leaving group and nucleophile, a new procedure for carbon–carbon bond formation would be available. Accordingly, a number of β-keto sulfides were prepared and their reaction with tris(dimethylamino)phosphine (**4a**) was examined. Previous work[2,5-9] suggested that the proposed reaction would probably involve a phosphonium salt intermediate **5**.[15a-c]



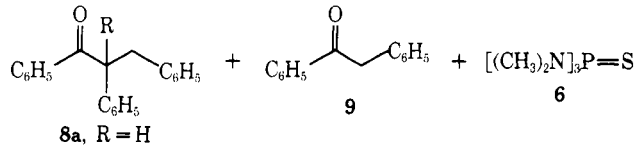
5

To facilitate displacement of the carbanion of **5**, a phenyl group was used at R_2. It appeared that a benzyl moiety at R_4 might encourage easy displacement of tris(dimethylamino)phosphine sulfide (**6**). α-Benzoyl-α-phenylmethyl benzyl sulfide (**7a**)[10] reacts extremely slowly with phosphine **4a** (in a variety of solvents), giving deoxybenzoin ($C_6H_5COCH_2C_6H_5$, **9**) as the principal product.

When the reaction was carried out in the absence of solvent, the starting materials were consumed in less than 1 hr to give three products as analyzed by quantitative vpc: 1-benzoyl-1,2-diphenylethane (**8a**, 69%), deoxybenzoin (**9**, 22%), and tris(dimethylamino)phosphine sulfide (**6**, 86%). **8a** was subsequently isolated in 43% yield.



7a, R = H
b, R = D



8a, R = H **9** **6**
b, R = D

It appears that **5** ($R_1 = R_2 = C_6H_5$; $R_4 = C_6H_5CH_2$; R_3 = H) is formed, but that the anion is partially diverted by proton abstraction to give deoxybenzoin (**9**). The proton attached to the α carbon atom in **7a** is likely to be the one abstracted. This was confirmed by isolation of $PhCOCD_2Ph$ after the reaction of keto sulfide **7b** with aminophosphine.

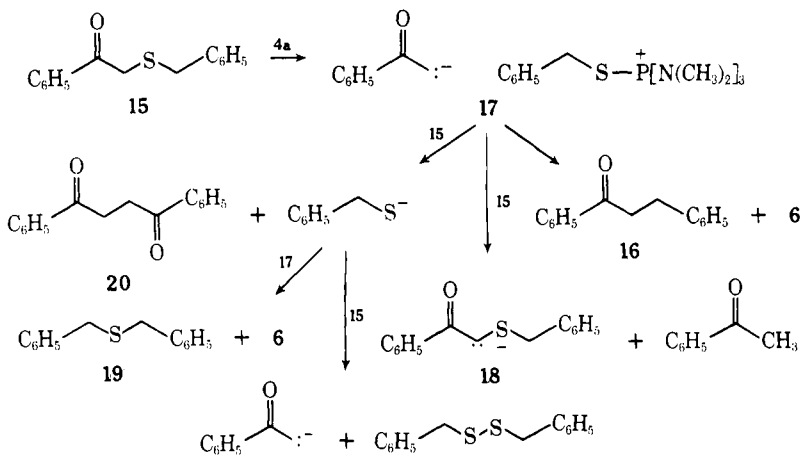
To determine whether alkylative coupling could occur for a β-keto sulfide that did not have a benzyl group as the second substituent on the sulfur atom, α-benzoyl-α-

Table I
Reaction of Tris(dimethylamino)phosphine with β-Keto Sulfides

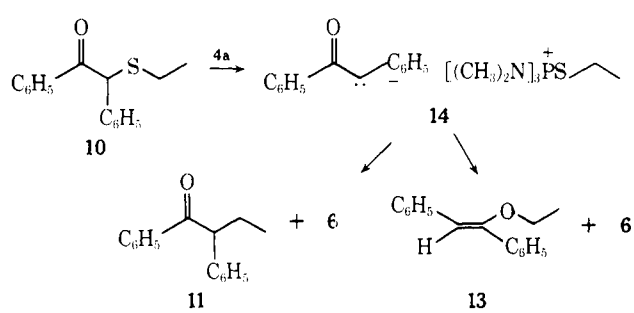
	Starting material				Products (%)		
	$R_1CCHR_2SCH_2R_3$			$R_1CCHR_2CH_2R_3$	$C_6H_5CCH_2R_2$	$[(CH_3)_2N]_3P{=}S$ (6)	
Compd	R_1	R_2	R_3				Other
7a	C_6H_5	C_6H_5	C_6H_5	69[a] (43)[b]	22[a] (12)[b]	86[a]	
10	C_6H_5	C_6H_5	CH_3	31[a]	9[a]	67[a]	**13**, 14[a] **12**, 28[c]
15	C_6H_5	H	C_6H_5	5[a]	30[a]	47[a]	$(C_6H_5CH_2)_2S$, 50[a]

[a] Crude yield (estimated by isolation of product and/or quantitative vpc and nmr of impure fractions). [b] Isolated pure. [c] Per cent of vpc integral trace.

Scheme I



phenylmethyl ethyl sulfide (**10**) was prepared[10] and treated with aminophosphine **4a**. Although 1-benzoyl-1-phenylpropane (**11**) was formed in reasonable yield (Table I), it proved difficult to isolate, as it and deoxybenzoin (**9**) behave in a very similar manner on column, thin layer, and gas chromatography. A third unidentified material **12** also had very similar chromatographic properties. The fourth product, *trans*-1-ethoxy-1,2-diphenylethene (**13**), gives further credence to the carbanion mechanism.[11]



In an attempt to simplify the mixture of products formed in the desulfurization of **10**, effects of solvent on the reaction were considered. It has been reported[12] that C-alkylation of ketonic anions is promoted by the use of hydroxylic solvents (such as water, polyfluorinated alcohols, or phenols). It is unlikely that the proportion of ketone **11** could be increased by the use of such solvents, as the anion of **14** would become irreversibly protonated, giving deoxybenzoin as the major product. Polar aprotic solvents, such as *N,N*-dimethylformamide or dimethyl sulfoxide, have a tendency to increase the proportion of O-alkylation.[12] Finally, use of volatile aprotic solvents such as benzene or 1,4-dioxane gives slow desulfurization to form a product mixture very similar to that obtained by treatment of β-keto sulfide **10** with neat aminophosphine.

It was found that temperature has little effect on product distribution; the major effect is on reaction rate. This observation suggests that the rate-determining step is the attack of phosphorus on sulfur to give **14**, or (less likely) that this step is fast and that the subsequent reactions of this intermediate all have similar thermodynamic parameters.

To test whether the α-phenyl group is required for desulfurization to occur, α-benzoylmethyl benzyl sulfide (**15**) was prepared[13] and treated with aminophosphine **4a** (Scheme I) to give benzyl sulfide (50%) as the only product isolable from the reaction. The reaction was slower than for the previous keto sulfides; starting material (2%) was present even after heating for 3 hr at 150°. Acetophenone (30%) was the other major product; only a small amount of 1-benzoyl-2-phenylethane (**16**, 5%) was produced.

The observed products (**6**, **16**, and **19**) can be rationalized (Scheme I) in a similar fashion as in the reaction of **7** and **10** with phosphine **4a**. This would yield **17**, the anion of which would not in this case be expected to attack starting material displacing benzyl mercaptide ion, since the more stable deoxybenzoin anion formed from **7a** and **10** does not undergo such an intermolecular reaction. Ketone **20** in fact is not observed in the reaction mixture.[14]

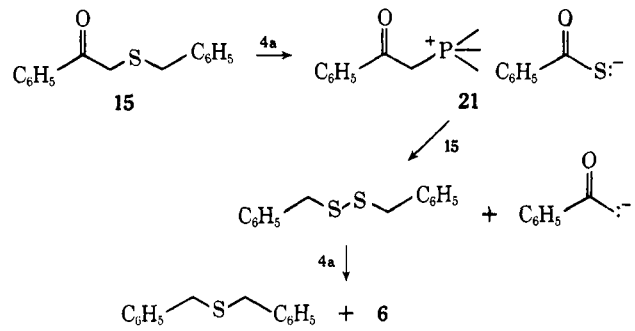
A plausible source of benzyl mercaptide ion involves an S_N2 process (Scheme II) analogous to that proposed for some reactions of trialkyl phosphites with aromatic thiocyanates.[15c,d] If this type of mechanism were in operation, mercaptide ion formation should be encouraged by the use of a β-keto sulfide containing an α-phenyl moiety. Also, if an ion pair such as **17** were formed, its fate should be similar to that of the corresponding ion pairs invoked as intermediates in the desulfurization of the α-phenyl-β-keto sulfides **7** and **10**. Finally, if phosphorus were attacking carbon, a low yield of phosphine sulfide **6** would be expected; this was, in fact, observed.

Table II
Reaction of Aminophosphines with RSXR

X	pK_a of RXH	X	pK_a of RXH
$-SO_2-$[a,b]	2[5]	$-S-$[a]	10[2]
$-\overset{O}{\overset{\|}{S}}-$[a,b]	>2[5]	$-O-$[a]	17[9]
$-SS-$[a]	8[7]	$-CH_2\overset{O}{\overset{\|}{C}}-$[b,c]	19
$-NHCO-$[a]	9[8]	$-CH_2CO_2-$[d]	23

[a] Smooth desulfurization to give RXR in good yield. [b] If X can provide an ambident anion (*e.g.*, $-SO_2^-$), more than one product may be formed. [c] Some desulfurization, competition from side reactions. [d] No reaction.

Scheme II



A direct substitution reaction such as that invoked in the thiocyanate-phosphine reaction would be encouraged by the reduction in crowding at the α carbon atom produced by removal of the phenyl group. Removal of this group would also increase the activation energy for the attack of phosphorus on sulfur to displace the carbanion of **17**, which is less stable than the anion formed from **7a** and **10**. This is probably the major factor in changing the direction of the reaction. No other compounds could be isolated from the reaction mixture because several of the products had similar chromatographic properties.

The reaction of S-substituted thioglycollic acid esters with aminophosphines was also investigated. Ethyl 4-phenyl-3-thiabutanoate (**22**)[16] gave no reaction with neat tris(dimethylamino)phosphine (**4a**), even when a mixture of the two compounds was maintained at high temperature for extended periods of time. The lack of reactivity of the ester can be rationalized by the relatively high pK_a associated with $^-:CH_2CO_2Et$ (pK_a = 24),[17] which must be displaced by phosphine for desulfurization to occur. The anion of **17** is more stable (pK_a = 19),[17] and is hence a better leaving group than the anion that must form from **22**. A nucleophilic substitution reaction involving attack of phosphine on the carbon atom α to the carbonyl group would be much slower for the ester than for the ketone.[18] Thus, the limit of the reaction of aminophosphines with sulfur-containing molecules emerges (Table II). Aminophosphines will not displace groups with a pK_a ≥ 20. Where the pK_a is near 20, higher temperatures and neat reactants are usually required to effect displacement.

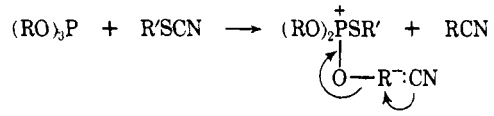
Reaction of Thiocyanates. Cyanide ion is similar to sulfide ion in that it is a good leaving group and nucleophile. It was thus felt that thiocyanates might be converted readily to nitriles on treatment with an aminophosphine. Early reports exist in the literature for the desulfurization of thiocyanates[20] and isothiocyanates[21] on treatment with trialkylphosphines, although few experimental data were given. More recently, the reactions of thiocyanates with trialkyl phosphites have been studied.[15]

Table III
Reaction of Benzyl Thiocyanate with Aminophosphine 4a

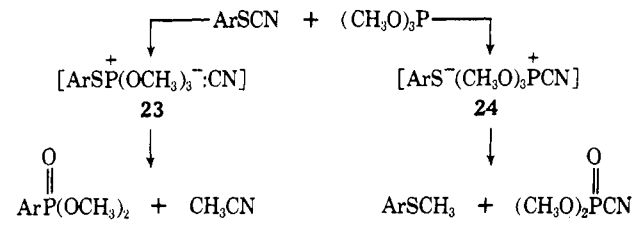
Solvent	Time,[a] min	Products, %[b] $(C_6H_5CH_2)_2S$	$C_6H_5CH_2CN$	$[(CH_3)_2N]_3P{=}S$
None	40	45	9	32
Acetonitrile	40	42	17	30
Dichloromethane	30	25	22	38
p-Dioxane	60	25	11	41
Benzene[c]	130	21	6	28

[a] Time for the reaction mixture to attain constant composition (vpc). [b] Determined by quantitative vpc. [c] Reflux.

Desulfurization accompanied by rearrangement was observed.[15b] Sheppard obtained evidence that the rearrangement occurs through an ionic pathway and proposed the following mechanism.[15b]



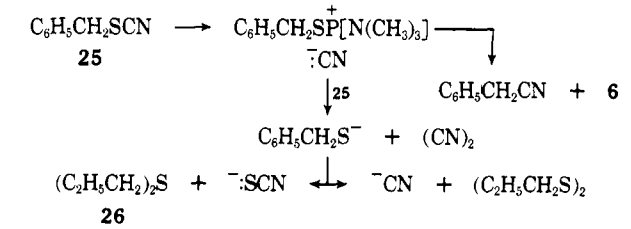
Pilgram and Phillips, in a detailed study of the reaction of a number of aryl thiocyanates with trimethyl phosphite, found that another reaction path is possible.[15c] Instead of preferentially attacking sulfur to form intermediate **23**, phosphorus can attack the carbon atom of the thiocyanate group, displacing a mercaptide ion to give intermediate **24**.



Treatment of benzyl thiocyanate (**25**) with tris(dimethylamino)phosphine gave an immediate exothermic reaction that produced a deep red color, even at room temperature. Vapor phase chromatography indicated that the reaction mixture was extremely complex (at least ten products). Preparative thin layer chromatography yielded only benzyl sulfide (**26**) and tris(dimethylamino)phosphine sulfide (**6**) as isolable materials. A large quantity of brown oil was obtained which contained many components. Vapor phase chromatography showed that benzyl cyanide was one of the major products.

The reaction was repeated in a variety of solvents. The yields of the major constituents of the mixture are shown below (Table III). The rate of formation of the red color increased with the polarity of the solvent.

If the appearance of the red color is indicative of the rates of the major reaction pathways, then it would seem that the mechanism is ionic. A plausible pathway is outlined below.



Benzyl cyanide could be formed by attack of aminophosphine on the sulfur atom, followed by attack of the displaced cyanide ion on the intermediate phosphonium

ion, in accord with the mechanisms of the other desulfurization reactions discussed. Attack of cyanide on this phosphonium ion may also give some isocyanide; although vpc did not rule out the presence of this compound, none was isolated.

If cyanide attacks a second molecule of thiocyanate instead of the phosphonium ion, it could displace mercaptide ion. The mercaptide ion could then attack the starting material to give either the observed sulfide or benzyl disulfide. Again, vpc did not rule out the presence of disulfide, but it was not isolated from the reaction mixture; if formed, it would be desulfurized by aminophosphine to give benzyl sulfide.[2]

Attack by **4a** on the carbon atom of the thiocyano group is also possible.[15c] Such an attack would lead to displacement of mercaptide ion, which could react with **25** to give benzyl sulfide.

Experimental Section[22]

Action of Tris(dimethylamino)phosphine on β-Keto Sulfides. α-Benzoyl-α-phenylmethyl Benzyl Sulfide. A. In the Presence of a Solvent. Refluxing a solution of α-benzoyl-α-phenylmethyl benzyl sulfide (**7a**, 0.318 g, 1.0 mmol) and tris(dimethylamino)-phosphine (**4a**, 0.16 g, 1.0 mmol) in benzene or 1,4-dioxane (1 ml) for 8 hr gave small amounts of deoxybenzoin (**9**) as the major product (qualitative vpc). A similar result was obtained using dichloromethane as solvent, either stirring for 24 hr at room temperature or refluxing for 12 hr.

B. Without Solvent. α-Benzoyl-α-phenylmethyl benzyl sulfide (**7a**, 1.00 g, 3.2 mmol) and tris(dimethylamino)phosphine (**4a**, 0.510 g, 3.2 mmol) were heated on an oil bath at 120°. After 30 min all starting material had been consumed (vpc). The mixture was then chromatographed on silica gel (60–100 mesh) using hexane (100 ml), hexane–dichloromethane mixtures (9:1, 100 ml; 4:1, 100 ml; 3:2, 500 ml; 1:1, 500 ml) and dichloromethane (100 ml) as eluents. The fractions collected were monitored by vpc. Separations were not completely efficient; combination of the first eluents and crystallization from ethanol gave 1-benzoyl-1,2-diphenylethane (**8a**, 0.39 g, 43%) as colorless needles, mp and mmp 119–120° (lit.[23] mp 120–121°). It was identical in all respects (vpc, tlc, ir, nmr) with an authentic sample. A later fraction was crystallized from aqueous ethanol to afford deoxybenzoin (9, 0.075 g, 12%), mp and mmp 55–56°, identical in all respects with an authentic sample.

α-Benzoyl-α-deuteriomethyl Benzyl Sulfide (7b). β-Keto sulfide **7a** (2.0 g) was crystallized from deuterioethanol (EtOD) to which a small piece of sodium had been added. The product was dissolved in carbon tetrachloride (10 ml); the resultant solution was filtered and evaporated to give, after crystallization (EtOH), the title compound **7b** (1.4 g, 70%) as colorless needles, mp 73–74°, and no detectable absorption in the nmr spectrum at δ 4.72, suggesting quantitative deuteration at the α position.

A portion of this material (0.79 g, 2.5 mmol) was mixed with tris(dimethylamino)phosphine (**4a**, 0.456 g, 2.8 mmol) and heated on an oil bath at 150° for 1 hr. The resulting mixture was chromatographed to give (a) 1-benzoyl-1-deuterio-1,2-diphenylethane (**8b**, 0.389 g, 55%), mp 121–123° after crystallization (ethanol) (mmp with nondeuterated material 121–122°, identical with **8a** by tlc and vpc); (b) $C_6H_5COCD_2C_6H_5$ (**9**, 0.045 g, 9%), mp 47–51°, pure by tlc (CCl_4) and vpc, containing 80% deuterium at the benzylic position (nmr, CCl_4); (c) a mixture of these two materials (0.130 g, tlc, vpc); and (d) tris(dimethylamino)phosphine sulfide (**6**, 0.340 g, 81%), identified by vpc and nmr.

α-Benzoyl-α-phenylmethyl Ethyl Sulfide. α-Benzoyl-α-phenylmethyl ethyl sulfide (**10**, 0.128 g, 0.5 mmol) and tris(dimethylamino)phosphine (**4a**) were mixed and heated on an oil bath for various time intervals and temperature conditions. Above 120° using varying molar amounts of phosphine (consumed in ~10 min) virtually constant yields of **9**, **11**, **12**, and **13** were obtained.

The reaction was also examined using benzene, 1,4-dioxane, and *N,N*-dimethylformamide as solvents (1 ml) and 1 mmol of each of the starting materials. Again, yields were approximately constant with each solvent.

Isolation of Products. α-Benzoyl-α-phenylmethyl ethyl sulfide (**10**, 640 mg, 2.5 mmol) and tris(dimethylamino)phosphine (**4a**, 450 mg, 2.7 mmol) were heated on an oil bath at 150° for 1 hr. The resulting mixture was chromatographed on silica gel (60–100 mesh, 60 g) using hexane (500 ml) and hexane–dichloromethane mixtures (9:1, 2 l.; 8:2, 2 l.; 7:3, 1 l.; 6:4, 1 l.; and 5:5, 1 l.) as eluents. The fractions collected were monitored by vpc. Separations were not completely efficient; however, the first fraction, a colorless oil (80 mg), was pure by tlc (hexane) and vpc; ν_{max} (liquid film) 2978, 1638, 1604, 1689, 1497, 1452, 1120 (v broad), 925, 772, and 700 cm^{-1}; nmr gave signals (CCl_4) at δ 1.8–2.8 (multiplet, 10 H), 3.8 (singlet, 1 H), 6.1 (quartet, 2 H), and 8.7 (triplet, 3 H); mass spectrum showed P^+ at 224. This information indicates that the material is an enol ether, $C_6H_5CH{=}C(C_6H_5)OC_2H_5$. Identification of a band characteristic of trans alkyl enol ethers in the ir[25] at 925 cm^{-1} suggests that this compound is *trans*-**1-ethoxy-1,2-diphenylethylene** (**13**, 14%). The second fraction was rechromatographed to give a sample of 1-benzoyl-1-phenylpropane (**11**, 61 mg, 11%) (vpc, tlc, nmr); after crystallization (EtOH) mp and mmp 49–52° (lit. mp 57°,[23c] 58°[24]); a mixture of **11** and **12** (160 mg) (vpc, tlc) was also obtained. Ketone **11** was also present in the next two fractions (vpc, tlc, nmr). Tris(dimethylamino)phosphine sulfide (**6**, 327 mg, 67%) was isolated in a further fraction (pure by vpc and tlc).

α-Benzoylmethyl Benzyl Sulfide. α-Benzoylmethyl benzyl sulfide (**15**, 2.42 g, 10 mmol) and tris(dimethylamino)phosphine (**4a**, 1.80 g, 11 mmol) were heated on an oil bath at 150° for 3 hr. The resulting mixture was chromatographed on silica gel (60–100 mesh) (250 g) using as solvents hexane (1.5 l.), hexane–dichloromethane mixtures (1:10, 1 l.; 1:9, 1 l.; 3:17, 1 l.; 1:4, 1 l.; 3:7, 1 l.; 2:3, 1 l.; 1:1, 1 l.; 7:3, 1 l.), dichloromethane (1 l.), chloroform (1 l.), ethyl acetate (1 l.), and methanol (1 l.). Efficient separation proved impossible; however, dibenzyl sulfide (540 mg, 50%) was isolated as yellow prisms, mp and mmp 47–49°, identical in all respects (tlc in benzene, vpc, ir, nmr) with an authentic sample of the sulfide.

Further fractions were obtained containing acetophenone, dibenzyl sulfide, 1-benzoyl-2-phenylethane (**16**),[26] starting material, and traces of other unidentified materials (vpc, tlc in cyclohexane or benzene, nmr).

Tris(dimethylamino)phosphine sulfide (**6**, 911 mg, 47%) was isolated in an almost pure state. Large quantities of polar material containing many unidentified components were also obtained.

Benzyl Thiocyanate. Benzyl thiocyanate (0.149 g, 1 mmol) and tris(dimethylamino)phosphine (0.163 g, 1 mmol) were mixed. An immediate reaction ensued, turning the mixture deep red. Mixing these materials in methylene chloride (1 ml) or acetonitrile (1 ml) gave a similar result. When benzene (1 ml) was used as solvent the reaction was much slower; the mixture turned yellow, orange, then red.

The methylene chloride solution obtained in this manner was separated into five fractions by preparative tlc on silica gel [solvents cyclohexane–ethyl acetate (1:1) and then benzene].

Dibenzyl sulfide, identical with an authentic sample (vpc, tlc, nmr, ir), and tris(dimethylamino)phosphine sulfide (**6**) (vpc, nmr) were isolated.

The other three fractions contained many components that were not identified, as they proved inseparable.

The reaction was then repeated in a variety of solvents; the product mixtures were analyzed for benzyl sulfide, benzyl cyanide, and **6** by quantitative vpc, using cumene as an internal standard. The results of these experiments are summarized in Table III.

Acknowledgment. We wish to thank the National Research Council of Canada for financial support of this work.

Registry No.—**4a**, 1608-26-0; **7a**, 23343-23-9; **7b**, 50311-41-6; **8b**, 50311-42-7; **10**, 16222-12-1; **15**, 2408-88-0; benzyl thiocyanate, 3012-37-1.

References and Notes

(1) (a) Organic Sulfur Chemistry. XVIII. For part XVII, see D. N. Harpp and T. G. Back, *J. Org. Chem.*, **38**, 4328 (1973). (b) Holder of NRCC Bursary, 1971–1972.
(2) D. N. Harpp and J. G. Gleason, *J. Amer. Chem. Soc.*, **93**, 2437 (1971), and references cited therein.
(3) M. Roth, P. Dubs, E. Gotschi, and A. Eschenmoser, *Helv. Chim. Acta*, **54**, 710 (1971).
(4) (a) C. C. J. Culvenor, W. C. Davies, and N. S. Heath, *J. Chem. Soc.*, 282 (1949); (b) R. E. Davis, *J. Org. Chem.*, **23**, 1767 (1958); (c) R. D. Schuetz and R. L. Jacobs, *ibid.*, **23**, 1799 (1958); (d) N. P. Neureiter and F. G. Bordwell, *J. Amer. Chem. Soc.*, **81**, 578 (1959); (e) D. B. Denny and M. J. Boskin, *ibid.*, **82**, 4736 (1960).
(5) (a) D. N. Harpp and J. G. Gleason, *Tetrahedron Lett.*, 1447 (1969); (b) D. N. Harpp, J. G. Gleason, and D. K. Ash, *J. Org. Chem.*, **36**, 322 (1971).

(6) J. E. McCormick and R. S. McElhinney, *J. Chem. Soc., Perkin Trans. 1*, 2795 (1972); D. N. Harpp and J. G. Gleason, unpublished results.
(7) D. N. Harpp and D. K. Ash, *Chem. Commun.*, 811 (1970).
(8) D. N. Harpp and B. A. Orwig, *Tetrahedron Lett.*, 2691 (1970).
(9) D. H. R. Barton, G. Page, and D. A. Widdowson, *Chem. Commun.*, 1466 (1970); D. N. Harpp and B. A. Orwig, unpublished results.
(10) D. N. Harpp and P. Mathiaparanam, *J. Org. Chem.*, **37**, 1367 (1972).
(11) Investigation of the alkylation of the anion of ethyl acetoacetate with alkyl halides suggests that increased SN2 activity of the alkylating agent is correlated with decreased O/C activity toward nucleophilic substitution.[12] This is in agreement with our observation that when two keto sulfides (which give the same ketonic anion) undergo desulfurization, ethyl keto sulfide **10** gives significant quantities of enol ether while the benzylic homolog **7a** does not.

$$C_6H_5CCH(C_6H_5)SR$$
7a, R = $C_6H_5CH_2$
10a, R = CH_3CH_2

(12) W. J. LeNoble and J. E. Piorta, *Tetrahedron Lett.*, 1087 (1966); W. J. LeNoble and H. F. Morris, *J. Org. Chem.*, **34**, 1969 (1969).
(13) L. M. Long, *J. Amer. Chem. Soc.*, **68**, 2159 (1946).
(14) It should be noted that while ketone **20** was not observed as a product in the reaction, thereby precluding significant benzyl mercaptide formation by this route, benzyl mercaptide does react with starting material **15** to give benzyl disulfide. This disulfide is known to desulfurize with **4a** to give benzyl sulfide.[2]
(15) (a) J. Michalski and J. Wieczorkowski, *Bull. Acad. Pol. Sci., Cl.* **3**, 4279 (1956); *Chem. Abstr.*, **51**, 4266 (1957). (b) W. A. Sheppard, *J. Org. Chem.*, **26**, 1460 (1961). (c) K. Pilgram and D. A. Phillips, *ibid.*, **30**, 2388 (1965). (d) This pathway contrasts with our initial mechanism (*vide supra*) as well as that of Borowitz[15e] on an analogous substrate. (e) I. J. Borowitz and R. Virkhaus, *J. Amer. Chem. Soc.*, **85**, 2183 (1963).
(16) (a) K. Schlogl, F. Wessely, and H. Woidich, *Monatsh. Chem.*, **87**, 425 (1956); (b) A. Ghavveau and R. Mathis-Noel, *Ann. Fac. Sci. Univ. Toulouse Sci. Math. Sci. Phys.*, **25**, 147 (1961); *Chem. Abstr.*, **60**, 11885*h* (1961); (c) C. Berse and G. Dupuis, *Can. J. Chem.*, **47**, 2174 (1965).
(17) (a) J. B. Conant and G. W. Wheland, *J. Amer. Chem. Soc.*, **54**, 1212 (1932); (b) W. K. McEwan, *ibid.*, **58**, 1124 (1936); (c) R. G. Pearson and R. L. Dillon, *ibid.*, **75**, 2439 (1953); (d) A. Streitweiser Jr., W. C. Langworthy, and J. I. Bravman, *ibid.*, **85**, 1761 (1963).
(18) For the analogous reactions of α-chloroacetophenone and ethyl chloroacetate with potassium iodide in acetone, exchange is about eight time more rapid for the former.[19]
(19) J. B. Conant, W. R. Kirner, and R. F. Hussey, *J. Amer. Chem. Soc.*, **47**, 488 (1925).
(20) A. W. Hofmann, *Ann. Chem. Pharm., Suppl. I*, 53 (1861).
(21) A. W. Hofmann, *Ber.*, **3**, 766 (1870).
(22) Gas chromatographic analyses (vpc) were performed on an F & M Model 5750 research chromatograph equipped with a Perkin-Elmer Model 194B printing integrator. Two 6 ft × 0.125 in. stainless steel column were used: 10% silicon gum rubber UC-W98 on Diaport S (80–100 mesh) and SE-30 ultraphase (10% by weight) on Chromosorb W AW/DMCS 80–100 mesh. Thin layer chromatographic analyses were performed on Eastman chromatogram sheets 6060 [silica gel with fluorescent indicator on poly(ethylene terephthalate) support; polyvinyl alcohol binder]. Solvent systems used are indicated in the text. Common intermediates were obtained from commercial sources and were purified as necessary. Melting points were obtained on a Gallenkamp apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 257 grating infrared spectrophotometer. Spectra were calibrated with 3027- and 1601-cm^{-1} bands of a polystyrene film reference. Refractive indices were measured on a Carl Zeiss 38341 refractometer at room temperature. Nuclear magnetic resonance (nmr) spectra were recorded on a Varian Associates T-60 spectrophotometer. All data are given in parts per million relative to TMS (used as an internal standard). Mass spectra were recorded on an AE1-MS-902 mass spectrometer equipped with a direct insertion probe.
(23) (a) S. Miyano and Y. Sako, *Chem. Pharm. Bull.*, **13**, 1372 (1965); (b) F. Klingemann, *Justus Liebigs Ann. Chem.*, **275**, 50 (1893); (c) H. Fiesselmann and J. Ribka, *Chem. Ber.*, **89**, 27 (1956); (d) E. J. Cragoe, Jr., A. M. Pietruszkiewicz, and C. M. Rbb, *J. Org. Chem.*, **23**, 1971 (1958).
(24) V. Meyer and L. Oelkers, *Ber.*, **21**, 1297 (1888).
(25) S. I. Miller, *J. Amer. Chem. Soc.*, **78**, 6091 (1956).
(26) R. Adams, J. W. Kem, and R. L. Schringer, "Organic Syntheses," Collect. Vol. I; H. Gilman and A. H. Blatt, Ed., Wiley, New York, N. Y., 1964, p 101.

Sulfuric Acid Catalyzed Rearrangements of 1- and 3-Homoadamantanols

Jelena Janjatović, Danko Škare, and Zdenko Majerski*

Rudjer Bošković Institute, 41001 Zagreb, Yugoslavia

Received July 5, 1973

Both 1- and 3-homoadamantanol yield homoadamantane, 1- and 2-methyladamantane, and 1-adamantylcarbinol in the reactions with 75% sulfuric acid (70°). The mechanism very likely involves formation of the 1- and 3-homoadamantyl cations, followed by hydride transfers and rearrangements of the resulting classical homoadamantyl cations into the corresponding bridged cations. A simple, good-yield preparation of 1-homoadamantanol is described.

Reactions with sulfuric acid leading to adamantane derivatives attracted considerable attention in the last few years.[1-8] *endo*-2,6-Trimethylene-*exo*-2-norbornanol in sulfuric acid was reported to rearrange smoothly into 1-adamantanol,[1] bicyclo[3.3.1]nonane-2,7-diol into 2-oxaadamantane,[2] while 3-hydroxymethylbicyclo[3.3.1]nonan-7-ol produced a mixture of 2-adamantanol, di(2-adamantyl) ether, and adamantane.[3] 2-Hydroxy-2-methyladamantane in 98% sulfuric acid gave various mixtures of methyladamantanones or methyladamantanes and hydroxymethyladamantanes depending on the temperature.[4] Synthetically useful reactions are also encountered. Treatment of deltacyclane with sulfuric acid gave either 1- or 2-noradamantanol or noradamantane, depending on conditions.[5] The reaction of adamantane or 1-adamantanol with 96% sulfuric acid (80°) resulted in a 50% yield of adamantanone,[6a] providing a very convenient method for the functionalization of the methylene position of adamantane. Both adamantanone oxime[7] and lactone 4-oxahomoadamantan-5-one[8] with sulfuric acid were reported to give fair yields of 4-hydroxyadamantan-2-one.[9]

The reaction of adamantanols with sulfuric acid were extensively investigated by Geluk and Schlatmann.[6] 2-Adamantanol was shown to rearrange to 1-adamantanol (>98%) at 28° in concentrated sulfuric acid.[6a,10] An equilibrium mixture containing small amounts of 2-adamantanol was rapidly achieved from either direction. However, with 70% H_2SO_4 (90°) a mixture of 1,4-adamantanediol, adamantane, 1-hydroxy-4-adamantanone, and adamantanone was obtained.[6b] 1-Adamantanol, under essentially the same conditions, disproportionated into 1,3-adamantanediol and adamantane.[6b] The mechanism of these reactions appears to involve an intermolecular hydride transfer of a bridgehead hydrogen from one molecule of the starting alcohol to an adamantyl cation which is generated from another molecule of the alcohol and is transformed into adamantane.[11]

An analogous mechanism would be reasonably expected to operate in reactions of homoadamantyl alcohols with sulfuric acid. However, the 3- and 4-homoadamantyl cations, if formed, could rearrange into the corresponding nonclassical cations, which may lead to adamantane de-