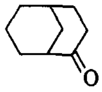
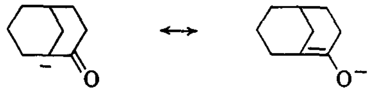


8

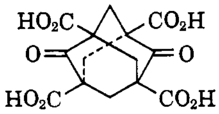


9a **9b**

pictures, structure **9b** must be an important resonance form.

A difficulty which arises when enolization data is used to evaluate the limits of Bredt's rule is that the degree of resonance stabilization of the enolate ion (and therefore, the acidity of the bridgehead hydrogen) is a function of the cosine of the projected angles between the interacting orbitals in the ion. Since it has not been ascertained low much orbital overlap is necessary to allow enolate formation, these data only require the conclusion that significant double-bond character can exist between C-1 and C-2 in the bicyclo[3.3.1]nonane series and not that a stable double bond can be formed between these carbon atoms.

Although there is ample evidence that the preferred conformation of bicyclo[3.3.1]nonanes is the chair-chair modification,[7] an examination of Dreiding models of **8** immediately shows that formation of a true enolate is not possible in this conformation since the C-1–H bond is orthogonal to the p-orbitals of the carbonyl group. However, if the ring containing the carbonyl group is in the boat form, the projected angle between the interacting orbitals decreases to 30° (cos 30° = 0.866) and resonance interactions in the transition state for removal of the proton and in the subsequent enolate ion can result in significant delocalization energies. The importance of the conformational factor on enol formation is dramatically illustrated by the stability of **10** toward decarboxylation[8] since all rings are locked in the chair conformation, in contrast to **6** where the rings are mobile.



10

Experimental

In a test tube was placed 200 mg. (1.45 mmoles) of bicyclo[3.3.1]nonan-2-one,[9] 5 ml. of freshly distilled dioxane, 5 ml. of deuterium oxide, and *ca.* 20 mg. of sodium. The tube was sealed, placed in a constant-temperature bath at 95°, and after several days (see Table I) was removed and cooled and the contents were poured into 100 ml. of pentane. The pentane solution was washed with five 50-ml. portions of ice–water to remove the dioxane and dried over magnesium sulfate. After removal of the pentane the ketone was sublimed and analyzed on the mass spectrometer.

Acknowledgment.—The authors wish to express their gratitude to the Petroleum Research Foundation (Grant PRF-789) for their generous support of the initial phases of this work.

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[8] O. Böttger, *Ber.*, **70B**, 314 (1937).

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Reduction of Sulfoxides by Triphenylphosphine and Carbon Tetrachloride

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While the reduction of sulfoxides by triphenylphosphine is acid catalyzed[2] and thus the reduction does not take place in an inert solvent such as benzene, it was found[3] that di-*p*-bromophenyl sulfoxide was reduced to the corresponding sulfide when heated with triphenylphosphine in the presence of carbon tetrachloride.

The purpose of this Note is to report this new reaction in view of its potential usefulness since, generally speaking, it produces good yields of sulfides even in the presence of nitro groups.

Experimental

The reductions of most diaryl sulfoxides were performed by refluxing, during 2 hr., a mixture of 0.01 and 0.02 moles of the sulfoxide and triphenylphosphine, respectively, in 100 ml. of carbon tetrachloride. The reaction mixture was then evaporated on a steam bath and the residue was worked up depending upon the solubility of the sulfide. Sulfides which crystallize readily from ethanol (di-*p*-bromophenyl and di-*p*-nitrophenyl sulfides) were obtained by dissolving the residue in ethanol in which triphenylphosphine oxide is readily soluble, while the lower melting sulfides were obtained by extraction of the residue with petroleum ether (b.p. 35–47°) and by evaporation of this extract.

In the case of di-*p*-hydroxyphenyl sulfoxide which is highly insoluble in carbon tetrachloride, the dry, finely ground powder was suspended in a mixture of 100 ml. each of carbon tetrachloride and benzene and the reflux period was extended to 18 hr. The reaction mixture was concentrated as described above and the oily residue was then extracted with aqueous sodium hydroxide. This left behind most of the triphenylphosphine oxide, and the sulfide was isolated by acidification of the alkaline extract, extraction with ether, crystallization from water, and recrystallization from benzene.

The reaction of dimethyl sulfoxide is highly exothermic and thus a solution of 0.01 mole of this sulfoxide in 50 ml. of carbon tetrachloride was added slowly to the solution of the phosphine in 100 ml. of carbon tetrachloride. The volatile dimethyl sulfide was swept by means of a stream of nitrogen into a 2.5% solution of mercuric chloride in water in order to precipitate the sulfide in the form of the metallic complex.[4]

The experimental results are summarized in Table I. The yields and melting points of the sulfides are those of the crude products. In all cases these were further purified and found to give satisfactory mixture melting points with samples of the authentic sulfides. The purity of the crude products was also examined by thin layer chromatography. Owing to the high solubility of triphenylphosphine oxide in ethyl alcohol the crudes obtained by crystallization from this solvent (*p*-bromo and *p*-nitro) were free from the oxide; conversely all the crudes obtained by petroleum ether extraction contained a trace of it. The crude of di-*p*-hydroxyphenyl sulfide contained a larger amount of the oxide but crystallization from water brought about a satisfactory purification of the sulfide.

The reaction between di-*p*-bromophenyl sulfoxide and triphenylphosphine in carbon tetrachloride was also carried out using equimolar quantities of the first-mentioned reagents, and the expected sulfide was isolated in 91% yield.

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[1] To whom all inquiries should be addressed.

[2] H. H. Szmant and O. Cox, manuscript in preparation.

[3] O. Cox, M.S. Thesis, University of Puerto Rico, 1964.

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Table I

Reduction of Sulfoxides by Triphenylphosphine and Carbon Tetrachloride

Sulfoxide	M.p. °C.	Lit. m.p., °C.	Sulfide Yield, %	Sulfide M.p., °C.	Sulfide Lit. m.p., °C.
Dimethyl[a]			82	157.5–163.5[b]	150–151[b]
Di-*p*-tolyl	94–95	92[c]	100	54–57.5	57.3[d]
Di-*p*-hydroxyphenyl	195–196	195[e]	27	135.5–147.5	151–151.5[f]
Di-*p*-methoxyphenyl	95–96	93–94[g]	90	38.5–42.5	46[f]
Di-*p*-bromophenyl	154–155	153[h]	94	114.5–115.5	112[i]
Di-*p*-nitrophenyl	182–187	178–180[j]	83	150–153	158–160[k]
Phenoxathiin-10-oxide	154–155	158–159[l]	91	51.5–55	57.5–58[m]

[a] Matheson Coleman and Bell product redistilled *in vacuo.* [b] Mercuric chloride complex reported in ref. 4. [c] H. C. Parker, *Ber.*, **23**, 1845 (1890). [d] E. Fischer, *ibid.*, **48**, 96 (1915). [e] S. Smiles and A. W. Bain, *J. Chem. Soc.*, **91**, 1119 (1907). [f] G. Tassinari, *Gazz. chim. ital.*, **17**, 83 (1887). [g] S. Smiles and A. Le Rossignol, *J. Chem. Soc.*, **93**, 755 (1908). [h] J. Boesecken, *Rec. trav. chim.*, **29**, 315 (1910). [i] K. W. Rosenmund and H. Harns, *Ber.*, **53**, 2234 (1920). [j] H. H. Szmant and J. J. McIntosh, *J. Am. Chem. Soc.*, **73**, 4356 (1951). [k] C. C. Price and G. W. Stacy, *Org. Syn.*, **28**, 82 (1948). [l] H. D. K. Drew, *J. Chem. Soc.*, 511 (1928). [m] C. M. Suter and Ch. E. Maxwell, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 485.

While the mechanism of this reaction is currently under study, it is very likely that the reduction of the sulfoxides is brought about by the dichloromethylidene derivative of the triphenylphosphine produced[5] according to this equation.

$$2Ph_3P + CCl_4 \longrightarrow Ph_3P{=}CCl_2 + Ph_3PCl_2$$

Furthermore, one is tempted to suggest that the ylide reacts subsequently with the sulfoxide to give an intermediate sulfur ylide, similar to the known reaction of carbonyl compounds.[5]

$$Ph_3P{=}CCl_2 + R_2SO \longrightarrow Ph_3PO + (R_2S{=}CCl_2)$$

Although the fate of the $=CCl_2$ moiety is not clear, the following possibility is suggested at this time.

$$(R_2S{=}CCl_2) + Ph_3PCl_2 \longrightarrow R_2S + CCl_4 + Ph_3P$$

In favor of this suggestion is the observation that a nearly theoretical yield of di-*p*-bromophenyl sulfide is obtained when equimolar quantities of the sulfoxide and triphenylphosphine are allowed to react.

We wish to add that a large-scale experiment employing dimethyl sulfoxide failed to provide evidence for the formation of tetrachloroethylene. This would indicate that the dichlorocarbene, a possible decomposition product of the sulfur ylide, is either not produced or efficiently scavenged[6,7] by triphenylphosphine.

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Solutions of Organic Compounds in Fused Alkali Thiocyanates

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The number of reports of reactions between organic compounds and fused salts is increasing.[1] These reactions, understandably, involve a gas in contact with the high-temperature melt. Homogeneous reactions are rare, though some interesting current research makes use of fused tetra-*n*-alkylammonium nitrates.[2]

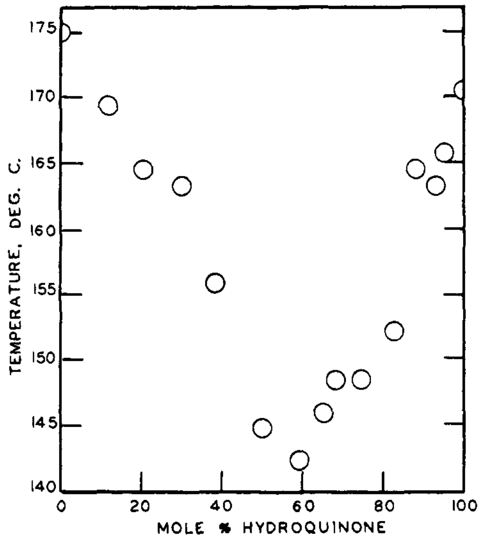

Figure 1.—Freezing point–composition plot for potassium thiocyanate–hydroquinone system.

The melting points of potassium thiocyanate (177°) and of a 3:1 mixture by weight of KSCN and NaSCN (about 130°) are low enough to permit the study of organic compounds in the fused salts. While investigating organic reactions in these media, we observed the high solubility of a number of polyhydroxy compounds. At 150° in fused KSCN-NaSCN, pentaerythritol, hydroquinone, ethylene glycol, methanol, and water are very soluble and sucrose, glucose, and *p*-nitroaniline are fairly soluble, glucose being recoverable as the osazone. The carbohydrate solutions begin to turn yellow after 10 min. at 150°. Triphenylmethyl chloride, triphenylcarbinol, hexyl bromide, phenol, borneol, *p*-toluidine, and pyridine are relatively insoluble. Benzoic acid is soluble and can be sublimed unchanged from the melt, but some decomposition of the thiocyanate occurs, probably due to the formation of HSCN.

The hydroxy compounds are apparently un-ionized in solution. Alizarin dissolves to form an orange solution and only when a trace of sodium hydroxide is added, does the deep blue color of the anion appear. The addition of solid benzoic acid changes the color back to yellow. The n.m.r. spectrum of pentaerythritol in KSCN-NaSCN at 150° shows two singlets, separated by 0.4 p.p.m. at 60 Mc.

The fused-salt solubility of the limited number of compounds observed shows some similarity to their water solubility. There are differences, for example ethanol is not miscible at 150°, though there is con-

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(2) J. E. Gordon, *J. Am. Chem. Soc.*, **86**, 4492 (1964).