

and the metal, but in **1** this bending would lead to decoordination of the most basic nitrogen atom in **1**, and it would be very unfavorable for this compound.

It thus seems most likely that mechanism II is involved here, and it is related to the one we had already described<sup>1</sup> for the hydration of **1**. The metal ion serves as a Lewis acid, and the very large catalysis is chiefly associated with a gain in coordination in the transition state for the addition.<sup>7</sup> In addition to this factor, the reaction of Tris with **2** in the presence of metal ions has extra help from the coordination of Tris with the metal, so that the well-known effects of neighboring group participation can operate even when these effects involve the development of a small amount of strain in the transition state.

(7) Either mechanism can account for the finding that the very large acceleration in this reaction is located chiefly in the  $\Delta S^\ddagger$  part of the activation parameters, since the Tris is already bound to the metal ion in the starting materials and thus loses no further translational freedom in the transition state. The positive value of  $\Delta S^\ddagger$  must reflect the liberation of solvent molecules in this transition state.

(8) National Science Foundation Predoctoral Fellow, 1965-1969. Support of this work by the National Institutes of Health is also gratefully acknowledged.

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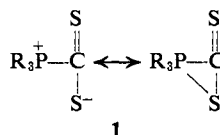
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Received April 26, 1971

## 2-Benzylidene-1,3-dithioles. A Remarkably Rapid Wittig Reaction

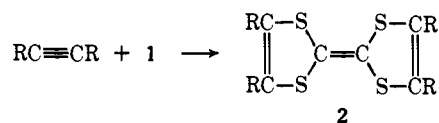
Sir:

Aliphatic phosphine-carbon disulfide complexes (**1**)

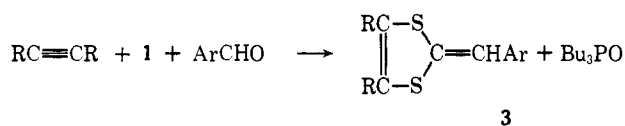


have been known for 90 years,<sup>1</sup> but very few chemical reactions of the complexes have been reported. We wish to report a general reaction of the complexes with acetylenes and aromatic aldehydes.

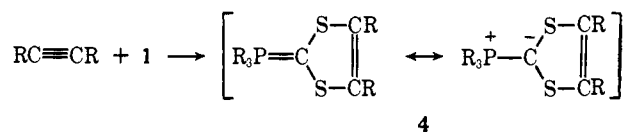
The adduct of carbon disulfide and tributylphosphine<sup>2</sup> reacted with acetylenes having at least one electron-withdrawing substituent at temperatures as low as  $-30^\circ$  as judged by the disappearance of the purple-red color of **1**. Poor yields of bidithioles **2** could be



obtained. When aromatic aldehydes were also present, excellent yields of 2-benzylidene-1,3-dithioles (**3**) were obtained.



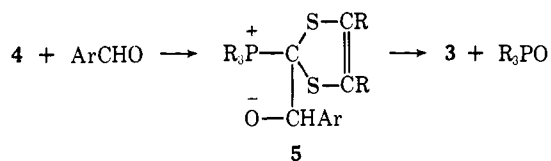
This reaction has proved to be a general one for acetylenes although requisite reaction conditions vary with the acetylene. Aryl acetylenes reacted slowly at room temperature, acetylene reacted at a useful rate at  $100^\circ$  or higher, and electronegatively substituted acetylenes reacted rapidly at 0 to  $-30^\circ$ . The rate differences observed with the acetylenes are consistent with the rate-determining reaction being a nucleophilic attack of **1** on the acetylene to give the phosphorane **4**. A subsequent Wittig reaction of **4** with the aromatic



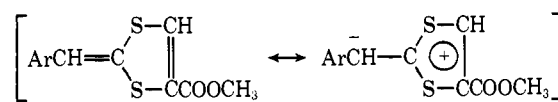
aldehyde would complete the reaction.

A remarkable feature of the reaction is its rapidity. As methyl propiolate is added to an ethereal solution of benzaldehyde, carbon disulfide, and tributylphosphine at  $-30^\circ$ , dimethyl 2-benzylidene-1,3-dithiole-4,5-dicarboxylate precipitates from solution. This reaction is several orders of magnitude faster than other Wittig reactions.<sup>3</sup> Moreover, the ease of reaction of **4** with aldehydes is the type of behavior normally characteristic of the stable, less reactive, resonance-stabilized alkylidene phosphoranes.<sup>3</sup>

A possible explanation of the abnormal reactivity of **4** is that in the zwitterionic structure contributing to **4**, although considerable stabilization of the negative charge by the two adjacent sulfur atoms might be expected,<sup>4</sup> any tendency toward planarity in the dithiole ring would lead to a cyclic 8- $\pi$ -electron system which would be antiaromatic and destabilized. The negative charge in **4** is removed from the dithiole ring in the transition state leading to the betaine **5**, and a lowered activation energy would be expected. Collapse of **5** to **3** and phosphine oxide should also be rapid because



the benzylidenedithioles themselves are quasiaromatic systems.<sup>5</sup>



**6a**, Ar = 4-pyridyl

**b**, Ar = 4-ClC<sub>6</sub>H<sub>4</sub>

**c**, Ar = 4-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>

When unsymmetrical acetylenes such as methyl propiolate are used in the reaction, geometric isomers of **6** are formed—usually in nearly equal yields. The existence of the two isomers is clearly shown by the two

(3) A. Maercker, *Org. React.*, **14**, 270 (1965).

(4) E. J. Corey and D. Seebach, *Angew. Chem., Int. Ed. Engl.*, **4**, 1075 (1965); D. Seebach, *ibid.*, **8**, 639 (1969).

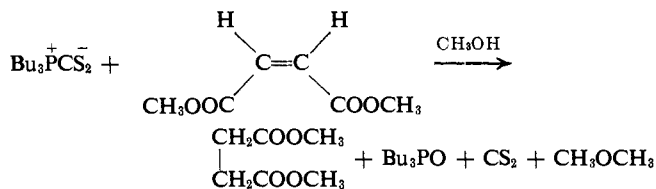
(5) E. Campaigne and R. D. Hamilton, *J. Org. Chem.*, **29**, 1711 (1964); H. Prinzbach and E. Futterer, *Advan. Heterocycl. Chem.*, **7**, 39 (1966).

(1) A. W. Hofmann, *Ann. Chem. Suppl.*, **1**, 26, 59 (1861); A. Hantzsch and H. Hibbert, *Chem. Ber.*, **40**, 1508 (1907).

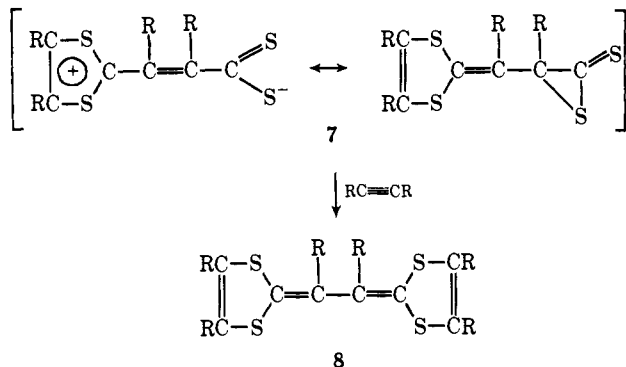
(2) W. C. Davies and W. J. Jones, *J. Chem. Soc.*, 33 (1929).

peaks attributable to the exocyclic hydrogen at  $\delta$  6.2–7.0 in the nmr spectra of **6**. The importance of the contribution which the dipolar structure makes to **6** is indicated by the low temperatures at which free rotation about the exocyclic double bond occurs. Coalescence of the exocyclic methine hydrogens occurs at 125° for **6a**, at 100° for **6b**, and at 80° for **6c**.

The phosphine-carbon disulfide complexes reacted with electron-poor olefins differently than with acetylenes. In an alcoholic solvent dimethyl maleate was reduced to dimethyl succinate.



The reaction observed between acetylenes and the phosphine-carbon disulfide complexes lends support to the suggestion that compounds of type **8** formed in the thermal reaction of carbon disulfide and electron-deficient acetylenes<sup>6</sup> could have arisen by reaction of the intermediate **7** with the acetylene.



(6) H. D. Hartzler, *J. Amer. Chem. Soc.*, **92**, 1412 (1970).

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## Photoelectron Spectra of Norbornanones and Norbornenones

Sir:

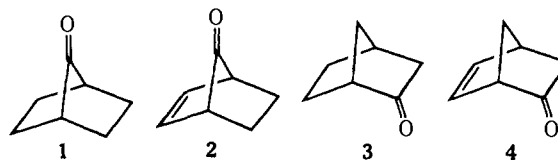
In a recent study we found photoelectron spectroscopy (PES) to be very useful in determining the interaction of the  $\pi$  levels in cyclopentenones.<sup>1</sup> We have now extended our investigations to the series of norbornane derivatives **1–4**. The measured ionization potentials (IP's) from the PE spectra<sup>2</sup> are given in Table I.

The first IP of norbornan-7-one (**1**)<sup>3</sup> at 9.01 eV is assigned to ionization from one of the oxygen non-

(1) D. Chadwick, D. C. Frost, and L. Weiler, *J. Amer. Chem. Soc.*, **93**, 4320 (1971).

(2) The PE spectra were obtained using a 584-Å spectrometer with a 2-in. radius hemispherical electrostatic energy analyzer.

(3) P. G. Gassman and P. G. Pape, *J. Org. Chem.*, **29**, 160 (1964). We are very grateful to Professors P. G. Gassman and J. Warkentin for generous samples of **2**.



bonding orbitals. The vibrational spacings in this band are 430 and 1210  $\text{cm}^{-1}$ , which indicate that this  $n$  orbital is delocalized to some extent. Unfortunately, no assignment of the ir spectra of any of these molecules (**1–4**) is available. The value for this  $n$  ioniza-

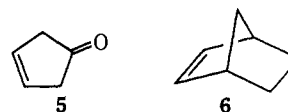
Table I. Vertical Ionization Potentials (Electron Volts)<sup>a</sup> of **1–4**<sup>b</sup>

Norbornan-7-one ( <b>1</b> )	Norbornen-7-one ( <b>2</b> )	Norbornan-2-one ( <b>3</b> )	Norbornen-5-one ( <b>4</b> )
9.01 (430 and 1210 $\text{cm}^{-1}$ )	9.19	8.94 (410 and 1270 $\text{cm}^{-1}$ )	8.90
10.3–15.0 <sup>c</sup>	9.62 11.0–14.6 <sup>c</sup> 15.12	10.65–14.8 <sup>c</sup>	10.10 11.0–15.3 <sup>c</sup>
15.72	15.90	15.96	15.95
16.82	16.77	16.74	16.87

<sup>a</sup>  $\pm 0.02$  eV for IP's less than 11 eV and  $\pm 0.05$  for IP's greater than 11 eV. <sup>b</sup> The vibrational spacings, where measurable, are given in parentheses and are  $\pm 40$   $\text{cm}^{-1}$ . <sup>c</sup> Several ionizations measured from the adiabatic onset.

tion is 0.24 eV lower than the corresponding value in cyclopentanone (9.25 eV).<sup>1</sup> It is a well-established observation that the first IP arising from ionization from a similar orbital tends to decrease with increasing size along a homologous series.<sup>4</sup>

The first IP of norbornen-7-one (**2**)<sup>3</sup> at 9.19 eV is assigned to ionization from the nonbonding level. The shift of 0.18 eV in the  $n$  level of **1** and **2** is attributed to the effect of replacing two  $\text{sp}^3$ -hybridized carbons in **1** by  $\text{sp}^2$  carbons. This agrees very well with the difference of 0.19 eV between the  $n$  levels of cyclopentanone and cyclopenten-3-one<sup>1</sup> (**5**). The band at 9.62 eV in the PE spectrum of **2** is attributed to ionization from the  $\pi_{\text{CC}}$  level. The  $\pi_{\text{CC}}$  IP in norbornene (**6**)



occurs at 8.97 eV.<sup>5</sup> This represents a stabilization of the  $\pi_{\text{CC}}$  level in **2** of 0.65 eV relative to **6** and it compares with the stabilization of 0.80 eV in **5** (9.98 eV)<sup>1</sup> relative to cyclopentene (9.18 eV).<sup>6</sup> The replacement of an  $\text{sp}^3$ -hybridized carbon by an  $\text{sp}^2$  carbon in the five-membered ring of a norbornene derivative should increase the IP of the  $\pi_{\text{CC}}$  level by *ca.* 0.2 eV.<sup>1</sup> Therefore, the major effect in the shift of the  $\pi_{\text{CC}}$  level in **2** compared to **6** is the interaction of the  $\pi_{\text{CC}}$  level with both  $\pi_{\text{CO}}$  levels in **2**. This interaction can occur directly through space<sup>7,8</sup> or through a  $\sigma$  level of the correct symmetry.<sup>8</sup> In **2** the through-space interaction of the two  $\pi$  levels

(4) See, for example, K. Watanabe, T. Nakayama, and J. Mottl, *J. Quant. Spectrosc. Radiat. Transfer*, **2**, 369 (1962).

(5) P. Bischof, J. A. Hashmall, E. Heilbronner, and V. Hornung, *Helv. Chim. Acta*, **52**, 1745 (1969).

(6) P. Bischof and E. Heilbronner, *Helv. Chim. Acta*, **53**, 1677 (1970).

(7) E. I. Snyder and B. Franzus, *J. Amer. Chem. Soc.*, **86**, 1166 (1964).

(8) R. Hoffmann, *Accounts Chem. Res.*, **4**, 1 (1971).