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Catalytic Behavior of Phenols in Pyrolytic Conversion of Allylic Dithiolcarbonates to Allylic Sulfides

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Pyrolytic conversion of *S*-(2-alkenyl) *S*-alkyl dithiocarbonates (allylic dithiolcarbonates) to 2-alkenyl alkyl sulfides (allylic sulfides) was catalyzed by phenols bearing electron-attracting substituents. The reaction is pseudo-first-order and the apparent first-order rate constants are proportional not only to the concentration of phenols but also to the hydrogen-bonding capability of phenols. The entropy of activation for the phenol-catalyzed reaction is *ca.* 8 e.u. smaller than that for the uncatalyzed reaction. The reactivity of *S*-(1-phenylallyl) *S*-alkyl dithiocarbonates did not obey Hammett's or Taft's equation.

Based on these findings together with the MNDO (modified neglect of diatomic overlap) calculation data, a possible role of phenols in the pyrolytic conversion of allylic dithiolcarbonates to allylic sulfides is discussed.

Keywords *S*-(2-alkenyl) *S*-alkyl dithiocarbonate; [3,3]-sigmatropy; allylic sulfide; phenol-catalyzed reaction; kinetics; mechanism; regioselectivity; xanthate

In previous papers,[1)] we reported that pyrolysis of allylic xanthates [I, *O*-(2-alkenyl) *S*-alkyl dithiocarbonates] caused consecutive [3,3]-sigmatropic rearrangements to give allylic sulfides (III, 2-alkenyl alkyl sulfides) with extrusion of carbon oxysulfide (COS) *via* allylically isomeric dithiol esters[2)] [II, *S*-(2-alkenyl) *S*-alkyl dithiocarbonates]. The pyrolytic reaction showed a typical concerted reaction behavior. On the other hand, we clarified that phenols catalyzed thione-thiol rearrangement of xanthates (IV) having a homoallylic electron system, such as *O*-cholesteryl[3a)] or *O*-(1-cyclopropylethyl)[3b)] *S*-alkyl dithiocarbonates, wherein the hydrogen bonding between the thione sulfur of IV and acidic hydrogens of phenols plays an important role. From these facts, we expected that the pyrolytic conversion of allylic dithiolcarbonates (II) to the allylic sulfides (III) would be catalyzed by phenols.

This paper describes the catalytic activities of phenolic compounds in the pyrolytic conversion of allylic dithiolcarbonates (II) to allylic sulfides (III).

Results and Discussion

When *S*-(1-phenylallyl) *S*-methyl dithiocarbonate (IIa) was heated at 150 °C in the presence of 3 molar eq of *p*-chlorophenol, *E*-3-phenylallyl (cinnamyl) methyl sulfide (IIIa) was produced regioselectively in nearly quantitative yield. The structure of IIIa was determined by comparison of the proton nuclear magnetic resonance (^{1}H-NMR) spectral data with those of an authentic sample.[1b)]

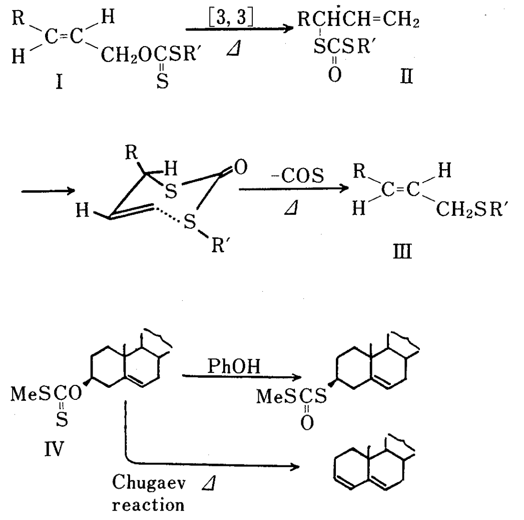


Chart 1

The decomposition rate was measured by following the decrease of the weight of IIa. Good first-order behavior was observed. The reaction in the presence of 3 molar eq of *p*-chlorophenol was found to proceed *ca.* twelve times faster than the reaction in the absence of *p*-chlorophenol. However, this reaction was considered to be phenolytic rather than catalytic. So we next studied the pyrolytic decomposition reaction of IIa using a catalytic amount of phenols. The effects of added phenols upon the pseudo-first-order rate constants (k) for IIa are illustrated in Table I.

Of the phenols used, *p*-nitrophenol appears to be the best

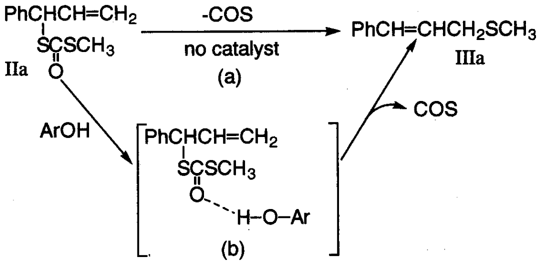


Chart 2

TABLE I. Rate Constants for Thermolyses of IIa in the Presence of Several Phenols at 120 °C

Phenol	(IIa/ArOH)	$k\times10^5$, s^{-1}	k/k_{uncat}
p-Nitrophenol	1 : 0.3	12.30	10.4
2,4-Dinitrophenol	1 : 0.3	4.90	4.2
o-Nitrophenol	1 : 0.3	4.00	3.4
Picric acid	1 : 0.3	3.45	2.9
p-Chlorophenol	1 : 0.3	3.21	2.7
Phenol	1 : 0.3	2.90	2.5
p-Cresol	1 : 0.3	1.49	1.3
No catalyst		1.18	1.0
p-Nitrophenol	1 : 0.09	2.60	
	1 : 0.19	7.37	
	1 : 0.33	13.63	
	1 : 0.37	15.98	
	1 : 0.52	21.90	

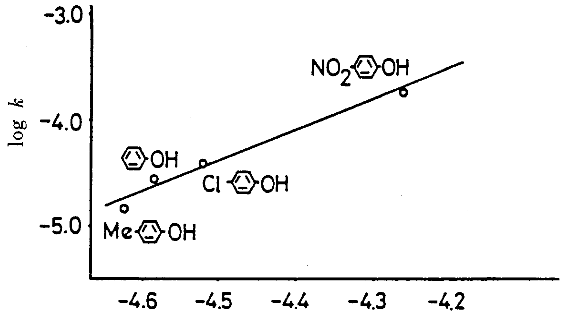
catalyst. In the presence of 0.3 molar eq of *p*-nitrophenol at 120 °C, the pyrolytic reaction of IIa proceeded *ca.* 10 times faster than the uncatalyzed reaction. *o*-Nitrophenol, 2,4-dinitrophenol or picric acid showed lower catalytic activity toward IIa than *p*-nitrophenol under the same reaction conditions.

In the case of *p*-nitrophenol, the activation parameters were calculated. To ensure the accuracy of the data, the rate constants (k_{cat}) for the catalytic reaction (route b) were evaluated according to the equation $k_{cat} = k - k_{uncat}$, in which k is apparent pseudo-first-order rate constant and k_{uncat} is the constant for the uncatalyzed reaction (route a). The activation energy for the pyrolytic conversion of IIa in the presence of *p*-nitrophenol is *ca.* 4 kcal/mol lower than that observed in the absence of *p*-nitrophenol. The reaction displays sizably negative entropy of activation, which is about 8 e.u. smaller than that of the uncatalyzed reaction, consistent with the cyclic mechanism involving phenol whose freedom of motion might be frozen out.[4)]

Table II. Activation Parameters[a)] for Thermolyses of IIa in the Presence of *p*-Nitrophenol and Picric Acid

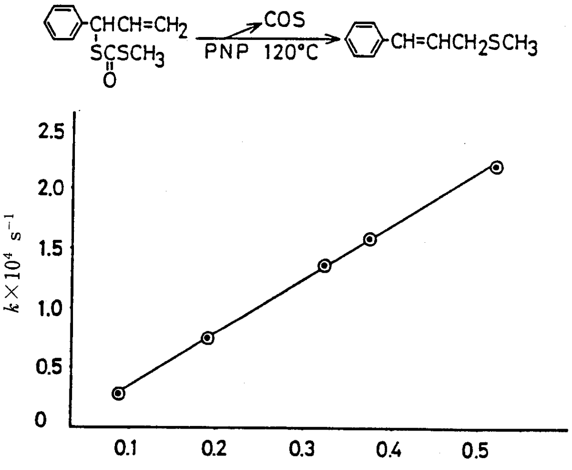
Phenol	$\Delta H^{\neq}$ (kcal/mol)	$\Delta S^{\neq}$ (e.u.)[b)]
p-Nitrophenol	17.8	−36
Picric acid	19.0	−34
No catalyst	22.1	−28

a) Based on k_{cat}. Measured by method B in the presence of 0.3 mol eq of phenols. *b)* Calculated for 130 °C.



log k_2

Fig. 1. Plot of Pyrolysis Rates (log$k$) of IIa *vs.* Catalytic Coefficients[5)] of Some Phenols
$r = 0.995$.



Amount of PNP (mol)

Fig. 2. Plot of Pyrolysis Rates of IIa *vs.* Amount of *p*-Nitrophenol (PNP)
slope $= 4.52 \times 10^{-4}$, $r = 0.999$.

Pocker showed that phenols catalyzed the solvolysis reaction of *tert*-butyl halide in the presence of pyridine in nitromethane, and the rates could be expressed in the form: $k_1 \times 10^5 = 0.367 + k_2 \times 10^5 \times [\mathrm{ArOH}]$. The value of k_2 has been used as a measure of the hydrogen bonding capacity to assist the ionization of *tert*-butyl halide.[5)] A plot of the rearrangement rates against the values of the catalytic coefficients, k_2 is roughly linear for our data, suggesting that hydrogen bonding plays an important role in the pyrolytic conversion reaction (Fig. 1).

In the reaction of IIa with *p*-nitrophenol, the apparent first-order rate constant is proportional to the amount of *p*-nitrophenol. A second-order rate constant was obtained from the slope of the line by means of the least-squares method.

In the uncatalyzed reaction, as we previously discussed,[1b)] the electron-withdrawing *S*-alkyl groups accelerate the reaction rate and a plot of the logarithm of the rate constant *vs.* Taft's constant is nearly linear. In the phenol-catalyzed reaction, a similar graph exhibited a much greater scattering of points. The conversion is retarded by incorporation of strongly electron-withdrawing substituents ($-CH_2COOR$, *etc.*) into the *S*-alkyl group. This may be attributable not only to the stabilization of the ground state due to the hydrogen bonding between the phenolic proton and another electron-rich functional group other than the carbonyl oxygen of the $-SC(=O)S-$ group of II but also to the decrease of the electron density of the sulfur atom of the $-CO-S-CH_2-COOR$ moiety.

Table III. Rate Constants for Catalytic Pyrolyses of *S*-Alkyl *S*-(1-Phenylallyl) Dithiocarbonates [$PhCH(SCOSR)CH=CH_2$]

R	$k \times 10^{5,a)}$ Uncatalyzed[b)]	Catalyzed	$\sigma^{*c)}$	$\sigma^{d)}$
Et–	4.72	20.60	−0.10	
Me– (IIa)	8.79	39.31	0.00	
$PhCH_2-$	10.08	36.81	0.215	0.00
Ph_2CH-	11.75	37.08	0.405	
$MeOCOCH_2-$	21.32	28.23	1.05	
p-$MeOC_6H_4CH_2-$	7.40	35.32		−0.11
p-$BrC_6H_4CH_2-$	14.03	62.21		0.27
p-$NO_2C_6H_4CH_2-$	23.34	42.56		0.78

a) Values at 150 °C, s⁻¹. *b)* See ref. 1*b*. *c)* Taft's values. *d)* Hammett's values.

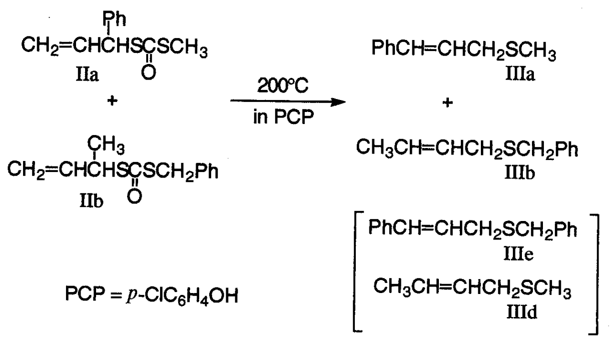


Chart 3

A crossover experiment in the presence of *p*-chlorophenol suggested that the intramolecular and concerted nature of this reaction was not affected by the presence of phenolic compounds: an equimolar mixture of *S*-(1-phenylallyl) *S*-methyl dithiocarbonate (IIa), *S*-(1-methylallyl) *S*-benzyl dithiocarbonate (IIb) and *p*-chlorophenol was heated at 200 °C for 2 h, and gas chromatographic (GLC) analysis showed the absence of crossover products, *e.g.*, benzyl cinnamyl (IIIe) and crotyl methyl (IIId) sulfides (see Chart 3).

These results indicate that the rate acceleration is not brought about by a simple "solvent effect" but by the specific solvation of the carbonyl carbon by hydrogen bonding. The ^{1}H-NMR spectrum of a mixture of IIa and *p*-chlorophenol showed a low-field shift (0.18 ppm) of the phenolic proton signal, indicating the presence of hydrogen bonding between the carbonyl oxygen of II and phenols. The possible role of intermolecular hydrogen bonding is also supported by the fact that *p*-nitrophenol shows higher catalytic reactivity than *o*-nitrophenol, 2,4-dinitrophenol or picric acid, in which the hydroxy group is linked with the *ortho* nitro group by intramolecular hydrogen-bonding.

To confirm this explanation deduced from the experimental data, we carried out a modified neglect of diatomic overlap (MNDO) calculation.[6] For simplicity, the calculation was performed on a protonated chair-form transition state of a model compound, *S*-allyl *S*-methyl dithiocarbonate (IIc), and the optimized structure was compared with the unprotonated one[1b] (Fig. 3). Inspection of the optimized structures of a linear form A, the cyclic transition state (B) with a $=CH_2\cdots SMe$ distance of 2.0 Å and its protonated cyclic transition state (C) indicates that the MeS–CO bond is shortened by protonation, whereas the S–CH_2 bond is lengthened. The increase of double bond character of the MeS–CO bond with the decrease of bond-order of S–CH_2 is considered to be favorable for [3,3]-sigmatropic rearrangement reaction.

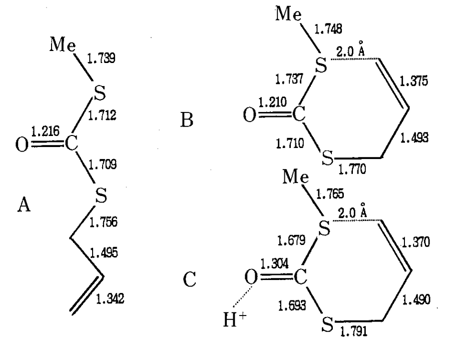


Fig. 3. Bond Length (Å) of the MNDO-Optimized Structures for *S*-Allyl *S*-Methyl Dithiocarbonate (A) and Cyclic Transition States [B and C (Protonated B)]

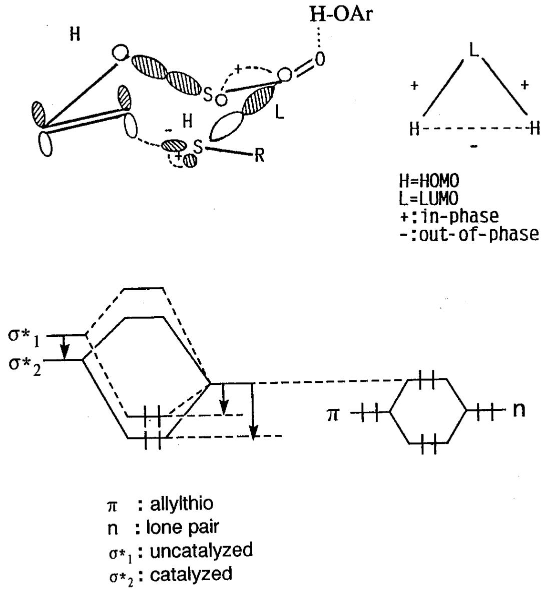


Fig. 4. Three System Interaction in the Transition State

The frontier orbital theoretical view on the rate enhancement for the catalyzed reaction based on the reactant dissection method (three system interaction)[7] is that the hydrogen bond to >C=O lowers[8] the lowest unoccupied molecular orbital (LUMO) of the RS–CO σ bond. This situation is very favorable for the three system interaction, which the interaction among the two highest occupied molecular orbital (HOMO)'s [π (allylthio moiety) and *n* (lone pair on the sulfur atom)] and LUMO of the σ bond may be increased in comparison with the uncatalyzed reaction.[1b]

After our communication concerning the uncatalyzed reaction had been published, Auburn *et al.*[9] reported a palladium catalyzed analogue of the present reaction. Their

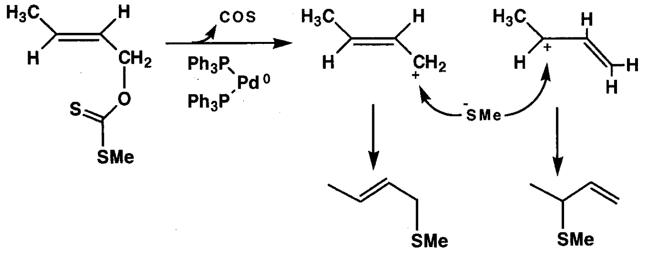
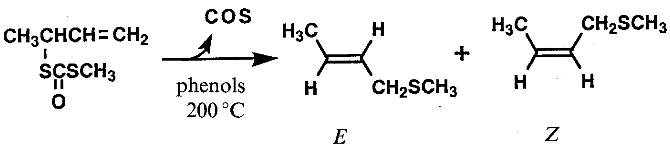
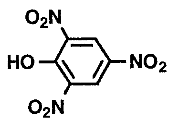
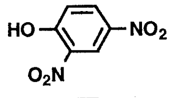
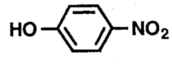


Chart 4

TABLE IV. Thermolysis of IId in the Presence of Some Phenols



Phenols	Yield (%)[a]	
	E	*Z*
	64.4	35.6
	69.8	30.2
	67.9	32.1
No Catalyst	67.1	32.9

a) Absence of 1-methylallyl methyl sulfide.

catalyzed reaction was proposed to proceed through an ionic intermediate under very mild reaction conditions. In the reaction of 1- or 3-alkyl-2-alkenyl substrates, allylation is not regioselective, giving mixtures of allylically isomeric sulfides because of an alteration of the reaction mechanism from the nonionic concerted pathway to the ionic one (a solvent-separated ion pair or carbonium ion intermediate).

On the contrary, allylation in the phenol catalyzed reaction proceeds regioselectively and the consecutive reactions can be carried out in a single operation. Therefore, the present reaction is considered to be practically important, though higher temperatures are necessary as compared with the palladium catalyzed reaction.[10)]

Finally, mention should be made of the effect of the catalysts on the formation ratio of the two geometrical isomers of the products. In the pyrolysis reaction of *S*-(1-methylallyl) *S*-methyl dithiocarbonate (IId) derived from [3,3]-sigmatropic rearrangement of *O*-crotyl methyl xanthate (Id), the two isomers (*Z*- and *E*-2-butenyl methyl sulfide, IIId) were produced without formation of the allylic isomer, 1-methylallyl methyl sulfide. The effect of some added phenols on the product distribution was studied (*p*-nitrophenol, 2,4-dinitrophenol and picric acid). However, the *Z*/*E* ratio (*ca.* 3/7) was found to be independent of the presence of phenols.

In summary, the pericyclic reaction of allylic xanthates is particularly valuable for regioselective conversion of sensitive allylic alcohols to the corresponding sulfides without rearrangement of the carbon skeleton and the pyrolytic reaction is effectively accelerated by phenols.

Synthetic applications using the phenol- and Lewis acid-catalyzed reactions are currently being investigated in our laboratory.

Experimental

The infrared (IR) spectra were taken with a Hitachi 270-30 spectrophotometer. The ^{1}H-NMR spectra were taken with Hitachi R-600 (60 MHz) and JEOL GX-400 (400 MHz) spectrometers using tetramethylsilane as an internal standard and the chemical shifts are expressed in δ values. High resolution mass spectra (HRMS) were taken with a JEOL JMS-DX303HF spectrometer. GLC analyses were performed with a Yanagimoto G-80 gas chromatograph equipped with thermal conductivity detector using a 10% SE-30 on Chamelite CK (60—80 mesh 3 mm × 3 m) column.

Molecular orbital calculations were performed on a FACOM M-360 computer in the Information Processing Center of Kumamoto University. Graphic analysis based on the molecular orbital (MO) calculation data and least-squares calculations were performed on Fujitsu FM-16β FDII, FM R-50LT and R-60HD personal computers.

S-(2-Alkenyl) S-Alkyl Dithiocarbonates (II) *O*-Cinnamyl *S*-methyl dithiocarbonate (Ia) was prepared according to a procedure developed in this laboratory and isolated in crystalline form.[2b)] Heating of Ia at 80 °C for 1 h gave *S*-(1-phenylallyl) *S*-methyl dithiocarbonate (IIa). *S*-(1-Phenylallyl) *S*-substituted alkly, *S*-(1-methylallyl) *S*-benzyl (IIb) and *S*-methyl (IId) dithiocarbonates were prepared according to the previously described method by the rearrangement of the corresponding xanthates.[1b)] Purification of the crude products by distillation or recrystallization gave II quantitatively.

Crossover Reaction A mixture of *S*-(1-phenylallyl) *S*-methyl dithiocarbonate (IIa), *S*-(1-methylallyl) *S*-benzyl dithiocarbonate (IIb) and *p*-chlorophenol (3 eq mol) was heated at 200 °C for 2 h. The reaction mixture was analyzed by GLC. The chromatogram showed the absence of benzyl cinnamyl (IIIe) and crotyl methyl (IIId) sulfides. The result is essentially the same as that obtained from the uncatalyzed reaction.

Pyrolysis of II (General Procedure) A dithiol ester (II, 5 mmol) was placed in a distillation flask and heated at 150—200 °C until evolution of COS gas ceased. The distillate was collected and purified by redistillation or chromatography on silica gel. In the case of sulfides having higher boiling points, the distillations were performed under a moderately reduced pressure.

Pyrolysis of II in the Presence of Phenols A mixture of II (5 mmol) and *p*-nitrophenol (0.16 mmol) was heated at 120—170 °C until disappearance of II as judged by thin layer chromatography (TLC). After cooling, the sulfide was extracted with *n*-hexane and the catalyst was easily removed by passing the *n*-hexane extract through a short column of silica gel. The *n*-hexane was evaporated off *in vacuo* by rotary evaporation, and the residue was purified by redistillation or chromatography on silica gel to give III.

Pyrolysis of S-(1-Methylallyl) S-Methyl Dithiocarbonate (IId) in the Presence of Phenols The progress of the reaction was monitored by Fourier transform (FT) pulse NMR spectroscopy. The *E*/*Z* ratio of IIId was determined from the signals of the *S*-methyl groups of the two compounds (2.05 ppm for *Z*-IIId and 2.01 ppm for *E*-IIId). Peak areas were based on the digital output data. The formation ratios (*E*:*Z*) for some phenols were as follows: picric acid 64.4:35.6, 2,4-dinitrophenol 69.8:30.2, *p*-nitrophenol 67.9:32.1, no catalyst 67.1:32.9.

Kinetics The rearrangement rate was followed at a given temperature by measuring the amount of evolved carbon oxysulfide gas by volumetry (method A) using a gas burette apparatus filled with a solution of concentrated H_2SO_4–NaCl or by weighing the decrease of the starting material due to loss of volatile reaction product (method B) using a Shimadzu AEL-200 electronic digital balance (readability 0.1 mg). The data were treated by means of a nonweighted least-squares program written in F-BASIC86 V3.1. The results are listed in Tables I—III (see also Figs. 1 and 2).

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References and Notes

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2) *a*) K. Harano and T. Taguchi, *Chem. Pharm. Bull.*, **20**, 2348, 2357 (1972); *b*) *Idem*, *ibid.*, **23**, 467 (1975).

3) *a*) K. Harano, K. Miyoshi and T. Hisano, *Chem. Pharm. Bull.*, **33**, 1861 (1985); *b*) K. Harano, H. Kiyonaga and T. Hisano, *ibid.*, **35**, 1388 (1987).

4) The entropy change of *p*-nitrophenol from the liquid state to the solid state is calculated to be about 8 e.u.

5) Y. Pocker, *J. Chem. Soc.*, **1959**, 1179.

6) M. J. S. Dewar and W. Theil, *J. Am. Chem. Soc.*, **99**, 4899, 4907 (1977); W. Thiel, MNDO Program 353, "Quantum Chemistry Program Exchange (QCPE)," Indiana University, Bloomington, IN, 1978.

7) S. Inagaki, H. Fujimoto and K. Fukui, *J. Am. Chem. Soc.*, **98**, 4693 (1976): There are two ways of dividing the three systems according to their roles. They are two donors and one acceptor (case 1) and two acceptors and one donor (case 2). In case 1, the orbital phase relation for stabilization has been found to be in-phase (+) between the HOMO of donor A and the LUMO of acceptor C, in-phase between the HOMO of donor B and the LUMO of acceptor C, and out-of-phase (−) between the $(\mathrm{HOMO})_A$ and $(\mathrm{HOMO})_B$. In case 2, each relation should be in-phase between $(\mathrm{LUMO})_A$ and $(\mathrm{HOMO})_C$, between $(\mathrm{LUMO})_B$ and $(\mathrm{HOMO})_C$, and between $(\mathrm{LUMO})_A$ and $(\mathrm{LUMO})_B$. The present reaction corresponds to case 1.

8) I. Fleming, "Frontier Orbitals and Organic Chemical Reactions," John Wiley & Sons, London, 1976, pp. 161—165.

9) P. R. Auburn, J. Whelan and B. Bosnich, *J. Chem. Soc., Chem. Commun.*, **1986**, 146.

10) For example, the dithiol ester IIa decomposed to IIIa on heating at 70 °C in *p*-chlorophenol.