2, R = CO$_2$CH$_3$; R' = H
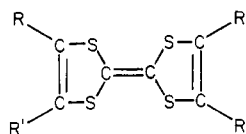3, R = R' = CO$_2$CH$_3$
4, R = CO$_2$H; R' = H

and
trans isomer

grating infrared spectrophotometer as KBr pellets. Melting points were measured with an electrothermal melting-point apparatus and are uncorrected. Dimethyl acetylenedicarboxylate, methyl propiolate, propiolic acid, and carbon disulfide were purchased from Aldrich and were used as received. Reactions at high pressure (4000–6000 atm) were run in Teflon capsules (3-mL capacity) placed in a steel die equipped with a heating band and pressed with a hydraulic press (Clifton 200 ton press). Reactions at low pressure (10–100 atm) were run in a Parr pressure reactor and were compressed with nitrogen.

Representative High-Pressure Reactions. Synthesis of 4,4'(or 5')-Bis(carbomethoxy)tetrathiafulvalene. Methyl propiolate (5 mL, 56 mmol) was dissolved in carbon disulfide (15 mL, 250 mmol) and a portion (3 mL) of this mixture was placed in a Teflon capsule. Pressure was applied at 5000–5500 atm and the capsule was heated at 100 °C for 26 h. Pressure was controlled within ±200 atm. After cooling, the capsule was opened and a dark red solid and a small amount of a red solution were obtained. The solid was isolated, washed repeatedly with CS$_2$, and dried in vacuum. The dark brown solid obtained was 1.28 g (96% yield, based on the acetylene compound used) and the melting point was 236–240 °C. Recrystallization from 1,2-dimethoxyethane gave red crystals: mp 242–244 °C (lit.[4] mp 244–245 °C); IR 3060, 3040, 1700, 1580, 1250, 820 cm^{-1}.

Synthesis of 4,4',5,5'-Tetrakis(carbomethoxy)tetrathiafulvalene. The reaction of dimethyl acetylenedicarboxylate and CS$_2$ was carried out and the solid 3 was isolated as described in the synthesis of 2. Recrystallization from ether–hexane gave red crystals: mp 163–167 °C (lit.[6] mp 168–169 °C); IR 1740, 1720, 1575, 1225 cm^{-1}.

Synthesis of Tetrathiafulvalene-4,4'(or 5')-dicarboxylic Acid. The reaction of propiolic acid and CS$_2$ yielded the crude compound 4 under high pressure as described above. It was found that CO$_2$ gas was evolved from the reaction mixture when the capsule was opened. The solid was washed with CS$_2$, dissolved in 1 N NaOH, filtered, and acidified with 2 N HCl. The product was filtered and dried overnight under reduced pressure at 60 °C: mp 360 °C (lit.[4] mp 360 °C); IR 3500–2500, 1660, 1550 cm^{-1}.

Typical experimental conditions for the synthesis of 2–4 under low pressure are as follows. Propiolic acid (10 mL, 163 mmol), CS$_2$ (15 mL, 250 mmol), and methylene chloride (15 mL) were mixed in a stainless-steel autoclave. The autoclave was repeatedly evacuated and filled with nitrogen and then nitrogen was admitted up to 70 atm. The contents were heated at 100 °C for 23 h (pressure increased to 100 atm). After cooling, the autoclave was opened and the CO$_2$ gas evolved was detected with Ba(OH)$_2$ solution. The compound was isolated as described above. The yield was 2.90 g, 12% based on the starting acetylene.

Registry No. (*E*)-2, 75444-58-5; (*Z*)-2, 75444-59-6; 3, 26314-39-6; (*E*)-4, 74857-63-9; (*Z*)-4, 74857-62-8; methyl propiolate, 922-67-8; propiolic acid, 471-25-0; dimethyl acetylenedicarboxylate, 762-42-5; CS$_2$, 75-15-0.

Effect of Metal Ions in Organic Synthesis. 6. Reactivity of the Azo Ene System of Phenylazostilbene in the Presence of Copper and Iron Ions

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Our previous papers discussed some effects of metal ions in organic synthesis.[1-4] Preliminary results were reported on the stereospecific 1,4-additions of certain alcohols to the azo ene system of phenylazostilbene (PAS) in the presence of copper and iron ions.[2] This paper reports further findings about the role of metal ions in these reactions.

A rapid decomposition of PAS in the presence of copper(II) chloride dihydrate (CCD) was previously mentioned.[2b] However, by reduction of the amount of CCD to a catalytic one, a very fast and quantitative conversion of PAS into the corresponding alkyl ethers of benzoin phenylhydrazone (AEBP) was observed. Under such conditions these reactions will occur either at room temperature or at lower temperatures. An activity lower than that of CCD, but considerably higher than that of the other inorganic salts, was revealed by anhydrous iron(III) chloride. Scheme I shows a general representation of this reactivity. The relative ratio between the syn–anti AEBP derivatives, the reaction times, and conditions are listed in Table I.

The stereospecificity of the 1,4-addition of the alcohols to the azo ene system of PAS appears to be considerably dependent upon the type of inorganic salt used. On the basis of the results reported in Table I, we can formulate the following reactivity order: copper(II) chloride dihydrate > anhydrous iron(III) chloride > iron(III) sulfate *n*-hydrate > copper(II) sulfate pentahydrate > iron(II) sulfate heptahydrate > anhydrous copper(I) chloride. The oxidized forms of the inorganic ions are much more effective than the reduced form and, for the same oxidation state of metal ions, chloride derivatives seem to be much more effective than the corresponding sulfate derivatives.

At this stage, we can hypothesize the formation of organometallic complexes which activate the azo ene system in these 1,4-addition reactions. Indeed, several metal ion–nitrogen derivative complexes are known.[1-4,6,7] Our

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(2) (a) O. Attanasi, *Studi Urbinati, Fac. Farm.*, **17**, 123 (1975); (b) O. Attanasi, P. Battistoni, and G. Fava, *Synth. Commun.*, **9**, 465 (1979); (c) XI Convegno Nazionale Società Chimica Italiana, Sorrento, Sept 16–21, 1979, and references therein.
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(6) M. F. Iskander and S. E. Zayan, *Z. Anorg. Allg. Chem.*, **320**, 261 (1963); C. G. Macarovici, V. Bota, and E. Hamburg, *Rev. Roum. Chim.*, **12**, 151 (1967); L. El-Sayed and M. F. Iskander, *J. Inorg. Nucl. Chem.*, **33**, 435 (1971); M. F. Iskander, S. E. Zayan, M. A. Kalifa, and L. El-Sayed, *ibid.*, **36**, 551 (1974); R. C. Agarwal and G. K. Agarwal, *J. Indian Chem. Soc.*, **53**, 655 (1976); E. M. Ivashkovich, *Koord. Chim.*, **3**, 983 (1977); H. Tanaka, H. Kuma, and S. Yamada, *Bull. Chem. Soc. Jpn.* **50**, 3259 (1977), and references therein.

Table I. Stereospecificity, Time, and Conditions of the 1,4-Additions of Alcohols, Water, and Phenol to the Azo Ene System of Phenylazostilbene in the Presence of Copper and Iron Ions

ROH	reacn condi-tions	Fe$_2$(SO$_4$)$_3$·nH$_2$O[e,g] time	syn/anti	FeCl$_3$[f,h] time, min	syn/anti	FeSO$_4$·7H$_2$O[e,g] time, h	syn/anti	CuSO$_4$·5H$_2$O[e,g] time	syn/anti	CuCl$_2$·2H$_2$O[f,h] time	syn/anti	CuCl[e,i] time, h	syn/anti	δ —CH⟨O syn	anti
methanol	a	20 min	38/62[d]	5	74/26	18	75/25[d]	2 h	41/59[d]	5 min	78/22	36	73/27[d]	5.15	5.66
	b	20 min	41/59[d]			2	84/16[d]	10 min	50/50[d]	10 min	95/5				
ethanol	a	40 min	27/73[d]	20	75/25	18	86/14[d]	2 h	32/68[d]	5 min	78/22	48	100/–[d]	5.32	5.82
	b	20 min	27/73[d]	10	50/50	2	91/9[d]	15 min	35/65[d]	10 min	89/11				
	c														
1-propanol	a	12 h	–/100[d]	40	25/75	18	100/–[d]	12 h	27/73[d]	10 min	75/25	48	100/–[d]	5.24	5.75
	b	30 min	–/100[d]	10	80/20	2	100/–[d]	30 min	33/67[d]	15 min	60/40				
	c														
2-propanol	a	12 h	–/100[d]	50	86/14	18	100/–[d]	12 h	74/26[d]	10 min	74/26	48	100/–[d]	5.43	5.91
	b	30 min	–/100[d]	30	79/21	2	91/9[d]	1 h	50/50[d]	15 min	42/58				
	c														
1-butanol	a	12 h	–/100[d]	50	77/23	18	100/–[d]	22 h	50/50[d]	15 min	68/32	56	100/–[d]	5.23	5.73
	b	30 min	–/100[d]	30	77/23	2	92/8[d]	1 h	50/50[d]	30 min	70/30				
	c														
2-butanol	a	14 h	–/100	75	86/14	20	100/–	24 h	60/40	15 min	64/36	60	100/–	5.21	5.71
	b	45 min	–/100	30	55/45	3	90/10	1 h	50/50	30 min	79/21				
	c														
phenol	c							30 min	79/21		81/19				
water	a			75	75/25			4 h	[m,n]					6.18	6.25
	b							4 h	81/19[n]						

[a] Room temperature. [b] Under reflux. [c] 0–5 °C. [d] From ref 3b. [e] Molecular ratio between PAS and inorganic salts = 1:2. [f] Molecular ratio between PAS and inorganic salts = 10:1. [g] The reactions at 0–5 °C and room temperature are very slow. [h] The reactions under reflux are very fast and give decomposition products of the 1,4-adduct. [i] The reactions at 0–5 °C and room temperature are very slow. [l] Carbon tetrachloride solution and tetramethylsilane as internal standard. [m] The syn–anti ratio was not possible to detect (see below). [n] The reactions were carried out in tetrahydrofuran solution and with different CCD amounts (see Experimental Section). [o] The syn–anti structure was assigned by ^{1}H NMR spectroscopy according to Karabatsos' method and assumptions.[5]
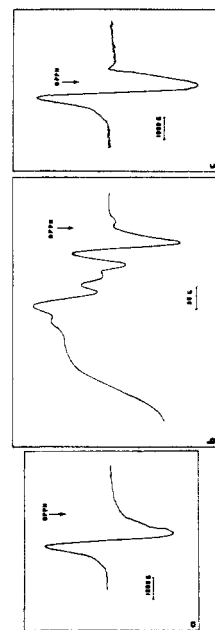

Figure 1. EPR signals obtained from the reaction between PAS and CCD in benzene solution: (a) CCD in benzene; (b) CCD + PAS in benzene; (c) adduct CCD + PAS in benzene.
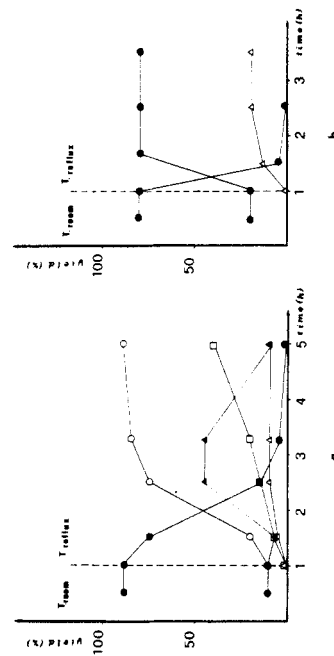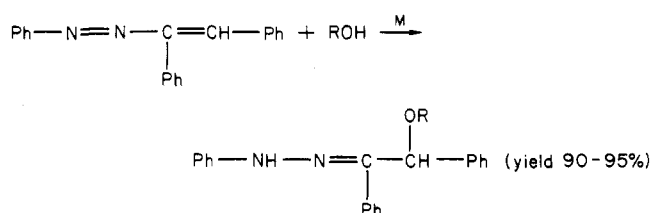

Figure 2. Decomposition of benzoin phenylhydrazone ethyl ether in the presence of CCD: ● benzoin phenylhydrazone ethyl ether (syn–anti), □ benzoin ethyl ether, △ benzoin ethyl ether, ▲ benzaldehyde, ○ ethyl benzoate; (a) condition A, (b) condition B.

Scheme I

$$Ph-N=N-\underset{\underset{Ph}{|}}{C}=CH-Ph \ + \ ROH \ \xrightarrow{M}$$

$$Ph-NH-N=\underset{\underset{Ph}{|}}{C}-\overset{\overset{OR}{|}}{C}H-Ph \quad (yield \ 90\text{-}95\%)$$

$$M = CuSO_4 \cdot 5H_2O, \ CuCl_2 \cdot 2H_2O, \ CuCl, \ FeSO_4 \cdot 7H_2O,$$
$$Fe_2(SO_4)_3 \cdot nH_2O, \ FeCl_3$$
$$R = Me, \ Et, \ 1\text{-}Pr, \ 2\text{-}Pr, \ 1\text{-}Bu, \ 2\text{-}Bu, \ H, \ Ph$$

Scheme II

Table II. Yields of the Products Derived from Decomposition of Benzoin Phenylhydrazone Ethyl Ether under A and B Conditions

	yield, %	
compd	condition A[a]	condition B[b]
benzoin	40	–
benzoin ethyl ether	10	20
benzaldehyde	10	90
ethyl benzoate	90	80

[a] After 5 h under reflux. [b] After 3 h under reflux.

of 1:1 (A) and 3:1 (B) led to the results reported in Table II.

The data were confirmed by the reaction of an authentic sample of a benzoin phenylhydrazone ethyl ether syn–anti mixture under the same conditions.[2b] Several substantial differences in the yields of the products for the different reaction conditions A and B are worth noting: (i) in A benzoin was detected, while in B it was not; (ii) in B benzaldehyde and ethyl benzoate were present in equimolecular amounts, while in A benzaldehyde was in a smaller amount relative to ethyl benzoate; (iii) in A benzoin ethyl ether was found in a smaller amount than in B. Since benzoin and benzoin ethyl ether under reflux did not manifest any reaction with alcohol in the presence of CCD, the hypothesis of a mutual interconversion could be rejected. Also, under the same conditions, benzaldehyde alone or with ethyl benzoate showed no reaction, while benzaldehyde with phenylhydrazine and CCD in an equimolecular ratio provided benzoin (yields 25%). On the other hand, varying the molecular ratio to 1:1:3 produced no benzoin. The analysis through high-performance LC of the reaction products between CCD and PAS with ethanol under A (Figure 2a) and B (Figure 2b) conditions was in good agreement with the observations reported above.

Figure 2 shows that under both conditions A and B, the decomposition of the benzoin phenylhydrazone derivative produces benzaldehyde, ethyl benzoate, and benzoin ethyl ether. The most important difference between the two conditions was that in A at a certain moment the amount of benzaldehyde rapidly decreased, and at the same time the formation of benzoin remarkably increased, while in B all the above-mentioned products remained unchanged. In addition, during the decomposition of the 1,4-adducts, a massive amount of copper(I) chloride was detected. The addition of this salt did not promote the reactions previously cited. There is, therefore, clear evidence that while the 1,4-addition is only catalyzed by metal ions, and the decomposition pathway comes from an oxidative mechanism requiring at least stoichiometric amounts of inorganic salts. This experimental evidence supports the hypothesis shown in Scheme III.
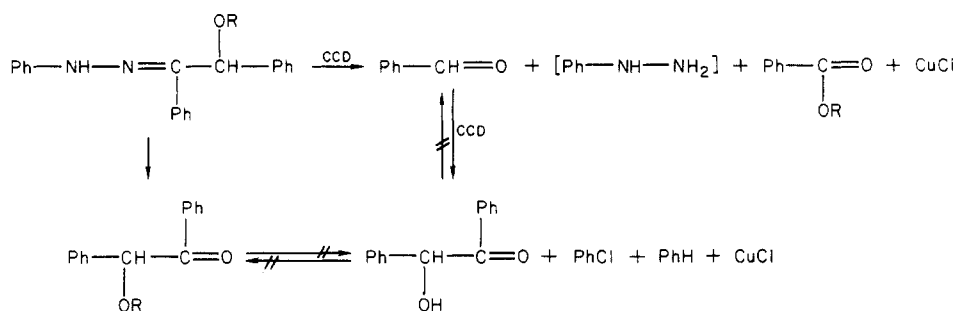
In conclusion, benzoin ethyl ether, benzaldehyde, and ethyl benzoate seem to form from benzoin phenylhydrazone ethyl ether by independent pathways. In both cases phenylhydrazine is produced, probably as phenyldiazene–copper complex.[7] In the presence of excess CCD, a large part of the latter compound decomposes rapidly, producing nitrogen, benzene, and chlorobenzene, while in the presence of an equimolecular amount of CCD, a partial interaction with benzaldehyde becomes possible producing benzoin.

attention was focused on finding an interaction between PAS and CCD. This interaction can be considered as a model for the participation of inorganic salts in these reactions. An attempt to follow the reaction in an EPR cavity failed because of a high rate of reaction and a high dielectric constant of the alcoholic solvent. On the other hand, the use of benzene exhibited three different EPR signals. Dissolved CCD showed no hyperfine structure and gave a resonance whose peak to peak width was 325 ± 10 G and g = 2.38 (Figure 1a). When PAS was added to the system, a stable signal lasting several hours was observed (Figure 1b). The peak to peak width measured 20 G and g = 2.124. On the basis of these observations, we studied the reaction of CCD with PAS in benzene, and we obtained a brown product. Its microanalysis was consistent with the molecular ratio of PAS–copper(II) chloride–water = 1:2:2. Moreover, this product reacted readily at room temperature with ethanol, giving the typical compounds coming from the decomposition of benzoin phenylhydrazone ethyl ether in the presence of CCD. The molecular ratio of 1:2 between PAS and CCD is also in agreement with the absence of a resolved paramagnetic resonance of this compound in benzene. The spectrum shows a peak to peak width of 325 ± 10 G and g = 2.149 (Figure 1c). The EPR signals can be interpreted as shown in Scheme II.

Further information on the activity of the inorganic salts was obtained from the subsequent and collateral reactions of the 1,4-adducts. In particular, after the formation of the benzoin phenylhydrazone derivatives, we observed the formation of the parent carbonyl compounds, benzoin, benzaldehyde, benzoic acid or esters, chlorobenzene, and benzene (yields 30%), when the reactions were carried out over several days under reflux with a 1:10 molecular ratio between CCD and PAS. By increasing the ratio up to 1:1 or 3:1 complete reactions were obtained at room temperature. In the case of CCD–PAS in ethanol, different ratios

Experimental Section

All products were identified by comparison with either authentic commercial specimens or specimens prepared in the usual

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Scheme III

way (TLC, high-performance LC, and IR, ^{1}H NMR, and mass spectra).

Phenylazostilbene. This compound was prepared as previously reported.[2a]

Benzoin Phenylhydrazone Derivatives. These compounds were obtained by reaction between phenylhydrazine and the corresponding carbonyl compounds, according to well-known methodologies.[2b,8] The *syn*-benzoin phenylhydrazone ethyl ether was obtained as previously reported.[2b]

1,4-Additions to Phenylazostilbene. A typical experiment for the 1,4-addition of alcohol to PAS was previously reported in detail.[2b] Anhydrous iron(III)chloride or copper(II) chloride dihydrate (0.035 mmol) was added to an alcoholic solution (25 mL) of PAS (0.35 mmol). The mixture was stirred magnetically at 0–5 °C until the reaction was completed (5–30 min). After evaporation of the alcohol under reduced pressure, the product was poured into ether and washed with saturated aqueous sodium chloride. The ethereal layer was dried with anhydrous magnesium sulfate, and after evaporation it provided the crude AEBP in good purity. Further purification can be obtained by usual methods. However, as reported, these compounds were highly reactive for facile oxygen absorption.[2b,5] For this reason it is convenient to work under a nitrogen atmosphere. The 1,4-addition of water to PAS was carried out in a monophasic 1:1 mixture of tetrahydrofuran and water, using a molecular ratio of 10:2 PAS–CCD. After 4 h under reflux, benzoin phenylhydrazone was obtained. The addition of phenol to PAS was carried out in tetrahydrofuran solution, using a PAS, CCD, and phenol molecular ratio of 1:1:65, respectively. The reaction mixture was kept at room temperature and stirred magnetically. Under these conditions benzoin phenylhydrazone phenyl ether, the 1,4-adduct of phenol to PAS, was detected as the intermediate of the reaction. After 4 h, the usual decomposition products of the benzoin phenylhydrazone derivatives were recovered.

Decomposition of Benzoin Phenylhydrazone Derivatives in the Presence of CCD. After the 1,4-addition to PAS, increasing the CCD amount up to a molecular ratio of 1:1 or 1:3, the benzoin phenylhydrazone derivatives decompose rapidly. The decomposition under reflux is faster than at room temperature and gives the parent carbonyl compounds, benzoin, benzaldehyde, benzoic esters, chlorobenzene, and benzene. As expected, in the case of benzoin phenylhydrazone (derived by 1,4-addition of water to PAS), after 24 h under reflux, in addition to benzaldehyde, benzoic acid, chlorobenzene, and benzene, only benzoin was obtained (60% yields). The reaction of benzoin phenyhydrazone ethyl ether was studied in detail.

Preparation and Decomposition of PAS–CCD Adduct. PAS (100 mg, 0.35 mmol) was dissolved in anhydrous benzene (50 mL) and CCD (6 mg, 0.035 mmol) was added. The mixture was stirred magnetically for 10 days at room temperature under a nitrogen atmosphere. The solid was filtered out and washed twice with 20 mL of anhydrous benzene. This filtration left a product free of residual CCD; mp 140 °C (uncorrected). The IR spectrum (4000–700 cm^{-1}) shows essentially the same features of PAS shifted to higher frequency (from 20 to 50 cm^{-1}). Anal. Calcd: C, 40.77; H, 3.42; N 4.75. Found: C, 40.59; H, 3.31; N, 4.86. This compound was reacted with absolute ethanol and produced benzoin ethyl ether, benzoin, benzaldehyde, ethyl benzoate, chlorobenzene, and benzene, which are the usual products derived

from the decomposition of benzoin phenylhydrazone ethyl ether.

Disproportionation in a Michael Addition Reaction

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The Michael addition reaction is one of the most synthetically useful reactions.[1] In its normal mode, a nucleophilic attack on the β position of an activated olefin is followed by protonation of the intermediate carbanion to give the neutral adduct (eq 1). An interesting exception
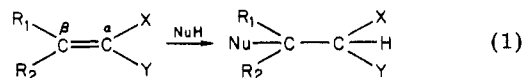
to this general behavior was reported by Juchnovski et al.[2] The reaction of 1-nitro-1-cyano-2-phenylethylene with amines in ethanol resulted in the bis onium salt of 2,4-dinitro-3-phenylglutaric acid dinitrile instead of the expected normal adduct.[2] The mechanism suggested by Juchnovski involved the formation of the normal adduct

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