Thione Photochemistry. Preparation and Properties of the α-Dithione System[1,2]

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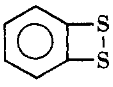
Abstract: The photolysis of diphenylvinylene dithiocarbonate leads to the formation of diphenyldithiete, but this substance is too reactive to allow isolation. The corresponding bis-*p*-dimethylamino compound has been similarly prepared and in the solid state exists in the α-dithione form. It is thus the first α-dithione to be studied. In solution the dithione and dithiete forms are in equilibrium, and this equilibrium is sensitive to light, temperature, and solvent. Thermodynamic and kinetic studies have yielded the energy parameters for this equilibrium. In preliminary experiments the α-dithione has been shown to react with hydrogen cyanide, diazomethane, and 1,2-dimethoxyethylene to give adducts. Complexes with metal carbonyls have also been isolated.

As far as we have been able to ascertain, the first attempt to prepare either an α-dithione or the valence tautomer, a 1,2-dithiete, was that of Guha and Chakladar.[4] These authors reported the preparation of benzo-1,2-dithiete (**1**) by the oxidation of dithiocatechol with iodine in ethanol. Later work showed that the reaction product was a polymeric mixture, and the simplest substance isolated was the dimer **2**.[5]



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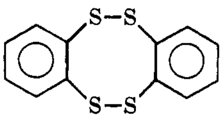

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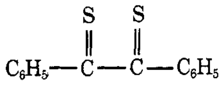
A later report[6] that dithiobenzil (**3**) had been prepared was subsequently[7,8] shown to be in error, and other attempts made to prepare dithiobenzil by standard procedures suitable for simple thiones were unsuccessful.[8]

Aside from these investigations there appears to have been little reported before 1960,[9] although rubeanic acid and substituted dithiooxamides[10,11] have been known for some time.

The first and, up to the present work, only successful preparation of a 1,2-dithiete or an α-dithione is that reported by Krespan and his collaborators.[12,13] These workers obtained bis(perfluoroalkyl)-1,2-dithietes by the action of sulfur on the corresponding fluoroacetylenes. The products were obtained in good yields, and spectroscopic evidence excluded the acyclic valence tautomeric α-dithione structure for these compounds. Shortly afterward Simmons and his collaborators[14] showed that dicyano-1,2-dithiete (**4**) was an intermediate in the oxidation of disodium dimercaptomaleonitrile (**5**). It proved impossible, however, to isolate the dithiete.



$C_6H_5-\overset{S}{\overset{\|}{C}}-\overset{S}{\overset{\|}{C}}-C_6H_5$

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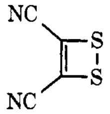

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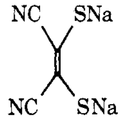

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Calculations were reported[14b] which set out to evaluate the relative stabilizing effect of substituents such as $-NMe_2$, $-Me$, $-CF_3$, or $-CN$ on the valence tautomeric forms in terms of their delocalization energies. The results obtained were in agreement with observation in as much as concerns the relative stability of the known dithiooxamides and dithietes, and the prediction was made that "conjugative electron release by the substituents stabilizes the α-dithione structure relative to the 1,2-dithiete structure, while both conjugative and inductive electron-withdrawing substituents stabilize the cyclic structure with respect to the open form."[15]

Thus, when the work to be described was undertaken, no α-dithione had been characterized as such, although metal complexes, prepared indirectly, were well known.[7,16] A study of the preparation and stability of such compounds was undertaken, the ultimate object being the study of their photochemistry.

Results and Discussion

Dithiobenzil. The most simple substance for which there was some hope of a stability such as to permit isolation was dithiobenzil (**3**). Classical approaches to the substance, both by us and by others,[6-8] led to no

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[1] Photochemical Synthesis. 56. This is the fifteenth of a series on thione photochemistry,

[2] Publication No. 98 from the Photochemistry Unit, University of Western Ontario.

[3] Recipient of a Canada Council Fellowship, 1971–1972.

[4] P. C. Guha and M. N. Chakladar, *Quart. J. Indian Chem. Soc.*, **2**, 318 (1925).

[5] L. Field, W. D. Stephens, and E. L. Lippert, *J. Org. Chem.*, **26**, 4782 (1961).

[6] S. K. Mitra, *J. Indian Chem. Soc.*, **15**, 58 (1938).

[7] G. N. Schrauzer and H. W. Fink, *Angew. Chem.*, **76**, 143 (1964).

[8] R. Mayer and M. Nitzschke, *Chem. Ber.*, **96**, 2539 (1963).

[9] A compound isolated from thiophene tar obtained by the action of sulfur on butane was tentatively classified as thiolane dithione but was not characterized: P. D. Caesar and P. D. Brantan, *Ind. Eng. Chem.*, **44**, 122 (1952).

[10] R. N. Hurd, G. Mater, G. C. McElheny, R. J. Turner, and V. H. Wallingford, *J. Org. Chem.*, **26**, 3980 (1961).

[11] B. Persson and J. Sandström, *Acta Chem. Scand.*, **18**, 1059 (1964).

[12] C. G. Krespan, B. C. McKusick, and T. L. Cairns, *J. Amer. Chem. Soc.*, **82**, 1515 (1960).

[13] C. G. Krespan, *J. Amer. Chem. Soc.*, **83**, 3434 (1961).

[14] (a) H. E. Simmons, R. D. Vest, D. C. Blomstrom, J. R. Roland, and T. L. Cairns, *J. Amer. Chem. Soc.*, **84**, 4746 (1962); H. E. Simmons, D. C. Blomstrom, and R. D. Vest, *ibid.*, **84**, 4756, 4772 (1962); (b) *ibid.*, **84**, 4782 (1962).

[15] Other calculations on the energetics of 1,2-dithiete have been made by G. Bergson, *Ark. Kemi*, **19**, 265 (1962).

[16] D. C. Dittmer and G. E. Kuhlmann have reported that the photolysis of dibenzoylstilbene episulfoxide gives monothiobenzil [*J. Org. Chem.*, **35**, 4224 (1970)]. This, the only known monothiono ketone, has also been prepared from *S*-desylthiosulfate: B. Saville and M. Steer, *J. Chem. Soc., Chem. Commun.*, 616 (1972). See, however, A. Schönberg and O. Schütz, *Justus Liebigs Ann. Chem.*, **454**, 47 (1927).

isolable product of relevance, nor were we able to adduce decisive evidence for the transitory existence of **3**. A different approach, in which the final product would be generated in the absence of reagents and under mild conditions, was, therefore, sought.

The decarbonylation of diphenylvinylene dithiocarbonate (**6**), having analogy in other systems, seemed promising. This substance was readily available by desulfurization of the corresponding trithiocarbonate[17] (**7**) with mercuric acetate in glacial acetic acid.

The products obtained after irradiation of **6**, in a variety of solvents, through Pyrex and at room temperature, were tetraphenyldithiin (**8**) in varying yields and a small amount of tolane. Despite considerable effort neither **3** nor the tautomeric diphenyl-1,2-dithiete (**9**) could be detected. Nonetheless, analysis of the gas evolved in the photolysis clearly indicated the formation of carbon monoxide and the absence of the possible alternative elimination product, carbonyl sulfide. That the photolysis did not take this alternative pathway was supported by the fact that the dithiafulvene (**10**) was not produced. Kirmse and Horner have shown[18] that irradiation of **11** leads, *via* **12**, to the formation of **8** and **10**. Elimination of carbonyl sulfide from **6** should have generated the same intermediate (**12**) and, hence, would be expected to give **10** besides the observed **8**.

Irradiation of **6** at −78° gave a somewhat different result. Carbon monoxide was again evolved, but the solid material was a yellow, probably polymeric, material having a very low solubility in all common organic solvents. Neither **8** nor tolane could be observed.

From these observations it seemed possible to us that the primary photochemical step was the chelotropic elimination of carbon monoxide to give **9** and that this dimerized rapidly. At low temperature this dimeric (or oligomeric) material polymerized further, but at room temperature it underwent at least partial thermal decomposition to give **8** and tolane. The following observations appear to support this view. Irradiation of **6** in the presence of molybdenum hexacarbonyl or nickel tetracarbonyl gave the metal complexes, **13** and **14**, which have already been prepared by Schrauzer and his collaborators by several other routes.[19] These complexes were not formed in the absence of irradiation nor was **13** detected following the addition of an irradiated solution of molybdenum hexacarbonyl to an irradiated solution of **6**. Furthermore, **13** was not observed upon the addition of molybdenum hexacarbonyl to an irradiated solution of **6**, nor vice versa (Scheme I).

To obtain further information about the reactions occurring at low temperature the irradiation of **6** at 77°K in EPA[20] solution was studied spectroscopically. At the outset there was little absorption in the 380-nm region (Figure 1, curve A), but on irradiation through Pyrex a new species was formed with maxima at 370 and 387 nm. On gradual warming to room temperature this absorption rapidly disappeared, with the concomitant appearance of an amorphous precipitate. We attribute the absorption at 370 and 387 nm to the presence of **9** and exclude the alternative **3** on the basis that such a compound would have $\pi^* \leftarrow n$ absorption at long wavelength as have all conjugated thiones so far prepared.

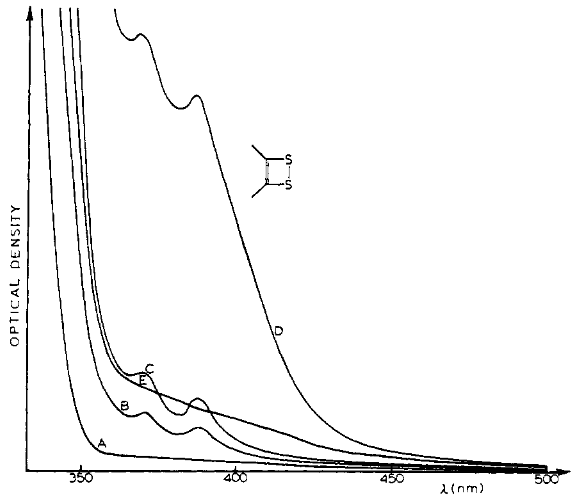
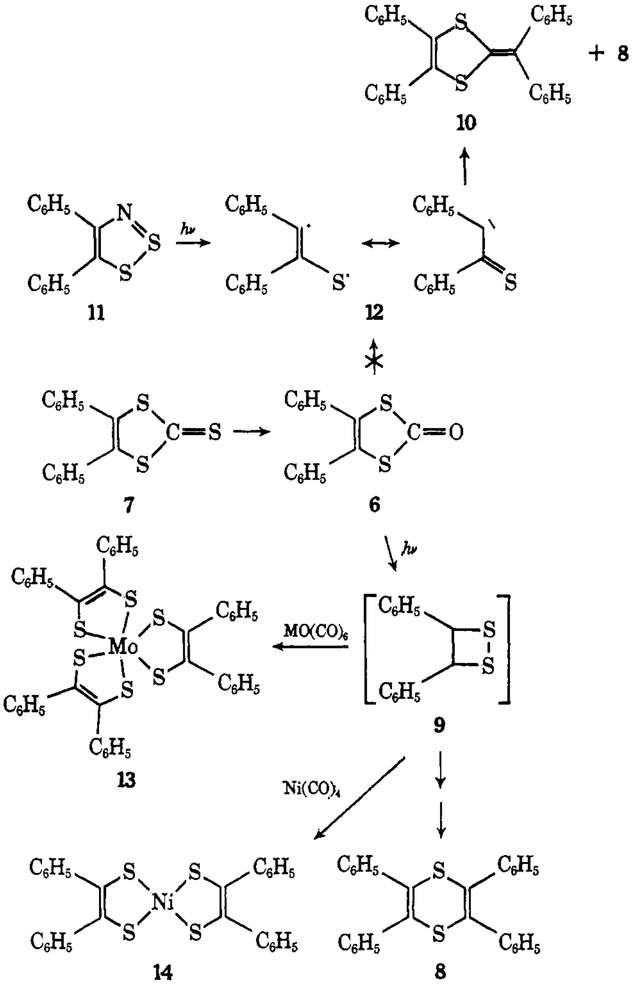


Figure 1. Spectral changes upon irradiation of a degassed solution of **6** in EPA at 77°K (A → B → C → D) and after warming to room temperature (E).

Scheme I



From this it is not surprising that we failed to detect **3** or **9** after flash thermolysis of **6** or 1,2-diphenyl-5,6-dihydro-1,4-dithiin (**15**).[21] Both **6** and **15** were

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[17] K. M. Pazdro, *Rocz. Chem.*, **43**, 1089 (1969).

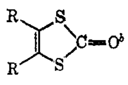
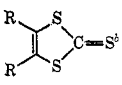
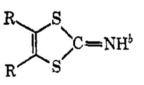
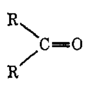
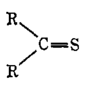
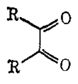
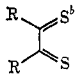
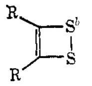
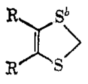
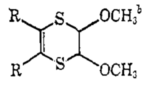
[18] W. Kirmse and L. Horner, *Justus Liebigs Ann. Chem.*, **614**, 4 (1958).

[19] (a) G. N. Schrauzer and V. P. Mayweg, *J. Amer. Chem. Soc.*, **87**, 1483 (1965); (b) *Z. Naturforsch.*, *B*, **19**, 192 (1964).

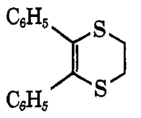
[20] EPA: ether–isopentane–alcohol, 5:5:2.

[21] H. Rubinstein and M. Wuerthele, *J. Org. Chem.*, **34**, 2762 (1969).

Table I. Nmr Data for Dithione **16** and Related Compounds[a]

					
H_o	6.54	6.56	6.53	6.68	6.61
H_m	7.08	7.08	7.05	7.75	7.75
$-N(CH_3)_2$	2.94	2.95	2.92	3.05	3.05
					
H_o	6.64	6.53	6.59	6.57	6.47
H_m	7.85	8.06	7.21	7.10	7.03
$-N(CH_3)_2$	3.05	3.07	2.95	2.92	2.87

[a] Chemical shift data (ppm) of some compounds structurally related to **16** and **22**. R = p-$Me_2NC_6H_4$–. H_o and H_m refer to the aromatic protons in ortho and meta positions to the dimethylamino group. (Solvent, $CDCl_3$). [b] Compound reported in this paper.



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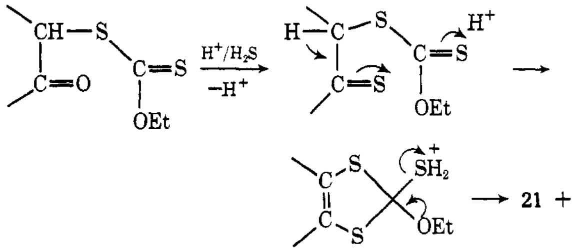
thermolyzed at 720° (0.1 Torr) using a technique described earlier.[22] In the case of **15** the expected retro-Diels–Alder reaction occurred to give ethylene. A yellow insoluble material was also obtained as main product, as was the case in the thermolysis of **6**. Both materials, in their infrared spectra, resembled the already described polymer formed on photolysis of **6**.[23] All three polymeric materials decomposed when heated in decalin for several hours to give **8** as the main product, together with sulfur and tolane. In addition, heating in xylene solution, in the presence of molybdenum hexacarbonyl, yielded **13**. Such behavior is reminiscent of that of the tetrameric dithiobenzil described earlier by Schrauzer and Fink[7] and supports the view that these insoluble materials are polymers of **3** or **9**.

Bis(p-dimethylamino)dithiobenzil (16). The starting material for the preparation of the α-dithione **16** was 4,4′-bis(dimethylamino)desoxybenzoin (**17**) which was prepared, according to the method of Allen,[24] by electrolytic reduction of p-dimethylaminobenzaldehyde and dehydration of the resultant pinacol. On treatment of **17** with hydrobromic acid and bromine in glacial acetic acid, the acetate **18** was obtained in 58% yield. Transesterification with potassium xanthate in ethanol gave the xanthate (**19**) in 44% yield, an important by-product being 4,4′-bis(dimethylamino)benzoin. However, reaction of the xanthate gave only very poor yields of the trithiocarbonate **20** although this method has been used successfully to cyclize other S-phenacyldithiocarboxylates.[17,25] The desulfurization to give the dithiocarbonate **21** could be achieved with mercuric acetate in chloroform. Fortunately it was found that **19** could be cyclized in anhydrous hydrofluoric acid–methanol in the presence of hydrogen sulfide to give **21** directly in 47% yield. A possible mechanism for this process is indicated below.



(20)

Irradiation of a benzene–vinyl ethyl ether solution of **21** at room temperature under nitrogen with light of wavelength greater than 350 nm gave the dithione **16** which crystallized from the irradiated solution in 50% yield, as dark red crystals, mp 184–185.5° dec. The manner of conducting the irradiation was critical because **16** remaining in solution remained inaccessible; attempted chromatographic separation led only to decomposition (Scheme II).

The nmr spectrum of a solution of **16** in $CDCl_3$ clearly indicated the presence of two species. Two singlets (dimethylamino protons) are observable at 3.07 and 2.95 ppm; on the basis of the analogies contained in Table I, they are assigned to **16** and **22**, respectively. The aromatic protons in **16** give rise to an AB pattern with resonances at 6.53 and 8.06 ppm, the signals for the corresponding protons in the dithiete being at 6.59 and 7.21 ppm.

Integration over methyl signals gave a ratio, at the temperature of the spectrometer (HA-100), of **16** to **22** of 6.1:1 in methylene dichloride. This ratio is reversed, to approximately 1:20, upon irradiation of the sample at −50° with light of wavelength greater than 500 nm. Upon warming of the sample so irradiated to the temperature of the spectrometer, the ratio regained its original value.

The infrared spectrum of **16** (most probably in the transoid form) as taken in a potassium bromide pellet is shown in Figure 2. It is very similar to that obtained in chloroform solution which is not unexpected in view of the preponderating presence of **16** in the equilibrium.

Attempts were made to isolate the dithiete by taking advantage of the already mentioned shift of equilibrium obtained by irradiation at long wavelength.[26]

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[22] J. F. King, P. de Mayo, C. L. McIntosh, K. Piers, and D. J. Smith, *Can. J. Chem.*, **48**, 3704 (1970); P. de Mayo, *Endeavour*, **31**, 135 (1972).

[23] Tolane was also formed as a minor product from the thermolysis of **6** and **15**.

[24] M. J. Allen, *J. Org. Chem.*, **15**, 435 (1950); *J. Amer. Chem. Soc.*, **73**, 1841 (1951).

[25] D. Leaver, W. A. H. Robertson, and D. M. McKinnon, *J. Chem. Soc.*, 5104 (1962).

[26] The spectral changes observed on irradiation at −0.4° of a degassed solution of **16** in methylene chloride have already been reported

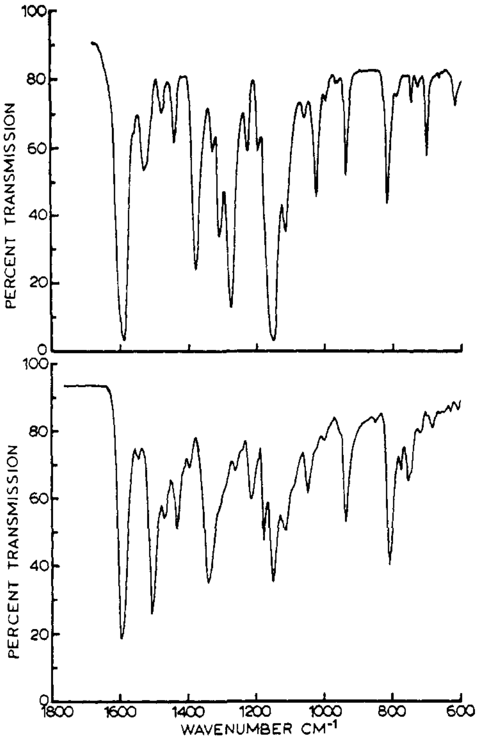
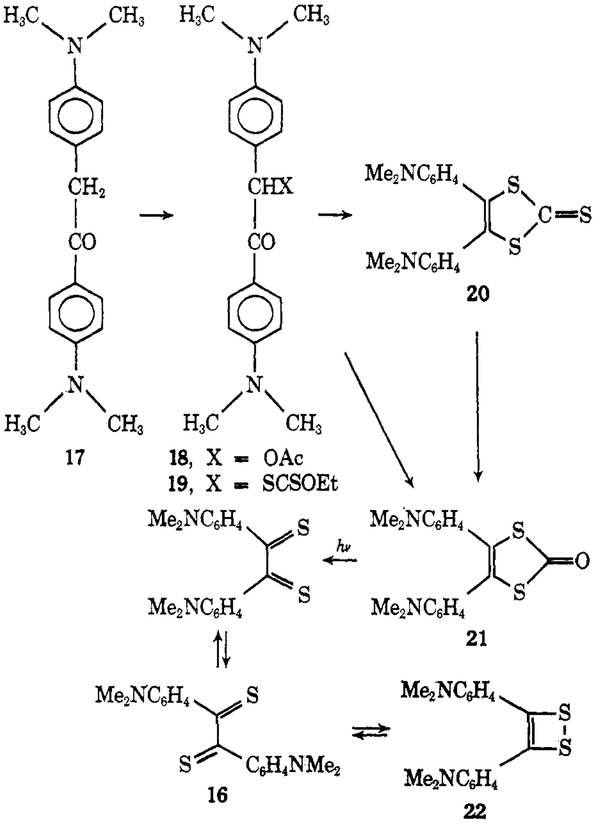


Figure 2. Infrared spectrum (KBr) of **16** (top). Infrared spectrum (KBr) of precipitated dithiete **22** (bottom).

Scheme II



The irradiation of the equilibrium mixture at −50° in methylene dichloride gave a yellow-orange solution from which a yellow precipitate was obtained by the addition of *n*-pentane. The infrared spectrum (KBr disk) of this material, believed to be essentially the dithiete **22**, is shown in Figure 2; however, it was not possible either to crystallize this material nor to determine the amount of **16**, if any, present.

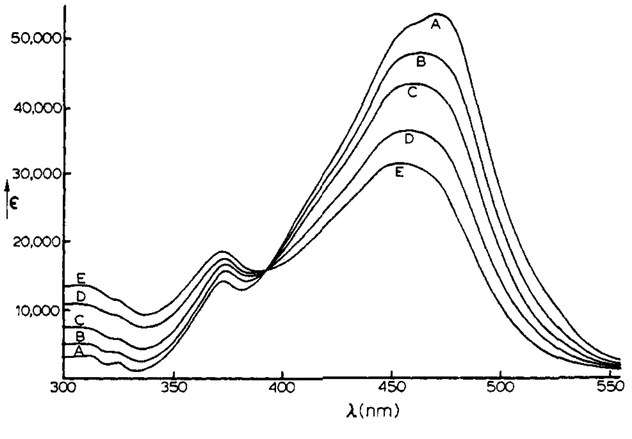


Figure 3. Absorption spectra of equimolar solutions of **16** in solvent mixtures of CH_3CN–CCl_4 at room temperature. Volume per cent of CCl_4 in CH_3CN: A, 0; B, 52; C, 72; D, 84; E, 92.

Solvent Effect on the Equilibrium 16 ⇄ 22. We have shown that the equilibrium between **16** and **22** depends on solvent, light,[26] and temperature. In fact, the demonstration that the tautomerization follows clean first-order kinetics (see below) is an integral part of the proof that the equilibrium involves monomeric species,[28] and hence is between the dithione and the dithiete. A contribution of the cisoid dithione to the, presumably predominating, transoid dithione was not discernible in the present experiments.

The ultraviolet and visible absorption spectra of **16** in solvents of different polarity have been determined. Those in methylene dichloride–hexane mixtures have already been reported,[27] while those in acetonitrile–carbon tetrachloride mixtures are shown in Figure 3. It may be seen that the extinction of the high intensity band at about 450 nm, mainly to be attributed to the α-dithione isomer, decreases with decreasing polarity of the solvent. Similar observations were made for solvent mixtures of ethanol and benzene and for ethanol and *n*-hexane. This suggests that the charge separation in the dithione is greater than in the dithiete, an observation in keeping with intuitive and theoretical predictions.[14b]

The presence of an isosbestic point at 392 nm (Figure 3) in acetonitrile–carbon tetrachloride (or at 385 nm in benzene–ethanol) indicates an equilibrium between only two absorbing species. In the case of the solvent mixtures methylene dichloride–hexane[27] and ethanol–*n*-hexane the actual individual absorptions of the two

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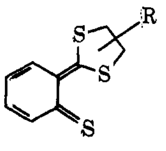
in a preliminary communication.[27] The mass spectrum is also there discussed.

(27) W. Küsters and P. de Mayo, *J. Amer. Chem. Soc.*, **95**, 2383 (1973).

(28) A deceptively similar equilibrium, thermally and photochemically reversible, has been observed (H. Y. Ng, unpublished observations from these laboratories) in connection with substances of type i where R is an



i

alkyl residue. In this case the equilibrium involves a dimeric species.

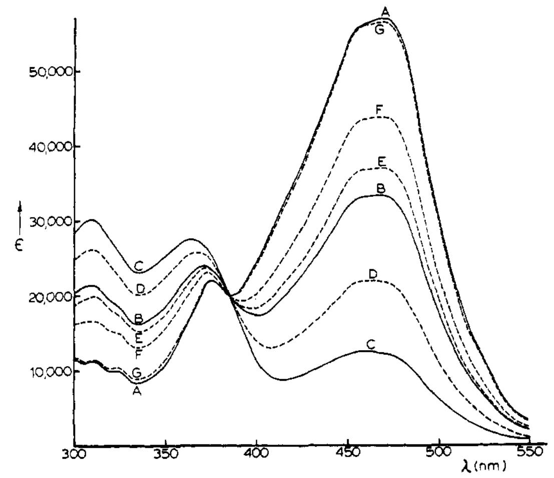


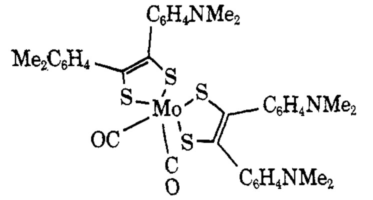
Figure 4. Spectral changes during irradiation (—) (λ >500 nm) and after irradiation (- - - -) of a degassed solution of thione in CH_2Cl_2 at 0.4°. Irradiation time (sec): A, 0; B, 5; C, 525. Time after irradiation (nm): D, 10; E, 30; F, 50; G, 200.

molecules are solvent dependent so that the isosbestic point cannot be observed.

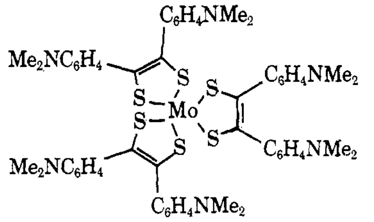
The displacement of the equilibrium in favor of **22** on irradiation with light of wavelength longer than 500 nm is shown in Figure 4. With removal of the light source the original equilibrium is reestablished. The fact that the final and original curves are superposable indicates that the photochemically induced tautomerization of **16** to **22** proceeds with appreciable formation of byproducts.

The foregoing discussion, together with that already reported,[27] serves to establish the identity of the chemical species generated by the photolysis of **21** and the nature of the equilibrium between them in solution. The substances have been further characterized by the formation of stable complexes.

Irradiation of a mixture of **21** and molybdenum hexacarbonyl gave two products: the bis adduct **23** which



23



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contains two carbonyl residues and the tris adduct **24**, analogous to **13** obtained from the phenyl derivative **6**.

The same adducts were formed by irradiating a mixture of **16** and molybdenum carbonyl, but no reaction was obtained in the absence of light. It thus appeared that irradiation of the carbonyl was necessary. This was confirmed by irradiation of a chloroform solution of molybdenum hexacarbonyl and subsequent addition of **16**. The formation of **23** was then observed. No adduct was formed under these conditions if **21** was substituted for **16**.

Kinetic and Thermodynamic Measurements. Kinetic and thermodynamic measurements were carried out to delineate the valence tautomeric system quantitatively.[29]

These were performed, utilizing both ultraviolet and nmr spectral techniques, in methylene dichloride solution between −2.9 and 42.5°. The direct determination of the temperature dependence of the equilibrium constant, K, by nmr measurements was unfortunately impractical since solutions of **16**/**22** were found to decompose slowly if of too high concentration (>0.02 M). The decomposition products, probably due to bimolecular reactions gave rise to signals in the nmr spectrum close to those of the methyl protons. However, dilute solutions (2×10^{-5} M) under nitrogen were stable for at least 100 hr at ambient temperatures.

The temperature dependence of K was, therefore, determined by following the absorbance of a methylene dichloride solution of **16**/**22** at 465 nm at eleven temperatures between −2.9 and 42.5°, the absorbances being measured alternately at higher and lower temperatures (Table II) thus approaching the equilibrium state from both sides.

For the equilibrium

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{B}$$

(**22** ⇄ **16**) Beer's law has the form

$$E = C_A\epsilon_A d + C_B\epsilon_B d \tag{1}$$

where E is the optical density of the solution, C_A and C_B the molarities of A and B, ϵ_A and ϵ_B their molar absorptivities and d the cell length. Introducing the mole fractions X_A and X_B *e.g.*, eq 1, for very dilute solutions, may be transformed to give

$$E^0 = X_A{}^0\epsilon_A dm\rho^0 + X_B{}^0\epsilon_B dm\rho^0 \tag{2}$$

$$E^1 = X_A{}^1\epsilon_A dm\rho^1 + X_B{}^1\epsilon_B dm\rho^1 \tag{3}$$

where the superscripts refer to temperatures T^0 and T^1, ρ is the solvent density, and m is the total molality of the solution. The ratio of the molar absorptivities (ϵ_r) is then, from eq 2 and 3, given by

$$\epsilon_r = \frac{\epsilon_B}{\epsilon_A} = \frac{X_A{}^0\rho^0E^1 - X_A{}^1\rho^1E^0}{X_B{}^1\rho^1E^0 - X_B{}^0\rho^0E^1} \tag{4}$$

With the equilibrium constant K defined as

$$K = X_B/X_A \tag{5}$$

the equilibrium constant K at temperature T can be formulated as

$$K = \frac{\rho^1E^0(1 - \epsilon_r)}{E\rho^0(X_A{}^0 + \epsilon_r - X_A{}^0\epsilon_r) - \epsilon_rE^0\rho} - 1 \tag{6}$$

Equation 6 allows for the change of the solvent density with temperature. To determine K it is necessary to know ϵ_r at 465 nm, together with $X_A{}^0$ at the standard temperature T^0.

The value for ϵ_r can be calculated from eq 4 if the

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[29] (a) E. W. Schlag and W. B. Peatman, *J. Amer. Chem. Soc.*, **86**, 1676 (1964); (b) J. P. Chesick, *ibid.*, **88**, 4800 (1966); (c) G. A. Doorakian and H. H. Freedman, *ibid.*, **90**, 3582 (1968).

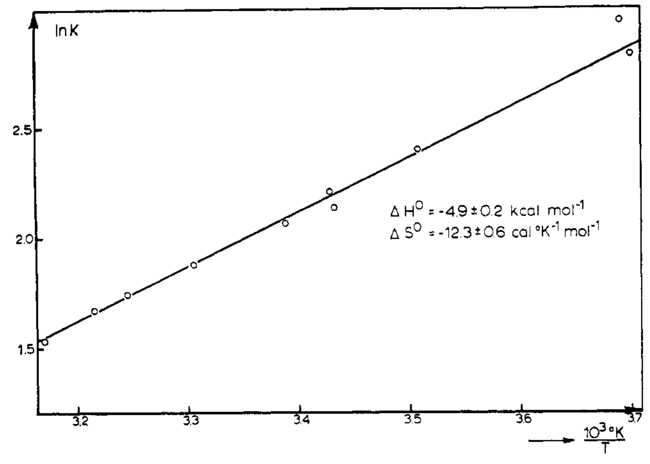

Figure 5. Plot of ln K as a function of the reciprocal absolute temperature, T.

mole fractions $X_A{}^0$ and $X_A{}^1$ at T^0 and T^1 are known together with the corresponding values for E^0 and E^1. The reference temperature T^0 was chosen to be 32° and $X_A{}^0$ found to be 0.141 ± 0.006 by nmr measurements of five freshly prepared solutions of **16**/**22**. Samples were irradiated at $-60°$ until the stationary state was attained; the mole fraction of **22**, $X_A{}^1$, was found to be 0.96 ± 0.1. A solution of **16**/**22** with an optical density (465 nm) of $E^0 = 1.49$ at 32° showed after irradiation at $-60°$ a residual absorption $E^1 = 0.24$. The value of ϵ_r was thus 11.5 ± 1.3, with the implicit assumption that the position of the photostationary state is not concentration dependent. The values obtained for the equilibrium constants K (eq 6) are given in Table II. A plot of ln K against the reciprocal of the absolute temperature gave a good straight line (Figure 5). From the slope of the plot the standard value of the tautomerization enthalpy for the process (**22** → **16**) was computed to be $\Delta H° = -4.9 \pm 0.2$ kcal mol^{-1}, together with $\Delta S° = -12.3 \pm 0.6$ eu.

Table II. Values of Equilibrium Constants, K, for **22** ⇄ **16** at Various Temperatures

Sequence of measurements	Temp, °C	K	% α-dithione (B, **16**) at equilibrium
7	−2.9	16.9	94.4
2	−2.2	19.6	95.1
3	11.8	11.0	91.7
9	18.1	8.4	89.4
1	18.5	9.1	90.1
10	21.9	7.9	88.8
4	29.3	6.5	86.7
11	32.0	6.1	85.9
5	34.9	5.7	85.0
6	37.8	5.3	84.1
8	42.5	4.6	82.3

For a first-order reversible reaction, followed spectrophotometrically, the sum of the rate constants $(k_1 + k_{-1})$ is given by

$$\ln\left(\frac{E^\infty - E^0}{E^\infty - E^t}\right) = (k_1 + k_{-1})t \qquad (7)$$

where E^∞, E^0, and E^t are the optical densities at equilibrium, time $t = 0$, and after time t. The measurements were carried out at nine temperatures between 0.7 and 27.3°. Before each run, the equilibrium was displaced photochemically in favor of the dithiete by irradiating the solution with light of wavelength greater than 500 nm. The equilibration process was then followed by recording the optical density at 465 nm as a function of time.[30] Figure 6 shows typical plots of ln $[(E^\infty - E^0)/(E^\infty - E^t)]$ against time for several temperatures. The excellent linearity confirms the equilibration process to be a first-order reversible reaction.

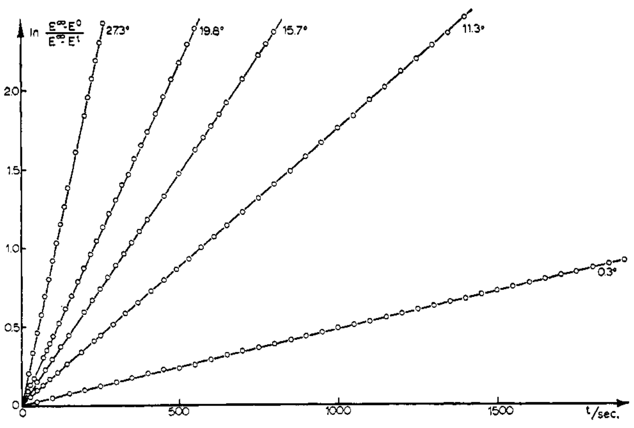

Figure 6. Plots of ln $[(E^\infty - E^0)/(E^\infty - E^t)]$ against time for several temperatures. The slopes of the lines represent the sum of the rate constants $(k_1 + k_{-1})$ at the indicated temperature.

The values for $(k_1 + k_{-1})$ together with the individual values of k_1 and k_{-1} [defined according to eq 1; k_1 is the rate constant for the formation of the α-dithione **16** (B)] are listed in Table III. From the Arrhenius plots for k_1 and k_{-1} illustrated in Figures 7 and 8 the temperature dependence of the two rate constants, estimated by the method of least squares, may be expressed as

$$k_1 = 4.32 \times 10^{10} \exp\left(\frac{-17.5 \text{ kcal mol}^{-1}}{RT}\right) \text{sec}^{-1}$$

$$k_{-1} = 2.29 \times 10^{13} \exp\left(\frac{-22.4 \text{ kcal mol}^{-1}}{RT}\right) \text{sec}^{-1}$$

Table III. Kinetic Data for the Equilibrium **22** $\underset{k_{-1}}{\overset{k_1}{\rightleftarrows}}$ **16**

Temp, °C	$10^4(k_1 + k_{-1})$, sec^{-1}	K^a	10^4k_1, sec^{-1}	10^5k_{-1}, sec^{-1}
−0.7	4.34	15.81	4.08	2.58
0.3	4.83	15.28	4.53	2.97
11.3	17.5	10.85	16.02	14.8
15.6	29.8	9.56	26.98	28.2
15.7	29.5	9.51	26.69	28.1
19.6	43.0	8.51	38.48	45.2
19.8	43.4	8.47	38.82	45.8
27.2	94.4	6.91	82.47	119.3
27.3	92.3	6.89	80.60	117.0

[a] Interpolated from Figure 5.

From the preexponential terms the standard values for the activation entropies[31] were evaluated as $\Delta S_1{}^{\ddagger} =$

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(30) No deviation from Beer's law was observed over four orders of magnitude in concentration using path lengths of 0.01–10 cm.

(31) With the assumption that the preexponential term is given by the expression $kT/h \cdot \exp \Delta S^{\ddagger}/R$.

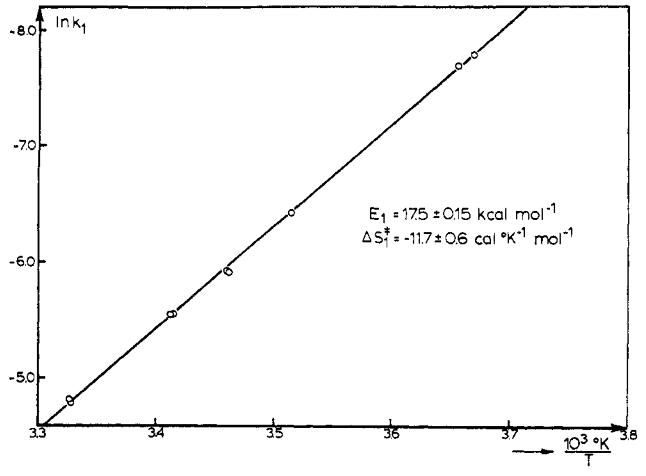


Figure 7. Arrhenius plot for the tautomerization of 1,2-dithiete **22** (A) to α-dithione **16** (B).

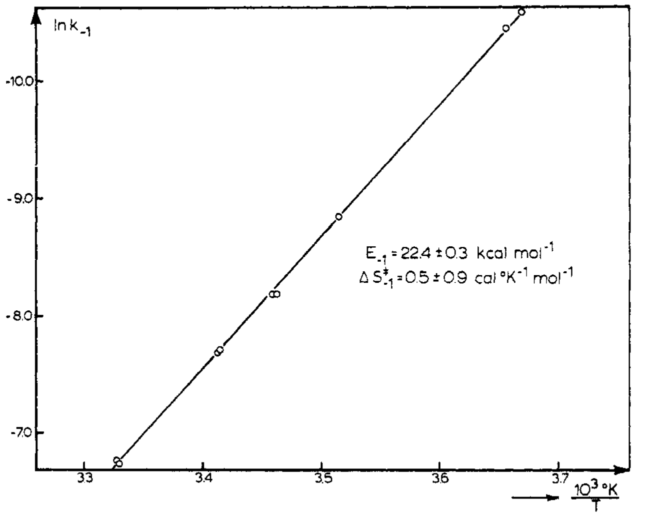
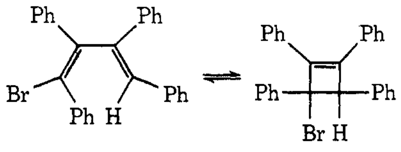


Figure 8. Arrhenius plot for the tautomerization of α-dithione **16** (B) to 1,2-dithiete **22** (A).

-11.7 ± 0.6 eu and $\Delta S_{-1}^{\ddagger} = 0.5 \pm 0.9$ eu. The values so extracted are summarized in Figure 9.

There are few data in the literature to which the cyclization reaction **16** → **22** may be compared. The only example known to us not involving fluorocarbons is that of *trans*-1-bromo-*cis*-1,2,3,4-tetraphenylbutadiene[29c] (**25**) to the corresponding cyclobutene.



25

For this reaction the energy of activation is comparable with that which we have observed, but perhaps one aspect requires comment. For the cyclization of **25** $\Delta S^{\ddagger}$ is reported to be -15.6 ± 1.7 eu which is understandable in terms of a concerted rearrangement without charge separation which is comparable to the Cope rearrangement. In the present instance the entropy of activation is of opposite sign, but there is also another important difference. This is that the equilibrium itself is strongly solvent dependent unlike that for **25**. It would seem likely that the organization of the solvent about the highly dipolar dithione is, as would be expected, much more important than that about the dithiete. In addition, the rotation of the phenyl groups may be more restricted in the dithione because of a higher bond order of the bond between the phenyl group and the thione carbon. Since we do not have evidence as to whether the bond rotation (t → c) and cyclization are simultaneous or not, and as we do not know the solvent effect on $\Delta S^{\ddagger}$, we can do no more than draw attention to these points.

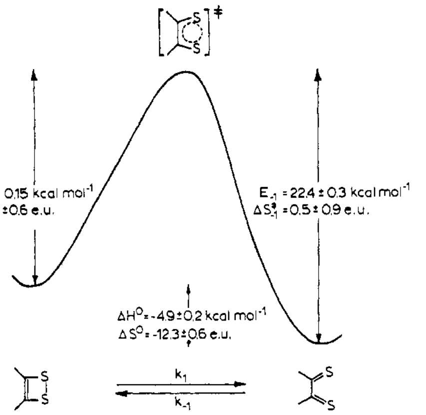


Figure 9. Schematic energy diagram for the dithione–dithiete tautomerization.

Reactions of α-Dithione 16. We have made a few preliminary studies of the ground state reactivity of **16** (or **22**). All involve 1,4 addition to the dithione system (or 1,2 addition across the disulfide linkage in the 1,2-dithiete).

Addition of diazomethane led to the smooth formation of a 1,3-dithiole **26** and the elimination of nitrogen. The reaction has no parallel in diketone chemistry as far as we are aware, but the addition of diazomethanes to simple thiones is well known.[32] The structure of **26** followed from its analytical data, mass spectrum, and the presence of a two-proton singlet at 4.42 ppm in the nmr spectrum. In this instance, as with certain simple thiones, the diazomethane carbon has added to the sulfur of the sulfur–carbon linkage.

A similar addition was observed in the reaction of hydrogen cyanide in acetonitrile with **16**. The product showed a band at 3280 cm^{-1} in the infrared spectrum to be attributed to N–H stretch, and this conclusion was confirmed by the observation of a broad singlet for one proton at 8.43 ppm (at −40°). These facts, together with the analytical data, the identical environment of the aromatic protons (Table I) requiring a symmetrical molecule, and the presence of a carbon–nitrogen double-bond stretching frequency at 1605 cm^{-1}, demand structure **27** for this substance.

Finally, we have made an attempt to assess the potential reactivity of **16** as a diene in the Diels–Alder reaction. Reaction of **16** in methylene dichloride with *trans*-1,2-dimethoxyethylene gave, *in the dark* at room temperature for 8 weeks, the adduct **28**. This reaction parallels, as far as product is concerned, the well-known photochemical addition of nonenolizable diketones to olefins.

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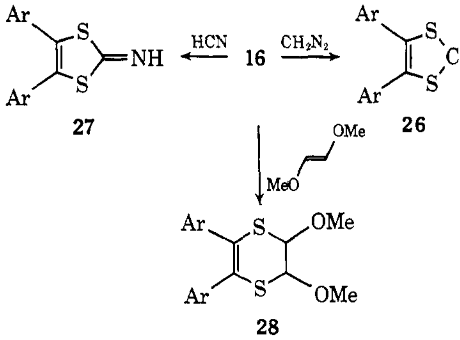
(32) S. Holm and A. Senning, *Tetrahedron Lett.*, 2389 (1973); A. P. Krapcho, D. R. Rao, M. P. Silvon, and B. Abegaz, *J. Org. Chem.*, **36**, 3885 (1971), and references cited therein.



Experimental Section

General Techniques. Melting points are uncorrected. Nuclear magnetic resonance spectra were recorded in $CDCl_3$ (unless otherwise noted) on a Varian T-60 spectrometer (unless otherwise mentioned); chemical shifts are given in δ values and TMS was used as internal standard. Mass spectra were obtained on a Varian M66 instrument. Mass peaks are reported at 70 eV followed by relative intensities. Molecular weights were determined in chloroform on a Hewlett-Packard vapor pressure osmometer, Model Mechrolab 301A. Irradiations were carried out with a 450W Hanovia high-pressure quartz-mercury vapor lamp, equipped with a double-walled immersion well. Light was filtered using Corning glass color filters as specified.

Diphenylvinylene Dithiocarbonate (6). To 24 g (0.075 mol) of $Hg(OAc)_2$ in 800 ml of glacial acetic acid was added a solution of 10 g (0.035 mol) of diphenylvinylene trithiocarbonate[17,33] in a little $CHCl_3$. After stirring overnight, 1500 ml of water was added; the precipitate was filtered and washed thoroughly with $CHCl_3$. The combined $CHCl_3$ extracts were washed with water and dried with $CaCl_2$. The solvent was evaporated and the crystalline residue crystallized twice from cyclohexane: yield 6.6 g (70%); mp 111°; colorless needles; ir (Nujol) 1700, 1642, 1448 cm^{-1}; nmr 7.12 (s); λ_{max} (C_6H_6) 312 nm (ϵ 5860); mass spectrum *m/e* 270 (100, M^+), 242 (40), 210 (19), 178 (62), 121 (90).

Anal. Calcd for $C_{15}H_{10}OS_2$: C, 66.64; H, 3.73; S, 23.72. Found: C, 66.88; H, 3.88; S, 23.96.

Irradiation of Diphenylvinylene Dithiocarbonate (6). (a) A solution of 168 mg (0.623 mmol) of **6** in 40 ml of chloroform was irradiated through Pyrex at room temperature, while a slow stream of N_2 was passed through the solution. The irradiation was stopped after 80 min and the reaction mixture worked up on silica gel by tlc (20% benzene in cyclohexane). Separation of the crude reaction mixture on silica gel (or alumina) by the tlc led to strong streaking to the solvent front. Therefore, the dithiine **8** and tolane had to be rechromatographed twice for purification. There was obtained 32–70 mg (19–42%) of **4**, identified by analysis and comparison (ir, tlc, and mixture melting point) with an authentical sample,[8] and 2–5 mg of tolane, identified by comparison (ir and tlc) with an authentic sample.

(b) A solution of 1.08 g (4 mmol) of **6** was irradiated for 1 hr through Pyrex in 35 ml of benzene and the evolved gas trapped in a burette. The gas was transferred to an ir gas cell and identified as CO by comparison of its spectrum with that of an authentical sample.

(c) A solution of 500 mg (1.85 mmol) of **6** in 30 ml of benzene was irradiated through Pyrex for 40 min, while a slow stream of N_2 was passed through the solution. The presence of COS was sought, according to the method of Brewer and Ghosh;[34] COS could not be detected.

(d) A refluxing solution of **6** (1.35 g) in 70 ml of benzene was irradiated for 100 min and the solution worked up, as described by Kirmse and Horner,[18] for the isolation of **10**. No **10** could be detected.

Irradiation of 6 in the Presence of $Mo(CO)_6$. A solution of 321 mg (1.19 mmol) of **6** and 325 mg (1.24 mmol) of $Mo(CO)_6$ in 50 ml of chloroform was irradiated for 50 min through Pyrex at room temperature, while a slow stream of N_2 was passed through the solution. The solvent was removed and the green-colored Mo complex **13** separated from the reaction mixture by preparative tlc on silica gel (20% benzene in cyclohexane): yield 30 mg (9%). The structure of **13** was proved by comparison (tlc, ir, and uv) with an authentically prepared sample.[19b]

A solution of 30 mg of **6** in 5 ml of CH_2Cl_2 and a solution of 30 mg of $Mo(CO)_6$ in 5 ml of CH_2Cl_2 were irradiated simultaneously through Pyrex under N_2 at room temperature for 25 min. The solutions were combined. No formation of **13** could be detected.

Neither upon addition of **6** to the irradiated solution of $Mo(CO)_6$ nor upon addition of $Mo(CO)_6$ to the irradiated solution of **6** could the complex **13** be detected.

Irradiation of 6 in the Presence of $Ni(CO)_4$. A solution of 175 mg (0.65 mmol) of **6** and 120 mg (0.7 mmol) of $Ni(CO)_4$ in 50 ml of benzene was irradiated under N_2 as described for $Mo(CO)_6$. The Ni complex **14** was separated by chromatography as described for **13**: yield 14 mg (8%). **14** was shown to be identical (tlc, ir, and uv) with an authentically prepared sample.[19a]

Thermal Decomposition of the Polymer from 9. The polymer (100 mg) was heated in 4 ml of decalin for 40 min at 180–190°. The decalin was distilled over a short column under reduced pressure and the residue separated on silica gel by preparative tlc (20% benzene in cyclohexane). There was obtained 6–11 mg of sulfur, 40–45 mg of tetraphenylthiophene [characterized by ir and mixture melting point), mp (from C_2H_5OH) and mmp 185–186° (lit.[35] 185°)], and 4–6 mg of tolane.

Thermal decomposition of the thermally obtained polymers from **9** and **15** gives similar results.

Thermal Decomposition of the Polymer from 9 in the Presence of $Mo(CO)_6$. The polymer (50 mg) and 55 mg of $Mo(CO)_6$ were refluxed in $CHCl_3$ for 100 hr. The reaction mixture was separated on silica gel by preparative tlc (20% benzene in cyclohexane) to give 5 mg of **13**. Similar results were obtained with the polymers from the thermal decomposition of **6** and of **15**.

4,4′-Bis(dimethylamino)benzoin Acetate (18). 4,4′-Bis(dimethylamino)desoxybenzoin (**17**)[24] (12.05 g, 0.0428 mol) and 140 ml of glacial acetic acid were placed in a 250-ml three-necked flask, fitted with a mechanical stirrer, gas inlet tube, and dropping funnel. While anhydrous HBr was slowly passed in at room temperature under stirring, **17** dissolved to give a green solution, which decolorized after some time with the formation of a white precipitate. This precipitate dissolved again on further passage of HBr. A solution of 6.83 g (0.0428 mol) of bromine in 50 ml of glacial acetic acid was then added dropwise over a period of 1.5 hr. The solution was transferred to a dropping funnel and added to 500 g of $NaHCO_3$ in 2 l. of water with vigorous stirring. The precipitate was filtered, thoroughly washed with water, and dissolved in benzene. The green-colored solution was washed with water and dried over $MgSO_4$. The benzene was evaporated and the remaining oil was dissolved with shaking in 50 ml of ethanol. After the solution was kept in the refrigerator overnight, a crystalline precipitate had been formed, which was filtered and washed with a little cold ethanol: yield 8.45 g (58%). This product was used for the next step without further purification. Crystallization from ether gave pure **18**: mp 142–143°; ir ($CHCl_3$) 1725 cm^{-1} (ester C=O); nmr 2.15 (s, 3 H), 2.95 (s, 6 H), 3.03 (s, 6 H), 6.83 (s, 1 H), 7.87 (d, 2 H, A part of AB pattern for aromatic protons in 2 position), 7.35 (d, 2 H, A′ part of A′B′ pattern for aromatic protons in 2′ position), 6.58 (d, 2 H, B or B′ part); 6.68 (d, 2 H, B or B′ part).

Anal. Calcd for $C_{20}H_{24}N_2O_3$: C, 70.57; H, 7.11; N, 8.23. Found: C, 70.44; H, 7.20; N, 7.79.

4,4′-Bis(dimethylamino)benzoin Xanthate (19). To a solution of 2 g (0.0125 mol) of potassium xanthate in 100 ml of absolute ethanol was added a solution of 2 g (0.0059 mol) of **18** in a solvent mixture of 8 ml of $CHCl_3$ and 200 ml of absolute ethanol over a period of 7 hr. After the addition the solution was stirred for another 40 hr, during which time **19** started to precipitate. The reaction mixture was evaporated to a total volume of 40 ml and the precipitate filtered and washed twice with 10 ml of absolute ethanol. Recrystallization from ethanol gave 1.05 g (44%) of **19**: mp 153–154°; ir (KBr) 1665 cm^{-1} (C=O); nmr 1.30 (t, 3 H), 2.90 (s, 6 H), 3.02 (s, 6 H), 4.55 (q, 2 H), 6.45–6.75 (m, 5 H), 7.92 (d, 2 H, A part of AB pattern for aromatic protons in 2 position), 7.30 (d, 2 H, A′ part of A′B′ pattern for aromatic protons in 2′ position).

Anal. Calcd for $C_{21}H_{26}O_2N_2S_2$: C, 62.65; H, 6.51; N, 6.96; S, 15.93. Found: C, 62.75; H, 6.75; N, 6.59; S, 16.19.

Bis(*p*-dimethylaminophenyl)vinylene Dithiocarbonate (21). To a mixture of 5 g (0.0124 mol) of **19** and 80 ml of methanol, placed in a polyethylene flask, was added 80 ml of anhydrous HF at −78°. Hydrogen sulfide was passed into the reaction medium for 250 hr,

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(33) Method of H. Behringer and D. Bender, *Chem. Ber.*, **100**, 4027 (1967).

(34) R. E. Brewer and J. K. Ghosh, *Ind. Eng. Chem.*, **41**, 2044 (1949).

(35) A. W. Chapman, *J. Chem. Soc.*, 1897 (1928).

while the temperature was allowed to become ambient. The solution was then poured with care into a stirred $NaHCO_3$ solution. If the reaction mixture was acid after the complete addition, the pH was adjusted to 7 by adding more $NaHCO_3$. The brownish precipitate was filtered, washed with water, and dissolved in benzene. This solution was washed with water and dried over $MgSO_4$. After evaporation of the benzene to a total volume of 20 ml, 50 ml of CH_3OH was added to give a precipitate of about 2.2 g of crude **21**, which contained the corresponding trithiocarbonate **20** as the main impurity. The mother liquor was worked up by column chromatography to give another 400–700 mg of impure **20** and **21**. [BDH silica gel (50 g), 60–120 mesh; eluent, benzene; **21** can easily be detected by tlc, since it gives rise to a deeply orange-colored spot upon uv irradiation on the plate.] Impure **20** and **21**, isolated by chromatography, were combined with crude **21**, obtained earlier and purified as follows. The product was dissolved in 140 ml of benzene and, portionwise, 1 g of $Hg(OAc)_2$ was added. The reaction mixture was stirred for 3 hr, the precipitate filtered and discarded, and an additional 500 mg of $Hg(OAc)_2$ added. After stirring for another 1.5 hr, the reaction mixture was filtered and the solvent evaporated. The solid residue was crystallized from benzene–methanol to give 2.1 g (47%) of pure, pale yellow **21**: mp 215–216°; ir (KBr) 1700, 1680, 1645 cm^{-1}; mass spectrum *m/e* 356 (31, M^+), 328 (7), 296 (2), 264 (68), 164 (100); λ_{max} ($CHCl_3$) 450 nm (ϵ 58, sh), 342 (14,900, sh), 298 (22,400).

Anal. Calcd for $C_{19}H_{20}ON_2S_2$: C, 64.02; H, 5.65; N, 7.86; S, 17.99. Found: C, 63.77; H, 5.57; N, 8.02; S, 17.88.

4,4′-Bis(dimethylamino)dithiobenzil (16). A solution of 100 mg (0.28 mmol) of **21** in 15 ml of benzene and 15 ml of vinyl ethyl ether was irradiated for 45 min at room temperature with light of wavelength $\lambda > 350$ nm (glass-color filter O-52), while a slow stream of N_2 was passed through the reaction medium. After keeping the irradiated solution in the refrigerator overnight, 44 mg (48%) of dark red crystals of **16** had precipitated, mp 184–185.5°. The irradiation can also be carried out in the absence of vinyl ethyl ether, but it was found that **16** crystallizes best from this solvent mixture. The dithione is stable in crystalline form and can be handled without taking any special precautions.

Anal. Calcd for $C_{18}H_{20}N_2S_2$: C, 65.70; H, 6.34; N, 8.51; S, 19.49. Found: C, 65.81; H, 6.20; N, 8.53; S, 19.52.

Bis(*p*-dimethylaminophenyl)-1,2-dithiete (22). A solution of 30 mg of **16** in 7 ml of CH_2Cl_2 was irradiated at −50° for 30 min with light of wavelength $\lambda > 500$ nm, while a slow stream of N_2 was passed through the solution. During the irradiation, the color of the solution changed from dark red to slightly red. *n*-Pentane was then added dropwise, and a slightly yellow precipitate was formed. The solvent was removed from the reaction flask and the solid residue dried by blowing N_2 through the reaction vessel at −30°.

Bis(*p*-dimethylaminophenyl)vinylene Trithiocarbonate (20). A mixture of 926 mg (0.0023 mol) of **19**, 3 g (0.0157 mol) of P_2S_5 (recrystallized from CS_2), and 50 ml of distilled decalin was heated under stirring at 155–160° for 70 min, while a stream of N_2 passed through the reaction medium. The reaction mixture was cooled to room temperature and filtered. The precipitate was added to 200 ml of $NaHCO_3$ solution, which was then extracted three times with 80 ml of $CHCl_3$. The chloroform layers were combined, washed with water, and dried over $MgSO_4$. The solvent was evaporated and the oily residue chromatographed on silica gel (BDH laboratory reagents, 60–120 mesh, eluent $CHCl_3$), and crystallization from $CHCl_3$–CH_3OH gave 51 mg (6%) of pure **20**: yellow crystals with mp 244–246°; ir (KBr) 1065, 1605 cm^{-1}; mass spectrum *m/e* 372 (100, M^+), 296 (44), 264 (37), 164 (8), no fragment corresponding to $M^+ - CS$.

Anal. Calcd for $C_{19}H_{20}N_2S_3$: C, 61.25; H, 5.41; N, 7.52; S, 25.82. Found: C, 61.01; H, 5.36; N, 7.45; S, 25.86.

Desulfurization of 20. $Hg(OAc)_2$ (150 mg, 0.47 mmol) and 40 ml of $CHCl_3$ were added to 55 mg (0.148 mmol) of **20**. The dark red reaction mixture was stirred for 50 min and filtered and the $CHCl_3$ evaporated. The remaining dark green oil was worked up by thin-layer chromatography (silica gel, $CHCl_3$) to give 20 mg (38%) of **21**, identical in every respect with the material obtained from **19** directly.

Irradiation of 21 in the Presence of Mo(Co)$_6$. A solution of 100 mg (0.281 mmol) of **21** and 100 mg (0.379 mmol) of $Mo(Co)_6$ (Alfa Inorganics) in 35 ml of benzene was irradiated through Pyrex for 65 min, while a slow stream of N_2 was passed through the solution. The solvent was evaporated and the black colored solid residue separated by tlc on silica gel (eluent, benzene). The brown and the green-colored fractions were rechromatographed under the same conditions.

Crystallization of the green fraction from $CHCl_3$–CH_3OH gave 24 mg (21%) of **23**: deeply green-colored needles; dec ~250°; ir (KBr) 1995, 1960 cm^{-1} (C═O); λ_{max} ($CHCl_3$) 750 nm (ϵ 15400), 420 (7200, sh), 310 (55,100).

Anal. Calcd for $C_{38}H_{40}O_2N_4S_4Mo$: C, 56.42; H, 4.98; N, 6.93; S, 15.85. Found: C, 56.54; H, 5.23; N, 6.90; S, 15.92.

Crystallization of the brown fraction from $CHCl_3$–benzene gave 24 mg (24%) of **24**: deeply brown-colored crystals; dec >250°; ir (KBr) 1595, 1350, 1193 cm^{-1}; λ_{max} ($CHCl_3$) 480 nm (ϵ 11,100), 318 (75,000).

Anal. Calcd for $C_{54}H_{60}N_6S_6Mo$: C, 59.98; H, 5.59; N, 7.77; S, 17.79. Found: C, 60.60; H, 5.52; N, 7.82; S, 17.90.

Reaction of 16 with Mo(Co)$_6$. (a) A solution of 1.5 mg of **16** and 1.5 mg of $Mo(Co)_6$ in 2 ml of $CHCl_3$ was irradiated through Pyrex for 12 min, while N_2 passed through the solution. Tlc ($CHCl_3$) indicated the formation of **23** and **24** in high yield. No complex formation was observed without exposing the solution to uv light. (b) A solution of 5 mg of $Mo(Co)_6$ in 5 ml of $CHCl_3$ (or benzene) was irradiated through pyrex for 8 min with the passage of N_2 through the solution. The irradiation was then stopped and 2 mg of **16** in a little $CHCl_3$ (or benzene) added. The solution turned black at once and tlc revealed the almost quantitative formation of **23**.

When a solution of 2 mg of **21** in a little $CHCl_3$ (or benzene) was added instead, no reaction was observed.

Preparation of Imine 27. Into a mixture of 44 mg (0.134 mmol) of **16** in 5 ml of CH_3CN was passed anhydrous HCN-N_2 for 20 min. After stirring the reaction mixture overnight, the solution had decolorized and a pale yellow precipitate had been formed. Removal of the solvent gave a solid residue (tlc revealed the quantitative formation of **27**) which was twice recrystallized from CH_2Cl_2–*n*-pentane: yield 20 mg (45%) of pale yellow crystals; mp 167–169°; ir (KBr) 3280 (═NH), 1605 cm^{-1}; nmr (see Table I), at −40°, 8.43 (broad singlet, 1 H); M^+ 355.

Anal. Calcd for $C_{19}H_{21}N_3S_2$: C, 64.19; H, 5.95; N, 11.82; S, 18.04. Found: C, 64.08; H, 6.00; N, 11.80; S, 17.92.

4,5-Bis(*p*-dimethylaminophenyl)-1,3-dithiole (26). To a solution of 63 mg (0.912 mmol) of **16** in 6 ml of benzene and 5 ml of CH_2Cl_2 was added an ethereal solution of diazomethane. The reaction mixture is stirred for 30 min, the solvent evaporated, and the oily residue separated by preparative tlc on silica gel (20% *n*-pentane in CH_2Cl_2). Recrystallization from CH_2Cl_2–*n*-pentane gave 50 mg of **26** (76%): mp ~180°; nmr 2.92 (s, 12 H), 4.42 (s, 2 H), 6.57 (d, 4 H, B part of AB pattern), 7.10 (d, 4 H, A part of AB pattern); mass spectrum *m/e* 342 (100, M^+), 296 (14), 264 (8).

Anal. Calcd for $C_{19}H_{22}N_2S_2$: C, 63.43; H, 6.77; N, 6.72; S, 15.39. Found: C, 63.64; H, 6.83; N, 6.84; S, 15.28.

1,2-Bis(*p*-dimethylaminophenyl)-5,6-dimethoxy-1,4-dithiine (28). A solution of 29.5 mg (0.09 mmol) of **16** and 27 mg (0.307 mmol) of *trans*-1,2-dimethoxyethylene in 10 ml of CH_2Cl_2 was kept in the dark at room temperature for 8 weeks. The solvent was evaporated and the residue separated on silical gel by preparative tlc ($CHCl_3$). After recrystallization from CH_2Cl_2–*n*-pentane, 12.5 mg of **28** (34%) was obtained: mp 232–233°; nmr 2.87 (s, 12 H), 3.60 (s, 6 H), 4.85 (s, 2 H), 6.47 (d, 4 H, B part of AB pattern), 7.03 (d, 4 H, A part of AB pattern).

Anal. Calcd for $C_{22}H_{28}N_2S_2O_2$: C, 63.43; H, 6.77; N, 6.72; S, 15.39. Found: C, 63.64; H, 6.83; N, 6.84; S, 15.28.

Kinetic and Thermodynamic Measurements. Apparatus and Materials. The uv experiments were carried out on the Cary Model 14 instrument using a spectrophotometer cell (path length approximately 0.8 cm), which could be thermostated. The Kryothermat Haake Model KT62 served as a constant temperature circulator. An iron–constantan thermocouple, equipped with a digital voltmeter, Dana Model 5330, allowed the temperature reading in the cell. (Temperature fluctuations were less than 0.2° during each experiment.) The nmr experiments were carried out on the Varian HA-100 spectrometer. For the integrations a sweep width of 5 Hz was chosen. Methylene chloride (Fisher, spectroanalyzed) was kept over molecular sieves, type 3A, for 24 hr, followed by fractional distillation through a 30-in. packed column. Only a middle fraction was used as solvent for the uv and nmr experiments.

Rate Measurements. The determination of the sum of the rate constants ($k_1 + k_{-1}$) at different temperatures was carried out as follows. The uv cell, containing a degassed CH_2Cl_2 solution of **16** (approximately 3×10^{-5} mol $l.^{-1}$), was placed into the λ_{max} spectrometer and the solution allowed to equilibrate at the particular temperature, until the optical density at 465 nm did not change more than 0.003 units within 60 min. The absorbance was noted, the cell taken out of the spectrometer, and the solution irradiated with light λ >500 nm (glass-color filter 3-69, Corning, N. Y.) for 10 min. The cell was then returned to the spectrometer as soon as possible and the absorbance at 465 nm continuously recorded by allowing the chart to move while the wavelength was set at 465 nm. This procedure could be started usually within 1 min after the irradiation had been stopped. The absorbance for the equilibrium state found after irradiation was always within 0.5% of the value, measured before irradiation.

Equilibrium Measurements. The reference temperature, T^0, chosen was 32° and X_A^0 was found to be 0.141 ± 0.006 from nmr measurements of five solutions, 0.01–0.015 *M* **16** in CH_2Cl_2. These were prepared in the dark and immediately placed in the nmr probe for equilibration. After 10–15 min a series of 6–10 integrals were run over the methyl peaks at 3.07 and 2.95 ppm. Impurities could not be detected in these solutions after this procedure. Two of these samples were irradiated at $T^1 = -60°$ with light of λ >500 nm under nitrogen until the photostationary state was reached (∼15 min); the mole fraction of dithiete, determined by nmr, was found to be (X_A^1) 0.96 ± 0.1. A solution of **16** under N_2 with an optical density of $E^0_{465} = 1.49$ at 32° showed, after irradiation at −60° with light λ >500 nm, a residual absorption of $E^1_{465} = 0.24$. (The uv spectrum, obtained after irradiation for 15 min, did not change on further irradiation for 30 min and was not changed after keeping the solution for 30 min at this temperature in the spectrometer.)

The density data for CH_2Cl_2 were taken from the literature.[36] The ratio of the molar absorptivities of **16** and **22** was thus determined as $\epsilon_r = 11.5 \pm 1.3$. It was assumed that the position of the photostationary state is not concentration dependent.

The temperature dependence of the optical density of solutions of **16** was determined as follows. Through a CH_2Cl_2 solution of **16** (∼3 × 10^{-5} mol $l.^{-1}$), placed in the uv cell mentioned above, was passed a stream of nitrogen for 30 min. The uv cell was closed and placed into the spectrometer. The optical density E_{465} at 465 nm was measured as a function of temperature. An increase of approximately 10% in E_{465} for a 20° decrease in temperature was observed. Solutions at higher temperatures reached the equilibrium state within a few minutes, while solutions at lower temperatures were allowed to equilibrate overnight. The sequence, in which the measurements were carried out, is given in Table II, along with the equilibrium constants and equilibrium concentrations for **16**.

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(36) Landoldt-Börnstein, 2. Band, 2. Teil, Bandteil a, p 199.

Photochemistry of Ketones in Solution. XXXIX. 3,4-Dimethyl-4-trichloromethyl-2,5-cyclohexadien-1-one[1a]

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Abstract: The photochemistry of the title compound **5** in a number of solvents is described and compared with that of the parent dienone **1** originally studied by Schuster and Patel. The effects on the photochemistry produced by introduction of the additional methyl group are varied and pronounced. In *tert*-butyl alcohol, both epimeric 6-methyl-6-trichloromethylbicyclo[3.1.0]hexenones (lumiketones) **7** and **8** are formed from **5**. The stereochemistry, assigned on the basis of spectral data, hydrogenation experiments, and an X-ray crystal analysis, shows the major product has the CCl_3 group in the exo orientation. It is concluded that the sole lumiketone formed from the parent dienone **1** also has an exo CCl_3 group. These results are rationalized mechanistically on the basis of a competition of steric effects, favoring an endo orientation in the intermediate and derived lumiketone of the bulkier dienone C-4 substituent (CCl_3 in these systems), and coulombic effects favoring an exo orientation of CCl_3 and other electron-rich groups. The electronic effects clearly dominate the reaction course in these systems. Other photoproducts include 2-chloro-3,4-dimethyl-4-trichloromethylcyclohex-2-en-1-one (**10**), a bicyclo[3.2.0]hexenone (**13**), 3,4-dimethylphenol (**14**), 3,5-dimethylphenol (**15**), and hydrogen chloride. Compounds **13** and **15** are formed by secondary photolyses of the initially formed lumiketones. Mechanisms for formation of all products are suggested. Noteworthy is the novel formation of **10**, which is proposed to involve trapping of zwitterion **37**, derived from **5**, by HCl generated *in situ*, a new mode of zwitterion trapping. The surprising formation of phenol **14** in good yield in benzene, *t*-BuOH, and other poor H-donor solvents, in contrast to the lack of phenol formation from **1** in such solvents, was shown in benzene to involve H abstraction not from the solvent but from ground state dienone, presumably from the allylic methyl group. Quantum yield data are presented. The triplet yield for **5** in benzene was found to be close to unity. Sensitization and quenching experiments in several solvents confirm that all products are triplet derived. As in earlier studies, quenching by 1,3-cyclohexadiene is somewhat more efficient than by *trans*-piperylene. The Stern–Volmer quenching slopes in 2-propanol for formation of lumiketone **7** decreased as dienone concentration was increased, while the slopes for formation of phenol **14** simultaneously increased. These results require two different triplets as precursors to these products, at least in 2-propanol. The triplet leading to lumiketones is suggested to be a π,π^* triplet, showing a typical self-quenching effect. The triplet which abstracts hydrogen from the solvent, leading to phenol **14**, is suggested to be the lowest n,π^* triplet. The increased quenching slopes in the latter case are tentatively attributed to trapping by ground state dienone of radicals, produced in the reaction, which could act as triplet quenchers. The "two triplet" mechanism required by the results is compared to previously proposed mechanisms in cyclohexadienone and cyclohexenone photochemistry. The broad emission of **5** at low temperature is likewise attributed tentatively to a low π,π^* triplet stabilized by the 3-methyl relative to the n,π^* triplet, which was suggested to be the lowest triplet in the case of the parent dienone **1**.

Previous papers from this laboratory have demonstrated the variety of reactions which ensue on electronic excitation of 4-methyl-4-trichloromethyl-2,5-cyclohexadienone (**1**).[2] The unusual richness of the photochemistry of this system, which is a sensitive

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(1) (a) Part XXXVII: D. I. Schuster and T. M. Weil, *J. Amer. Chem. Soc.*, **95**, 4091 (1973). (b) Address correspondence to this author at Department of Chemistry, New York University, Washington Square, New York, N. Y. 10003.

(2) D. J. Patel and D. I. Schuster, *J. Amer. Chem. Soc.*, **90**, 5137 (1968); D. I. Schuster and D. J. Patel, *ibid.*, **90**, 5145 (1968).