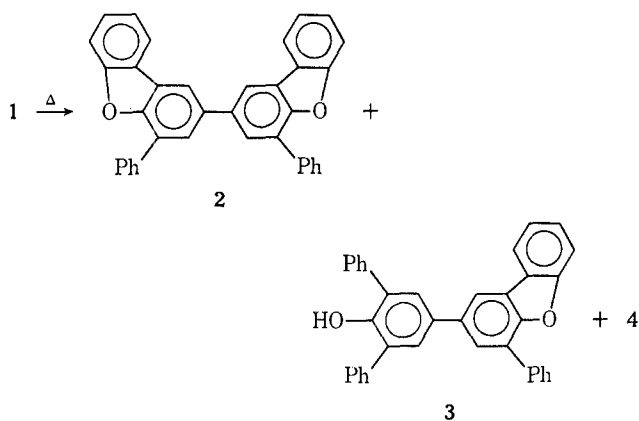
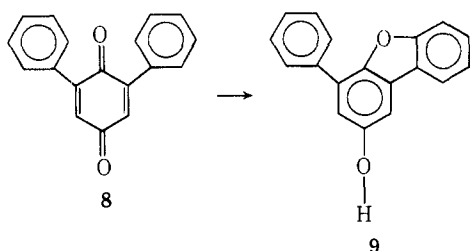


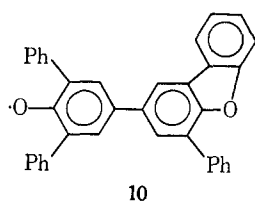
Thus it is apparent that the course of the reaction is



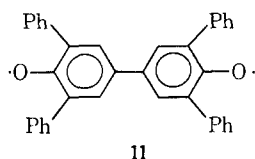
A related reaction has recently been observed. Hageman<sup>2</sup> irradiated 2,6-diphenyl-1,4-benzoquinone (**8**) in acetonitrile with ultraviolet light and isolated the dibenzofuran **9** in high yield.



Separation of the bisdibenzofuran **2** from **3** and **4** is readily accomplished by column chromatography or alternatively by crystallization from benzene. Oxidation of the mixture of **3** and **4** with oxygen in alcohol solution in the presence of a copper-amine catalyst<sup>3</sup> converts **4** to insoluble **1**. By analogy, with the oxidation of 2,4,6-triphenylphenol to the stable phenoxy radical,<sup>4</sup> the oxidation of **3** should yield **10**, and thus reduction of the filtrate from the preceding step regenerates **3**.



Dimroth<sup>5</sup> has examined the esr spectrum of **1** and observed a weak signal at room temperature. It has also been demonstrated that diphenylmethane to *s*-tetraphenylethane proceeds readily in high yield at 150°.<sup>6</sup> Hence it appears reasonable to assume that species such as **11** on the quinhydrone are



present especially at elevated temperatures. In the absence of a species to dehydrogenate, attack would occur on the pendant phenyl and subsequent aromatization by dehydrogenation would yield **2** or **3**.

### Experimental Section

**Preparation of 1.**—Oxygen was passed through a vigorously stirred solution of 50 g (0.20 mol) of 2,6-diphenylphenol and 4.0 g of copper(I) chloride in 500 ml of *n*-butyronitrile at 100° for 5 hr. The reaction mixture was cooled and filtered to yield 42 g (0.086 mol, 85% yield) of **1**, mp 290° dec. Reduction with hydrazine in hot acetic acid gave the corresponding biphenol **4**, mp 196°. *Anal.* Calcd for C<sub>36</sub>H<sub>26</sub>O<sub>2</sub>: C, 88.13; H, 5.34. Found: C, 88.30; H, 5.28.

**Thermolysis of 1.**—To a test tube was added 9.80 g (0.02 mol) of **1** which was then heated to 300° for 0.5 hr at which point the melt was light amber in color. The reaction mixture was cooled and diluted with 2 vol of benzene. The solution was chromatographed over activated alumina (column 2 in. in diameter, 12 in. long) using benzene as eluent. The first fractions obtained contained 2.56 g (0.0053 mol, 26.5% yield) of **2**, mp 231–234°. *Anal.* Calcd for C<sub>36</sub>H<sub>22</sub>O<sub>2</sub>: C, 88.86; H, 4.56; mol wt, 486. Found: C, 88.7; H, 4.7; mol wt, 495.

Elution with ethanol–benzene gave a mixture of the two products, **3** and **4**. After evaporation of the solvents, the residue was dissolved in 150 ml of ethanol. To this solution was added 0.5 g of CuCl and 2 ml of *N,N,N',N'*-tetramethylethylenediamine. Oxygen was passed through the vigorously stirred solution for 0.5 hr and then the green solid which separated was removed by filtration. The solid was dissolved in 250 ml of hot chloroform and filtered to separate copper salts, and the filtrate evaporated to yield 5.63 g (0.0115 mol, 57.5% yield) of **1**, identified by comparison with an authentic sample. The intense red-colored filtrate from the oxidation was treated with hypophosphorous acid until the red color of the reaction mixture disappeared and then flooded with water. The solid obtained was recrystallized from acetic acid to yield 1.24 g (0.0025 mol, 12.5% yield) of **3**, mp 196–198°. *Anal.* Calcd for C<sub>36</sub>H<sub>24</sub>O<sub>2</sub>: C, 88.50; H, 4.95. Found: C, 88.6; H, 5.17.

**Registry No.** —**1**, 3550-01-4; **2**, 26675-14-9; **3**, 26675-15-0; **4**, 2416-96-8.

### Intramolecular Hydrogen Bonding in $\beta$ -Amino $\alpha,\beta$ -Unsaturated Esters

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Received May 21, 1970

This note comprises studies on hydrogen bonding of 1-ethylpyrazolyl-5-aminomethylenemalononic acid diethyl ester (Ia) and of its 3-methyl derivative (Ib) utilizing nmr and ir spectroscopy. These compounds could exist as II, III, or IV, where R' is the pyrazol ring. Although nmr studies have been reported on closely related Schiff bases<sup>1</sup> and vinylogous imides,<sup>2</sup> studies on our system have not been previously reported.

\* To whom correspondence should be addressed.

(1) G. O. Dudek and E. P. Dudek, *J. Amer. Chem. Soc.*, **88**, 2407 (1966), and preceding papers of the series.

(2) D. L. Ostercamp, *J. Org. Chem.*, **30**, 1169 (1964), and references cited therein.

(2) H. J. Hageman and W. G. B. Huysmans, *Chem. Commun.*, 837 (1969).

(3) A. S. Hay, *Advan. Polym. Sci.*, **4**, 496 (1967).

(4) K. Dimroth and A. Berndt, *Angew. Chem.*, **76**, 434 (1964).

(5) K. Dimroth, W. Unbach, and K. H. Blöcher, *ibid.*, **75**, 860 (1963).

(6) A. S. Hay, *Tetrahedron Lett.*, 4241 (1965).

Results<sup>3</sup>

The infrared spectra of Ia and Ib in deuteriochloroform (CDCl<sub>3</sub>) and deuterioacetonitrile (CD<sub>3</sub>CN) are very similar. The broad weak band at 3250 cm<sup>-1</sup> is assigned to N-H stretching absorption, which was not affected by a 20-fold dilution of the concentrated CDCl<sub>3</sub> solution (0.071–0.003 *M*). No free NH stretching frequency in the 3400–3500-cm<sup>-1</sup> region was observed.

In the ir spectra of Ia and Ib, the absorptions at 1711 (CD<sub>3</sub>CN) and 1702 cm<sup>-1</sup> (CDCl<sub>3</sub>) are assigned to unassociated ester carbonyl, while the bands at 1691 (CD<sub>3</sub>CN) and 1685 cm<sup>-1</sup> (CDCl<sub>3</sub>) are assigned to associated ester carbonyl.<sup>4</sup> The difference, Δν, of 15–20 cm<sup>-1</sup> arises from participation of the C=O group in the hydrogen bonding. The absence of a large downward carbonyl shift suggests that the ionic resonance form, IV, does not contribute appreciably to the ground state.<sup>5</sup> The band at 1652 cm<sup>-1</sup> is assigned to the C=C absorption frequency, while the absorption at 1612 cm<sup>-1</sup> is assigned to NH bending (deformation) vibrations, based upon the disappearance of the latter band and the appearance, after deuteration, of a strong ND band at 1568 cm<sup>-1</sup>. From ir results, it can be concluded that Ia and Ib exist predominantly as enamine, II, stabilized in intramolecular hydrogen bonding.

Proton resonance data for Ia and Ib are listed in Table I. The spectrum of Ia in CDCl<sub>3</sub> consists of two

TABLE I  
PROTON RESONANCE DATA

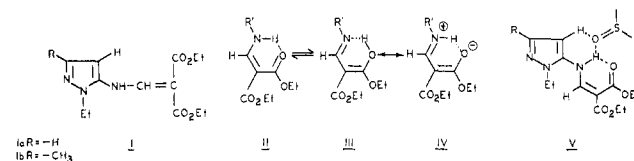
Compd	Solvent	Concn, <i>M</i>	δ, ppm			
			Ring protons 4 H <sup>a</sup>	3 R <sup>a</sup>	Vinyl H <sup>b</sup>	NH <sup>b</sup>
Ia	CDCl <sub>3</sub>	0.36	6.04	7.42	8.16	11.08
		0.14	6.05	7.42	8.17	11.07
		0.08	6.03	7.39	8.16	11.07
		0.04	6.05	7.41	8.17	11.06
	DMSO- <i>d</i> <sub>6</sub>	0.4	6.27	7.39	7.98	10.57
	CD <sub>3</sub> CN	0.3	6.10	7.32	8.29	11.65 <sup>d</sup>
	CF <sub>3</sub> COOH	0.3	6.71	8.07	8.45 <sup>e</sup>	<i>g</i>
Ib	C <sub>6</sub> D <sub>6</sub> N	0.4	6.17	7.53	8.40 <sup>f</sup>	11.27 <sup>f</sup>
		0.05	5.88 <sup>c</sup>	2.25	8.17	11.07
	CDCl <sub>3</sub>	0.4	6.05 <sup>c</sup>	2.12	7.99	10.56
		0.3	5.90 <sup>c</sup>	2.13	8.05	10.66 <sup>d</sup>
	DMSO- <i>d</i> <sub>6</sub>	0.3	5.90 <sup>c</sup>	2.13	8.05	10.66 <sup>d</sup>
		0.3	6.47 <sup>c</sup>	2.53	8.42 <sup>e</sup>	<i>g</i>
	C <sub>6</sub> D <sub>6</sub> N	0.4	5.92 <sup>c</sup>	2.27	8.38 <sup>f</sup>	11.23 <sup>f</sup>

<sup>a</sup> Doublet with *J* = 2.0 Hz; in CF<sub>3</sub>COOH, *J* = 3.0 Hz.  
<sup>b</sup> Doublet with *J* = 13.0 Hz. <sup>c</sup> Singlet when R = CH<sub>3</sub>. <sup>d</sup> Broad doublet. <sup>e</sup> Fully collapsed or very broad resonance. <sup>f</sup> Broad singlet. <sup>g</sup> Not located.

doublets at δ 6.05 and 7.42, with spin-spin coupling constant, *J* = 2.0 Hz, which are assigned to protons at carbons 4 and 3 of the pyrazol ring, respectively. In Ib, the 3-methyl resonance occurs at δ 2.25, while the C<sub>4</sub>H appears as a singlet at δ 5.88, slightly upfield of the resonance in Ia because of substitution. The doublets at δ 8.17 and 11.08 are assigned to vinyl and hydrogen-bonded NH protons, respectively. The observed spin-spin coupling of 13.0 Hz indicates a *trans* spatial ar-

angement of the CH-NH moiety.<sup>6</sup> The variation in concentration from 0.36 to 0.04 *M* had no significant effect on the proton resonance spectrum of Ia. In dilute solutions, the *trans* coupling constant (*J*<sub>NH-CH</sub>) of 13.0 Hz could still be observed, although the NH signal became somewhat broader. Dilution might be expected to influence the chemical shift of the NH proton resonance if it were intermolecularly hydrogen-bonded. In CDCl<sub>3</sub>, the enaminoic NH exchanged more slowly in the presence of D<sub>2</sub>O than in dimethyl sulfoxide-*d*<sub>6</sub> (DMSO), due to the solubility differences of D<sub>2</sub>O in the solvents. Usually, nonbonded NH protons exchange instantaneously under these conditions, which is another indication of intramolecular hydrogen bonding. Molecular models indicate a distance of *ca.* 1.5 Å for the NH-O=C bond in structure, II, which is a favorable distance for bonding.

Once it had been established that Ia and Ib exist mainly as the enamine, II, in CDCl<sub>3</sub>, the effect of other solvents on the proton resonance spectrum was studied. Of particular significance are the results in DMSO, a hydrogen-bonding solvent. The coupling constants, *J*<sub>NH-CH</sub> and *J*<sub>H,H</sub> were found to be insensitive to change of solvent. The upfield shift of 0.5 ppm in NH resonance includes about 0.2 ppm for diamagnetic anisotropic shielding, while the C<sub>4</sub>H shifted downfield by 0.2 ppm (equivalent to a total shift of 0.4 ppm). The preferred conformation of the pyrazol ring places the C<sub>4</sub>H



adjacent to the NH group. While the downfield shift of the C<sub>4</sub>H can be explained by anisotropy of DMSO, it is also possible that DMSO hydrogen bonds intermolecularly to the C<sub>4</sub>H, at the same time bonding to the NH, with the concurrent weakening of the NH-O=C hydrogen bond, as depicted in V. In CD<sub>3</sub>CN, the paramagnetic shift of 0.4 ppm of the NH indicates that the intramolecular hydrogen bond is weakened. In trifluoroacetic acid, a strong hydrogen-bonding medium, the NH proton resonance was probably obscured by the signal due to the solvent, but the broadening or collapse of the vinyl proton resonance indicates some perturbation of the NH-O=C bond.<sup>7</sup> The ring protons in Ia are shifted downfield by 0.65 ppm, with an increase in *J*<sub>H,H</sub> from 2.0 to 3.0 Hz because of protonation at nitrogen 1 and subsequent charge delocalization in the pyrazole ring. This conclusion is reinforced by the downfield shift (0.3 ppm) of the 3-methyl resonance in Ib. Finally, in pyridine, a proton acceptor base, NH and CH resonances appear as collapsed singlets with a downfield shift as a result of π-electron interaction (magnetic anisotropy) and proton exchange between NH and the solvent.

Our results confirm the observations of previous workers<sup>1,2</sup> who have shown that suitably substituted β-amino-α,β-unsaturated ketones were present as hydro-

(6) *J*<sub>NH-CH</sub> of 13.0 Hz for *trans* and of 7.5 Hz for *cis* have been reported (ref 1).

(7) The infrared spectra of Ia before and after contact with trifluoroacetic acid were identical.

(3) Nmr measurements were carried out on a Varian A-60 spectrometer using TMS as an internal reference. Perkin-Elmer Model 621 was used for ir studies. Both instruments were operated at ambient temperatures.

(4) The C=O absorption band at 1702 cm<sup>-1</sup> in CDCl<sub>3</sub> was broad, with a shoulder at 1685 cm<sup>-1</sup>, but was resolved in CD<sub>3</sub>CN into two peaks.

(5) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Wiley, New York, N. Y., 1959, Chapter 14; "Advances in Infrared Group Frequencies," Methuen, London, 1968, Chapter 8.

gen-bonded complexes of the type II at low concentrations. We have also shown the influence of various solvents on intramolecular hydrogen bonding.

**Registry No.**—Ia, 26823-99-4; Ib, 26824-00-0.

**Acknowledgment.**—We thank Dr. H. Höhn of Squibb Regensburg, Germany, for these compounds.

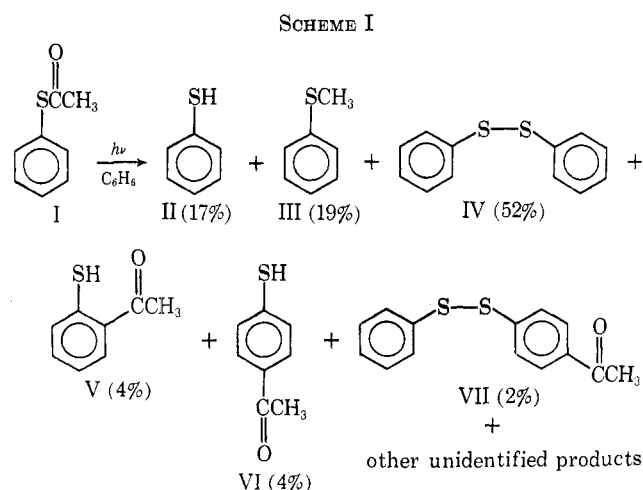
### The Ultraviolet Irradiation of S-Phenyl Thiolacetate<sup>1-3</sup>

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Received May 26, 1970

A recent communication<sup>4</sup> prompted us to report the results of our study of the ultraviolet irradiation of S-phenyl thiolacetate (I). When a 0.1 M solution of I in benzene was irradiated for 4 hr with a medium-pressure mercury lamp, the products shown in Scheme I were



produced. Approximately 40% of the starting material was recovered. The products were isolated by preparative gas chromatography and identified by ir and nmr spectroscopy.

Products II, III, and IV were identified by comparison with authentic samples. The structure assignments for the photo-Fries reaction products (V and VI) were made from their ir and nmr spectra, which we believe are definitive. The nmr peak, attributable to the S-H proton, was shifted from  $\delta$  3.40 for VI to  $\delta$  5.10 for V. This type of shift is always observed when protons, which are capable of hydrogen bonding, are ortho to carbonyl groups.<sup>5</sup> The nmr of VI also exhib-

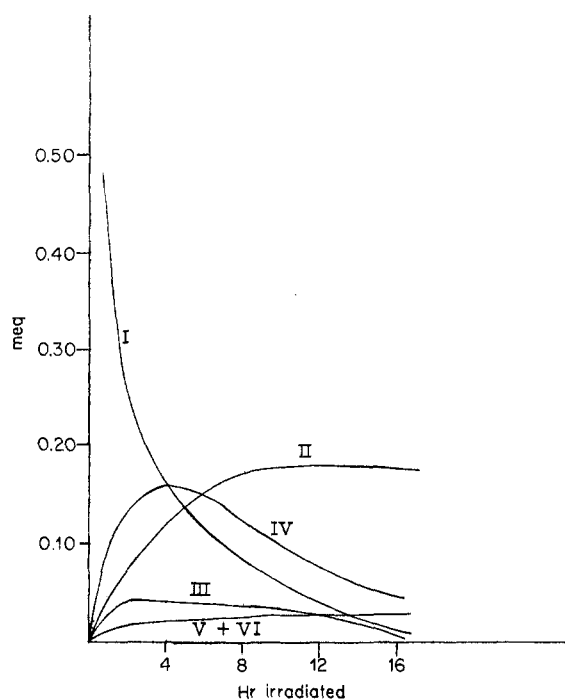


Figure 1.—0.1 M solution of S-phenyl thiolacetate in benzene.

ited a symmetrical AB pattern (really AA'XX') centered at  $\delta$  7.45. This is typical of benzene compounds which have different substituents in the para positions.<sup>6</sup> The structure assignment for compound VII is consistent with the spectral data. The ir of VII exhibited strong bands at 688 and 742  $cm^{-1}$  which are indicative of the monosubstituted benzene moiety, as well as a strong band at 890  $cm^{-1}$  which can be attributed to para-disubstituted benzene.<sup>7</sup> One of the small peaks which could not be isolated could be the ortho analog of VII.

The ratio of these products changed significantly as irradiation time was increased. As shown in Figure 1, the amount of II increased steadily while III and IV increased to a maximum at about 4 hr, then decreased in yield until the light was turned off after 16 hr. These results show that this is not a simple reaction. We feel the change in product ratios is due to secondary reactions. For example, diphenyl disulfide has been reported to form thiophenol when irradiated by ultraviolet light.<sup>8</sup> Compounds similar to thioanisole have been reported to form disulfides when irradiated.<sup>9</sup> The disulfide then would react to form thiols. We obtained thiophenol when we irradiated either thioanisole or diphenyl disulfide under our reaction conditions.

Table I gives a summary of the results of the irradiation of I in various solvents. The samples were irradiated until polymer build-up prevented further reaction. No products were observed when I was irradiated in either methyl carbitol ( $CH_3OCH_2CH_2OH$ ) or ethanol. When a solution of I in benzene was irradiated by a low-pressure mercury lamp, the products were the same but ratios were different (see Table I). Apparently thioanisole is converted to diphenyl disulfide faster than the

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(1) Supported by the Brigham Young University Research Division and the United Fund of Utah County.

(2) Nuclear magnetic resonance spectra were obtained on a Varian A-60A spectrometer purchased under the National Science Foundation Grant GP-6837.

(3) Presented at the Pacific Northwest Regional Meeting of the American Chemical Society, Salt Lake City, Utah, June 1969.

(4) J. R. Grunwell, *Chem. Commun.*, 1437 (1969).

(5) See R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," Wiley, New York, N. Y., 1967, p 122.

(6) See ref 5, p 127.

(7) See Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, San Francisco, Calif., 1962, p 26.

(8) Y. Schaafsma, A. F. Bickel, and E. Y. Kooyman, *Tetrahedron*, **10**, 76 (1960).

(9) W. Carruthers, *Nature*, **208**, 908 (1961).