

[CONTRIBUTION FROM THE CHEMICAL RESEARCH DEPARTMENT, CENTRAL RESEARCH DIVISION, AMERICAN CYANAMID CO., STAMFORD, CONN.]

## Chemistry of Dianions. II. Anion Radical and Dianion of Diethyl Azodicarboxylate

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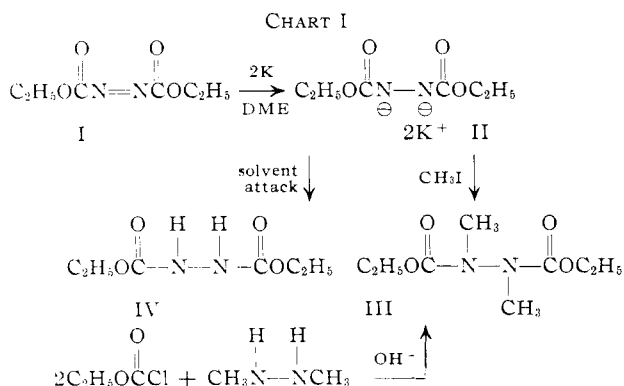
The anion radical and dianion of diethyl azodicarboxylate (I) have been prepared. Several derivatives of the dianion are reported. The e.s.r. spectrum of the anion radical has been obtained and from its hyperfine structure, the methylene proton and nitrogen coupling constants have been measured. Hückel molecular orbital calculations have been made on I and the calculated molecular orbital energies and spin densities have been compared with both the polarographic reduction potential of I and the e.s.r. of its anion radical.

### Introduction

Although alkali metal adducts of azo compounds were discovered along with the alkali metal adducts of conjugated hydrocarbons,<sup>1,2</sup> there have since been few investigations of the reactions of these substances.<sup>3,4</sup> Virtually no further attempts have been made to determine how the nature of the substituents on the azo linkage affects its metalation.<sup>5</sup> This is particularly surprising since the early work<sup>2</sup> indicates that a disodium adduct could be prepared from azomethane in diethyl ether. Since under similar conditions, a corresponding adduct cannot be prepared from butene-2, it would appear that the scope of the reaction of alkali metals with azo linkages is considerably broader than with olefins.

### Results and Discussion

**Dianion of Diethyl Azodicarboxylate.**—The reaction of diethyl azodicarboxylate with two equivalents of potassium in 1,2-dimethoxyethane (DME) gives a chocolate-brown dianion II. Treatment of II with methyl iodide gives diethyl N,N'-dimethylbicarbamate (III), identified by comparison with an authentic sample of III prepared from N,N'-dimethylhydrazine and ethyl chloroformate.<sup>6</sup> These reactions are shown in Chart I.



Reaction of II with other primary alkyl halides also gives N,N'-disubstituted diethylbicarbamates in yields up to 60%. Reaction with 1,4-dibromobutane results in the synthesis of N,N'-dicarbethoxytetrahydropyridazolidine, prepared earlier by the hydrogenation of the Diels-Alder adduct of 1,3-butadiene and I.<sup>7</sup> The compounds prepared together with their

physical properties are listed in Table I. In addition to its nucleophilic behavior, dianion II also cleaves solvent at room temperature so that if alkylation is attempted 48 hr. after preparation of II, the major product is diethyl hydrazodicarboxylate (IV); cf. Chart I. Since the ambident anions of amides give N-alkylation products under these conditions,<sup>8</sup> dianion II appears to react as a bis analog of the amide anion. A planar configuration for dianion II, with both negative charges in the same  $\pi$ -orbital, would have a considerably altered  $\pi$ -electron distribution as compared to a simple amide anion. Electrostatic repulsion in the dianion would undoubtedly demand higher charge density at the extremities of the  $\pi$ -systems (*i.e.*, on the oxygen atoms) and concomitant lower charge densities on the nitrogen atoms. Such a charge distribution pattern would be expected to result in an appreciable amount of O-alkylation, in a kinetically-controlled situation. Since O-alkylation is not observed, a reasonable explanation is simply that the dianion II assumes a nonplanar configuration to minimize the interaction of its two negative charges.

Although compound I reacted smoothly with potassium, no reaction with lithium could be detected, even using a high-speed stirring technique<sup>9</sup> which produces finely divided, highly reactive lithium.

**Anion Radical of Diethyl Azodicarboxylate.**—It was noted in some of our experiments (*cf.* Experimental section) that a transitory green color could sometimes be observed during the formation of II. Polarographic reduction of I in acetonitrile<sup>10</sup> gave a single electron reduction with a half-wave potential of  $-0.497$  v. (*vs.* s.c.e.). The lack of further reduction through  $-2.7$  v. suggests that the single electron adduct to I should be readily detectable by e.s.r.

Examination of the e.s.r. spectrum of DME solutions of the green reaction product of I with potassium in a sealed tube<sup>11</sup> at room temperature showed (*cf.* Fig. 1) a quintet of well-resolved lines with intensity ratios very nearly 1:2:3:2:1. This quintet was further split into a smaller quintet which had an intensity ratio close to 1:4:6:4:1. The larger quintet is attributed to a hyperfine interaction of the unpaired electron with two equivalent nitrogen nuclei with a measured coupling constant,  $a_N$ , of  $5.9 \pm 0.1$  gauss. The smaller quintet is ascribed to the hyperfine interaction of the unpaired electron with the four equivalent hydrogens on the methylene carbon atoms of the diethyl ester. The measured coupling constant,  $a_H$ , is  $0.9 \pm 0.1$  gauss.

(8) N. Kornblum, R. A. Smiley, R. K. Blackwood, and D. C. Iffland, *J. Am. Chem. Soc.*, **77**, 6269 (1955).

(9) H. E. Zimmermann and A. Zweig, *ibid.*, **83**, 1196 (1961).

(10) We wish to thank W. H. Jura of these laboratories for obtaining the polarographic half-wave reduction potential.

(11) The technique used in examining the reactions of various substances with alkali metals in the e.s.r. was described by A. Zweig and A. K. Hoffmann, *J. Am. Chem. Soc.*, **84**, 3278 (1962).

(1) W. Schlenk, J. Appenrodt, A. Michael, and A. Thal, *Ber.*, **47**, 473 (1914).

(2) W. Schlenk and E. Bergmann, *Ann.*, **463**, 1 (1928).

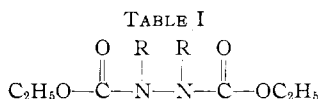
(3) J. W. B. Reesor and G. F. Wright, *J. Org. Chem.*, **22**, 375 (1957).

(4) M. V. George, D. Wittenberg, and H. Gilman, *J. Am. Chem. Soc.*, **81**, 361 (1959).

(5) G. Wittig and A. Schuhmacher, *Chem. Ber.*, **88**, 234 (1955).

(6) The preparation of III from N,N'-dimethylhydrazine was made by R. A. Hardy, Jr., and his group at Lederle Laboratories, Pearl River, N. Y. We wish to thank Dr. Hardy for supplying information and a sample for comparison.

(7) P. Baranger and J. Levisalles, *Bull. soc. chim. France*, **24**, 704 (1957).



Compound, diethyl	R	M.p. or b.p. (mm.), °C.	Analyses, %		Yield, %	$n_D^{25}$
			Calcd.	Found		
N,N'-Dimethylbicarbamate	CH <sub>3</sub> -	71-72 <sup>a</sup> (0.7)	C, 47.05 H, 7.90 N, 13.72	46.9 <sup>a</sup> 7.86 13.6	11.3	1.431
N,N'-Diethylbicarbamate	C <sub>2</sub> H <sub>5</sub> -	78-81 (0.1)	C, 51.70 H, 8.68 N, 12.06	51.77 8.21 12.30	27	1.4333
N,N'-Diallylbicarbamate <sup>c</sup>	C <sub>3</sub> H <sub>5</sub> -	92-93 (0.5)	C, 56.23 H, 7.87 N, 10.93	56.17 7.56 10.80	40	1.4539
N,N'-Dibenzylbicarbamate <sup>c</sup>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> -	70-71	C, 67.39 H, 6.79 N, 7.86	67.73 6.71 7.90	60	...
Tetrahydro-1,2-pyridazinedicarboxylate	-(CH <sub>2</sub> ) <sub>4</sub> -	102-104 (0.25)	C, 52.16 H, 7.88 N, 12.17	52.17 7.73 12.41	15	1.4632 <sup>b</sup>

<sup>a</sup> Obtained by R. A. Hardy, Jr. (private communication); cf. ref. 6. <sup>b</sup> Reported<sup>7</sup>  $n_D^{25}$  1.4642. <sup>c</sup> N.m.r. data described in Experimental section.

**Molecular Orbital Calculations.**—The relative stability of the anion radical and dianion of I and the e.s.r. spectrum of the anion radical suggests that an extended delocalized  $\pi$ -orbital system is present in I. To gain better understanding of this system, a set of Hückel m.o. (HMO)<sup>12</sup> calculations were made on the delocalized orbitals consisting of the atomic orbitals shown in Fig. 2. Each atom in the  $\pi$ -system was assumed to contribute one electron except the ether-type oxygens which were assumed to contribute two electrons each. The net result is ten electrons distributed over an eight-atom system for the neutral molecule. An eight by eight determinant written in the usual fashion<sup>12</sup> was set equal to zero. This determinant was factored into two four by fours and the eigenvalues of the residual determinants were solved by a Burroughs 204 computer using an iterative procedure.

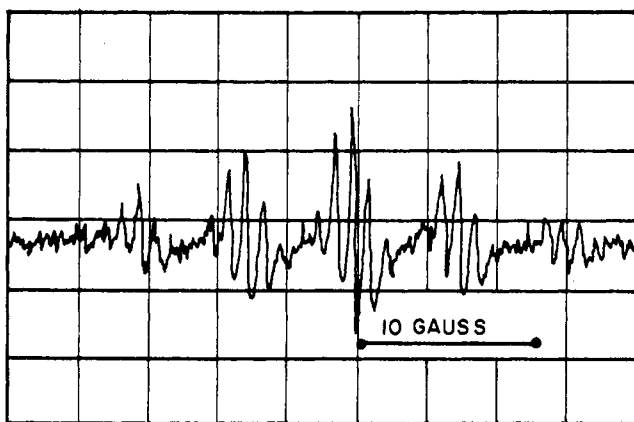


Fig. 1.—E.s.r. derivative spectrum of diethyl azodicarboxylate anion radical.

Use of the HMO method in heteroatom  $\pi$ -systems requires an appropriate choice of values for the coulomb ( $\alpha_x$ ) and exchange ( $\beta_{xy}$ ) integrals. For  $\pi$ -systems involving nitrogen and oxygen, fairly narrow ranges of these parameters have been shown to give good agreement with a wide variety of experimental results.<sup>13</sup> The hetero parameters are conveniently described in terms of the coulomb integral ( $\alpha_c$ ) and resonance in-

tegral ( $\beta_c$ ) employed for benzene and take the forms  $\alpha_x = \alpha_c + h_x\beta_c$ ,  $\beta_{xy} = k_{xy}\beta_c$ , where  $h_x$  and  $k_{xy}$  are the hetero parameters.

It has been shown<sup>14</sup> that the polarographic half-wave potential for many aromatic hydrocarbons and polyenes correlate with the coefficients of their lowest vacant molecular orbital (LVMO) calculated by the HMO method. For  $\pi$ -electron systems containing heteroatoms a correlation is also obtained, although the slope of the correlation line is sensitive to the choice of heteroatom parameters.<sup>15</sup> If it is assumed that differences in solvation do not, to an appreciable extent, affect the reduction potential of I relative to that of aromatic hydrocarbons,<sup>16</sup> then the energy of the LVMO of I on

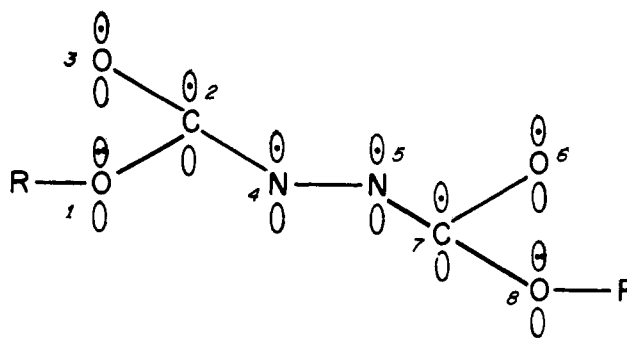


Fig. 2.—Assumed  $\pi$ -system in azodicarboxylic ester.

the hydrocarbon scale should be  $-0.18 \pm 0.05 |\beta|$ . Several sets of m.o. parameters were investigated for the  $\pi$ -system of Fig. 2. There are four types of atoms and four types of bonds that go into the secular equation and any result desired can be obtained by adjusting the parameters. We limited our selection of the integrals, in particular the coulomb integrals, to values which others have found satisfactory for the atoms involved in the same hybridization situation. Although the  $\pi$ -system is not rigidly constrained in a ring, we used established values for the resonance integrals or in some instances slightly lower values. The effect of parameter selection on the LVMO is shown in Table II. As can be seen from the table, the results that come

(14) Reference 12, chapter 7, p. 173, and references therein.

(15) P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 2795 (1962).

(16) The fact that solvent changes usually have only a small effect on polarographic reduction potentials suggests that this approximation may be permissible. Cf. P. H. Given, *J. Chem. Soc.*, 2684 (1958); M. E. Peover, *Nature*, **191**, 702 (1961).

(12) A. Streitwieser, Jr., "Molecular Orbital Theory," John Wiley and Sons, Inc., New York, N. Y., 1961.

(13) For a comprehensive review of heteroatom parameters in the HMO method, see ref. 12, chapter 5, p. 117.

TABLE II

EFFECT OF HETEROATOM PARAMETERS ON THE LOWEST UNFILLED MOLECULAR ORBITAL (LUMO) OF AZODICARBOXYLIC ESTER

M.o. parameter	Parameter values <sup>a</sup>			
	Set 1	Set 2	Set 3	Set 4
$h_O$	2.00	2.00	2.00	2.00
$h_C$	0.00	0.00	0.00	0.00
$h_O$	1.00	1.00	1.20	1.00
$h_N$	0.50	0.75	0.75	0.75
$h_{C=O}$	0.80	0.80	0.80	0.80
$k_{C=O}$	1.00	1.00	1.56	1.00
$k_{C-N}$	0.80	1.00	1.00	1.00
$k_{N=N}$	1.00	1.00	1.00	0.80
LUMO ( $\beta$ )	+0.0084	-0.2573	-0.1190	-0.3733

<sup>a</sup> Set 1 contained the "suggested" values of Streitwieser<sup>13</sup>; set 2 is modified by values for  $h_N$  and  $k_{C-N}$  suggested from e.s.r. data<sup>17</sup>; set 3 is further modified by values of  $h_O$  and  $k_{C=O}$  suggested from e.s.r. data<sup>18</sup>; set 4 examines the effect of reducing  $k_{N=N}$ .

closest to the hydrocarbon correlation value are those that use bond and core parameters obtained from e.s.r. studies.<sup>17,18</sup> A decrease of the N-N bond integral from what would be used in a ring situation sharply changes the LUMO away from the value expected from the reduction potential.

The importance of checking heteroatom parameters in molecular orbital calculations against more than one type of experimental result has previously been commented on.<sup>18</sup> In this study we have examined the polarographic reduction potential which is related to molecular orbital energy levels. On the other hand, the e.s.r. hyperfine structure is related to the spin density distribution in the lowest unfilled molecular orbital. Thus, a severe test, although not a proof, of both the parameter selections and soundness of the assumed  $\pi$ -system can be made by comparison of the observed e.s.r. spectrum of the anion radical with that predicted by the model.

When the coefficients of the molecular orbitals and the electron density distributions were calculated, they were found to be less sensitive to the parameter adjustments that had been made than were the orbital energy levels. Normalized values for the electron density distribution in the neutral molecule I and its LUMO are shown in Table III.

TABLE III

EFFECT OF HETEROATOM PARAMETERS ON UNPAIRED ELECTRON DISTRIBUTION IN THE ANION RADICAL OF I

Position	Electron distribution <sup>a</sup>			
	Set 1	Set 2	Set 3	Set 4
Nitrogen	0.2811	0.3462	0.2790	0.2978
Carbon	.0724	.0471	.0734	.0534
Carbonyl oxygen	.1312	.0981	.1351	.1359
Ethereal oxygen	.0153	.0085	.0125	.0129

<sup>a</sup> Parameter values for each set are the same as in the corresponding set in Table II.

An equation has been developed<sup>19</sup> which relates hyperfine coupling constants to the spin density on the nuclear sites involved. For the nitrogen hyperfine coupling constant in the anion-radical of I, this equation takes the form<sup>20</sup> of eq. 1, where  $S^N$  is the 1s-

$$a_N = (S^N + Q_{NN}S^N + Q_{NC}S^N)\rho_N^\pi + Q_{NN}S^N\rho_N^\pi + Q_{NC}S^N\rho_C^\pi \quad (1)$$

polarization and the contribution to the 2s-polarization arising from the unshared pair, the  $\rho^\pi$ 's are the  $\pi$ -electron spin densities on the atoms involved, and the  $Q$ 's are the  $\sigma$ - $\pi$  interaction parameters. These param-

eters are not known. However, it has been shown,<sup>15,17</sup> that an approximation to this equation, a simple proportionality of coupling constant to spin density (eq. 2), often gives reasonable agreement. For  $sp^2$ -hybridized nitrogen bonded only to carbon, the value

$$a^N = Q\rho_N^\pi \quad (2)$$

of  $Q$  was found to be  $25.3 \pm 2.3$  gauss for a series of azaaromatic anion-radicals.<sup>17</sup> If  $Q_{NN}S^N$  has a magnitude comparable to  $Q_{CN}S^N$  in eq. 1, then eq. 2 should be a satisfactory approximation for the anion-radical of I. Using  $25.3 \pm 2.3$  gauss for  $Q$  and the observed  $5.9 \pm 0.1$  gauss value for  $a^N$ ,  $\rho_N^\pi$  should be  $0.234 \pm 0.025$ . Table III shows the calculated unpaired spin densities for the various parameter sets. Parameter set 3, employing values suggested from other e.s.r. results, gives  $\rho_N^\pi = 0.279$ . Parameter set 3 also gave a value for the energy of the LUMO which was close to that suggested by the reduction potential, so that this set is the most satisfactory of those examined.<sup>21</sup>

The small methylene proton coupling constant that was experimentally obtained can be qualitatively accounted for by the small ( $\sim 1$ -2%) unpaired electron density predicted on the ether-type oxygens by all of the parameter sets studied. A rather large direct proportionality  $Q$  (as in eq. 2) is suggested here. No attempt has been made to obtain parameters for  $h_O$  and  $k_{C=O}$  which consistently fit e.s.r. data although several similar situations where hyperfine coupling involves methoxy groups are known.<sup>22,23</sup>

### Experimental<sup>24</sup>

**Materials.**—Diethyl azodicarboxylate (I) was used as received from Aldrich Chemical Co., after it was found that distillation of I gave a center cut with an infrared spectrum and index of refraction essentially identical with that of undistilled material. 1,2-Dimethoxyethane (DME) was distilled from lithium aluminum hydride immediately before use. Alkali metals were freshly cut under a petroleum solvent before use and all reactions involving alkali metals were run in flamed glassware under a positive head of ketyl-purified nitrogen.<sup>9</sup>

**Diethyl N,N'-Dimethylbicarbamate.**—In a 250-ml. heavy-wall erlenmeyer flask was placed 2.23 g. (0.0128 mole) of diethyl azodicarboxylate, 50 ml. of DME, 1.00 g. (0.0256 g.-atom) of potassium, and some glass chips. The mixture was stirred magnetically at  $-10^\circ$  and, when no reaction was apparent, was warmed to room temperature where the color of the solution turned to a chocolate brown. Stirring was continued under nitrogen for 18 hr. by which time only traces of potassium metal remained unreacted. Excess methyl iodide was added, and after further stirring for 1 hr. some barely visible slivers of unreacted potassium were removed. The DME solution was filtered and the filter cake was washed with 25 ml. of methanol. The methanol filtrate was combined with the DME solution and solvents were removed under reduced pressure. The residue was taken up in 25 ml. of water and extracted with 25 ml. of ether. Concentration of the ether extract gave 0.887 g. (11.3%) of oil with an infrared spectrum similar to that of authentic diethyl N,N'-dimethylbicarbamate<sup>6</sup> but with some extraneous absorptions. Molecular distillation at 1.0 mm. and  $80^\circ$  gave a clear, colorless liquid whose infrared spectrum was virtually superimposable with that of an authentic sample.

**Diethyl N,N'-Dibenzylbicarbamate.**—Into a 100-ml. Morton flask fitted with a nitrogen inlet, condenser, dropping funnel, and high speed (12,000 r.p.m.) stirrer was placed 2.34 g. (0.060 g.-atom) of potassium metal and 25 ml. of DME. The reaction mixture was stirred for 2 min. and the potassium cut into small slivers at room temperature. The reaction flask was then kept at  $25^\circ$  by cooling, while 5.22 g. of I in 25 ml. of DME was added to the stirred suspension of potassium over 15 min. The reaction mixture was deep brown and most of the potassium disappeared within a few minutes of completion of the addition. Stirring was continued for 1 hr. further, then 12.65 g. (0.10 mole) of benzyl

(21) Parameter sets that are fitted to several properties of the same molecule should be of broader general use than those parameter sets which are selected to obtain maximum agreement with a single physical property. Attempting to obtain precise agreements in these m.o. systems is meaningless as the methods available for determining such m.o.'s are not sufficiently accurate.

(22) H. Judeikis and D. Kivelson, *J. Am. Chem. Soc.*, **84**, 1132 (1962).

(23) Y. Matsunaga and C. A. McDowell, *Can. J. Chem.*, **38**, 1158 (1960).

(24) All melting and boiling points are uncorrected.

(17) A. Carrington and J. dos Santos-Veiga, *Mol. Phys.*, **5**, 21 (1962).

(18) G. Vincow and G. K. Fraenkel, *J. Chem. Phys.*, **34**, 1333 (1961).

(19) M. Karplus and G. Fraenkel, *ibid.*, **35**, 1312 (1961).

(20) We are thankful to a referee for pointing this out.

chloride in 20 ml. of DME was added dropwise. The mixture was moderately stirred under nitrogen at room temperature overnight, treated cautiously with about 5 ml. of methanol to ensure the complete absence of potassium, then poured into excess water and extracted with a total of 200 ml. of benzene. Concentration of the benzene solution was followed by distillation through a Vigreux column. Benzyl chloride was removed below 50°, at 0.05 mm. The pressure was lowered to 40  $\mu$  by means of an oil diffusion pump and after a forerun of 0.15 g., 6.44 g. (60%) of oil distilled at 147–155° at 36–47  $\mu$ . The oil solidified on cooling and the colorless solid melted at 70–71°. Recrystallization from hexane did not change the melting point.

The n.m.r. spectrum of the 70–71° solid in deuteriochloroform, with tetramethylsilane (TMS) as internal standard, showed phenyl ( $\sim 2.8 \tau$ ), methylene (multiplet  $\sim 5.9 \tau$ ), and methyl (triplet  $\sim 8.9 \tau$ ) protons in a ratio of 5.0:3.8:3.2; calcd. 5:4:3. An absorption, presumably due to an impurity, with a relative intensity of 0.25 was observed at 8.42  $\tau$ .

**Diethyl N,N'-Diallylbicarbamates.**—The procedure was identical to that used for the dibenzyl derivative, except that 12.1 g. (0.10 mole) of allyl bromide in 20 ml. of DME was added to the dianion solution. Work-up as before gave 3.1 g. (40%) of oil, b.p. 92–93° (0.5 mm.); n.m.r. analysis of this oil in carbon tetrachloride solution with TMS as internal standard showed vinyl (multiplet  $\sim 4.2 \tau$ ), vinylidene (multiplet  $\sim 4.9 \tau$ ), methylene (overlapping doublet and quartet  $\sim 6.0 \tau$ ), and methyl (triplet

centered at 8.8  $\tau$ ) protons in a ratio of 1.00:1.93:3.83:2.95; calcd. 1:2:4:3.

**Diethyl N,N'-Diethylbicarbamate.**—The procedure was similar to that used for the dibenzyl derivative, except that in this case the dianion was prepared from 10.44 g. (0.06 mole) of I in 30 ml. of DME added to 4.68 g. (0.12 g.-atom) of potassium in 60 ml. of DME. The color of the solution soon after the beginning of the addition was green and turned brown only after about half the addition was complete. Treatment with 20.0 g. (0.13 mole) of ethyl iodide in 20 ml. of DME gave, after work-up and distillation, 3.77 g. (27%) of oil, b.p. 78–81° (0.1 mm.).

**Diethyl Tetrahydro-1,2-pyridazinedicarboxylate.**—The procedure was the same as for the diethyl derivative except that 13.0 g. (0.06 mole) of 1,4-dibromobutane was added to the dianion. Work-up and distillation afforded 2.1 g. (15%) of colorless liquid which darkened after standing several days.<sup>7</sup>

**Electron Spin Resonance Analysis.**—The e.s.r. signal was obtained at room temperature in a sealed tube by a technique previously described.<sup>11</sup>

**Acknowledgments.**—Assistance with the computations by J. H. Lehnson is gratefully acknowledged. The authors also wish to thank W. G. Hodgson for obtaining the e.s.r. spectrum and for stimulating discussions.

[CONTRIBUTION FROM THE ESSO RESEARCH AND ENGINEERING CO., PROCESS RESEARCH DIVISION, EXPLORATORY RESEARCH SECTION LINDEN, N. J.]

## Base-Catalyzed Elimination Studies on Sulfones, Sulfoxides, Sulfides, Disulfides, and Mercaptans in Dimethyl Sulfoxide<sup>1</sup>

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Elimination studies on a large number of sulfur compounds and some compounds containing both nitrogen and oxygen functional groups have been carried out at 55° in the base-solvent system, potassium *tert*-butoxide-dimethyl sulfoxide (DMSO). The ease of elimination for a series of isopropyl derivatives was found to be  $\text{Br}^\ominus = \text{RSO}_2^\ominus = \text{RSO}^\ominus > \text{NO}_3^\ominus > \text{SCN}^\ominus > \text{RS}^\ominus > \text{NO}_2^\ominus > \text{S}^\ominus > \text{CN}^\ominus$  based on the yield of propylene. A variation in the structure of the alkyl moiety of the sulfur compounds indicated that the ease of carbanion formation follows the order  $p > \text{sec} > \text{tert}$  which is consistent with a  $\beta$ -elimination. The yields of olefinic products were markedly dependent on the solvent and size of the alkali metal cation of the *tert*-butoxide base. The rate of olefin production followed the order  $\text{Cs} > \text{Rb} > \text{K} > \text{Na} \gg \text{LiO}t\text{Bu}$ . Some novel double elimination reactions to produce butadiene were observed with tetramethylene sulfoxide and sulfide.

### Introduction

The mechanisms for the formation of olefins by 1,2-elimination of HX from  $\text{RCH}_2\text{X}$  ( $\beta$ -elimination) have been the subject of a large number of investigations.<sup>2,3</sup> Three principal mechanisms for this reaction are recognized. The E1 mechanism involves stepwise loss of HX by a carbonium ion intermediate. The E2 mechanism involves simultaneous loss of HX from  $\text{RCH}_2\text{X}$  in the presence of base. Finally, the carbanion mechanism involves initial abstraction of a proton by base to give an intermediate  $\beta$ -carbanion. Subsequent loss of  $\text{X}^\ominus$  from the  $\alpha$ -carbon atom yields the olefinic product. The last mechanism has only recently been established with any certainty.<sup>4</sup> The leaving group, X, in these reactions is usually a halogen, sulfonyl ( $\text{RSO}_2\text{O}^\ominus$ ), sulfonio ( $\text{R}_2\text{S}^\ominus$ ), or ammonio ( $\text{R}_3\text{N}^\ominus$ ) group. Some studies involving elimination of the sulfonyl group ( $\text{RSO}_2^\ominus$ ) have also been reported.<sup>5,6</sup> Until recently, little work has been reported on base-catalyzed elimination reactions involving sulfenoxyl ( $\text{RSO}^\ominus$ ),

mercapto ( $\text{RS}^\ominus$ ), and sulfhydro ( $\text{SH}^\ominus$ ) groups.<sup>7,8</sup> In addition, it should be noted that no systematic study on the base-catalyzed elimination reactions of sulfur compounds has been carried out in the past. For these reasons, the base-catalyzed elimination reactions of sulfones, sulfoxides, disulfides, sulfides, mercaptans, and some compounds containing nitrogen and oxygen functional groups have been investigated in the dipolar solvent dimethyl sulfoxide. The unusual solvating properties of this solvent for carbanion reactions have recently been reviewed.<sup>9</sup> In the present study, the scope of our base-catalyzed elimination studies in DMSO will be described. No attempts to distinguish between a bimolecular or stepwise carbanion elimination mechanism will be made in the present paper.

### Results

The base-catalyzed elimination reactions of a large number of sulfur compounds and some compounds containing both nitrogen and oxygen functional groups have been studied in the base-solvent system potassium *tert*-butoxide-dimethyl sulfoxide at 55  $\pm$  0.1°. The reaction mixtures were sampled at the desired time and the olefinic products were determined by gas chromatography according to the method outlined in

(1) This work was presented before the Petroleum Division of the American Chemical Society, 145th National Meeting, New York, N. Y., September, 1963.

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(3) J. F. Bunnett, *Angew. Chem. Intern. Ed. Engl.*, **1**, 225 (1962).

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