ylvinylsilanes absorb at lower wave length and much lower intensity than vinyl sulfides.

These facts suggest that it is misleading to refer to the radical-sulfide resonance interaction as "*d*-orbital" resonance. A 3*d* orbital must be utilized in the process but it appears likely that it must be used to hold the unshared 9th electron on the sulfur atom (B). If the double bond in (B) were indeed a 2*p*-3*d* double bond, it could be expected that silicon could participate in such interaction equally well.

The electrical factors observed for the vinylsilanes seem to be about as expected, intermediate between sulfide ($e = -1.4$)[1] and sulfone ($e = 1.2$).[1] The more positive *e*-value for the triethoxy compound could be ascribed to the electron-withdrawing inductive effect of the oxygen atoms as compared to the methyl groups of the trimethyl compound.

NOTRE DAME, IND.
PHILADELPHIA, PENNA.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENTS, UNIVERSITY OF NOTRE DAME AND UNIVERSITY OF PENNSYLVANIA]

Divinyl Sulfide: Copolymerization and Spectra

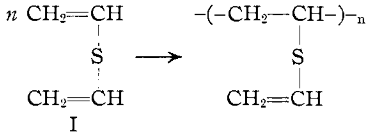
BY CHARLES E. SCOTT AND CHARLES C. PRICE

RECEIVED DECEMBER 18, 1958

Divinyl sulfide has a very intense absorption in the ultraviolet, λ_{max} 240 and 255, E_{max} 41,800 and 38,000. Earlier values are very probably those for the corresponding sulfoxide. The high degree of conjugation is reflected in the polymerization characteristics of divinyl sulfide. The material can be converted to soluble high polymer in 50% yield by azobisisobutyronitrile catalysis. Copolymerization studies indicate the resonance stabilization factor, $Q = 0.6 \pm 0.1$, to be appreciably higher than that for methyl vinyl sulfide, $Q = 0.35$.

The similarity of conjugating properties of the vinylene and sulfide groups has been emphasized by many authors.[1] The particular case of the similarity of ultraviolet spectra between divinyl sulfide and 1,3,5-hexatriene[2] has stimulated this further investigation of the conjugative properties of the former.

One example of the enhanced conjugation in divinyl sulfide (I) is the increased ease of its conversion to homopolymer, as compared to methyl vinyl sulfide. The fact that the polymer produced after 50% conversion is still soluble is itself evidence of the greater reactivity of the divinyl sulfide system than of a vinyl sulfide system. Normal vinyl polymerization of I would produce a polymer with pendant vinyl groups.



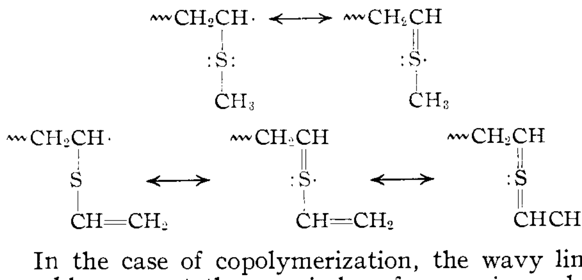
I

The presence of these pendant vinyl groups is evident from the ultraviolet spectra of copolymers of I (Table IV) and from the crosslinking and insolubilization of these polymers which occurs on standing. The fact that the polymer is not highly crosslinked initially must mean that either double bond in I is far more reactive in polymerization and copolymerization than the pendant double bond in the polymer. This in turn would be most readily explained if the two vinyl groups were mutually activated by conjugation through the sulfur atom.

This through conjugation is clearly supported by the ultraviolet spectra data on I. It is pertinent to point out that we now believe that earlier reports of the spectra of I are indeed that of its sulfoxide.[3] The data in Table IV indicate the need for great care in using solvents free of peroxide impurities capable of readily oxidizing sulfide groups to sulfoxides. Thus isopropyl vinyl sulfide showed essentially the same λ_{max} and log E_{max} in alcohol and in *freshly purified* dioxane. In dioxane which had been purified earlier and stored without exclusion of air, there was an appreciable shift of the absorption to longer wave length and lower intensity, closely resembling the sulfoxide.

The ease of oxidation of the sulfide group by peroxide is also supported by the ineffectiveness of benzoyl peroxide as a catalyst. In many monomer systems, benzoyl peroxide and azoisobutyronitrile are roughly equally effective as catalysts. In divinyl sulfide polymerizations, the former is ineffective, presumably due to its rapid destruction by reaction with the sulfide group.

Copolymerization studies of I (M_1) with methyl methacrylate and styrene lend further support to the through conjugation in I. The resonance parameter, $Q_1 = 0.6 \pm 0.1$, is considerably higher than that for methyl vinyl sulfide, $Q = 0.35$. This suggests an added degree of resonance stabilization for the intermediate free radical from I.



In the case of copolymerization, the wavy line would represent the remainder of a growing poly-

---

[1] See, *e.g.*, (a) A. D. Walsh, *Quart. Revs.*, **2**, 85 (1948); (b) C. C. Price and J. Zomlefer, THIS JOURNAL, **72**, 14 (1950); (c) M. R. Padhje and J. C. Patel, *Trans. Faraday Soc.*, **49**, 1119 (1953).

[2] C. C. Price and H. Morita, THIS JOURNAL, **75**, 4747 (1953).

[3] H. Mohler and J. Sorge, *Helv. Chim. Acta*, **23**, 1200 (1940), give λ_{max} 255 and 275, log E_{max} 3.7 and 3.75 (in hexane) as contrasted to our values of λ_{max} 240 and 255, log E_{max} 4.62 and 4.58 (in dioxane). The shift to longer wave length and lower intensity would correspond to that we observe for isopropyl vinyl sulfide and its sulfoxide (Table IV).

TABLE I

COPOLYMERIZATION OF METHYL METHACRYLATE (M_2) WITH DIVINYL SULFIDE (M_1)[a]

M_1[b]	Time, min.	Conversion, %	Softening point, °C.	S, %	C, %	H, %	m_1[c]
0.204	24	8.0	145–150	6.33	60.33	8.19	0.199
.402	30	11.0	104–110	10.57	58.75	7.91	.317
.504	22	17.0	120–130	12.47	58.94	8.56	.372
.604	25	9.9	170–178	14.31	58.49	7.09	.425
.801	20	4.9	190	20.00	57.37	7.61	.576

[a] Benzoyl peroxide catalyst. [b] Mole fraction of divinyl sulfide in monomer mixture. [c] Mole fraction of divinyl sulfide in copolymer as calculated from sulfur analysis.

TABLE II

COPOLYMERIZATION OF STYRENE (M_2) WITH DIVINYL SULFIDE (M_1)[a]

M_1[b]	Time, min.	Conversion, %	Softening point, °C.	S, %	C, %	H, %	S,[c] %	m_1[d]
0.302	67	1.0	145–150	5.73	85.86	7.77	5.78	0.182
.431	130	3.0	124–130	8.78	83.28	7.51	8.82	.273
.494	65	4.3	114–120	11.22	80.60	7.38	11.32	.346
.603	150	3.9	100–109	14.25	77.35	7.36	14.42	.433
.689	63	1.4	90–95	17.25	72.63	7.34	17.74	.524
.801	165	3.9	77–82	22.33	68.57	7.36	22.70	.654

[a] Azo-bis-isobutyronitrile catalyst. [b] Mole fraction of divinyl sulfide in monomer mixture. [c] Sulfur analysis corrected for oxygen uptake; oxygen calculated by difference. [d] Mole fraction of divinyl sulfide in copolymer calculated from sulfur analysis, corrected for oxygen uptake.

TABLE III

COPOLYMERIZATION PARAMETERS FOR DIVINYL SULFIDE (M_1)

M_2	r_2	r_1	Q_2[a]	e_2[a]	Q_1	e_1
Methylmethacrylate	0.85 ± 0.05	0.13 ± 0.05	0.74	0.40	0.48	−1.08
Styrene	1.90 ± 0.1	0.47 ± 0.05	1.00	−0.80	0.68	−1.13

[a] C. C. Price, *J. Polymer Sci.*, **3**, 772 (1948).

TABLE IV

ULTRAVIOLET ABSORPTION CHARACTERISTICS

	Solvent	Concn., moles/liter	λmax, mμ	ϵ_{max}[a]
Methyl methacrylate–divinyl[b] sulfide copolymer (%S = 12.47)	Dioxane	6.25×10^{-4b}	252	930
Methyl methacrylate–divinyl[b] sulfide copolymer (%S = 20.00)	Dioxane	1.06×10^{-5c}	254	764
Styrene–divinyl sulfide[b] copolymer (%S = 14.25)	Dioxane	1.94×10^{-4c}	254	2,080
Vinyl isopropyl sulfide	95% Ethanol	6.0×10^{-5}	230	6,000[d]
Vinyl isopropyl sulfide	Dioxane	1.23×10^{-4}	253	4,710
Vinyl isopropyl sulfide	Purified dioxane	4.7×10^{-5}	229	6,200
Vinyl isopropyl sulfoxide[e]	95% Ethanol	6.4×10^{-5}	235	2,800[f]
Vinyl isopropyl sulfoxide	Purified dioxane	7.04×10^{-5}	250	3,000
Divinyl sulfide	95% Ethanol	8.14×10^{-6}	240	41,800[g]
			255	38,000

[a] The low and variable extinction coefficient for the vinyl sulfide group in the divinyl sulfide copolymers is ascribed to the great propensity of the copolymers to crosslink, a tendency which is greatly enhanced in solution. [b] ϵ_{max} for copolymers calculated on the basis of divinyl sulfide incorporated in the copolymer. [c] Based on moles of divinyl sulfide present. [d] Price and Zomlefer[1b] report λ_{max} 230, log E_{max} 4.1 for methyl vinyl sulfide. [e] Prepared by sodium hypochlorite oxidation, n^{25}_D 1.4863, b.p. 97–98° (26 mm.). [f] Note the very considerable shift to shorter wave length in a hydrogen-bonding solvent (ethanol) *vs.* dioxane. [g] Mohler and Sorge[3] report λ_{max} 255 and 275, log E_{max} 3.7 and 3.75.

mer chain. In the case of the excited state formed by adsorption of ultraviolet light, the wavy line would represent a second "unpaired" electron (of opposite spin).

The electrical factor for divinyl sulfide, $e = -1.1$, is less negative than for methyl vinyl sulfide, $e = -1.35$.[1b] Since electron donation by sulfur, by mesomeric or by electrical effects, to either a radical or a double bond would be weakened by competition of a second electron-accepting group on the sulfur, this less negative electrical term seems reasonable for divinyl sulfide.

Experimental

Divinyl Sulfide (I).—β,β-Dibromodiethyl sulfide, m.p. 31–32°, was prepared from thiodiglycol in 82% yield.[4] Crude material obtained by the method of Burrow and Reid[5] was converted to divinyl sulfide by treatment with hot ethanolic potassium hydroxide,[6] b.p. 84.5–85.5°, n^{25}_D 1.5040, 42% yield (lit.[6] b.p. 83.5–84°, 29% yield).

β-Hydroxyethyl Isopropyl Sulfide.—To a boiling solution of 39 g. of mercaptoethanol and 28 g. of potassium hydroxide in 125 ml. of ethanol, 62.5 g. of isopropyl bromide was added during 90 minutes. The cooled reaction mixture was diluted with water and extracted with ether. The extract was washed, dried and distilled to yield 37 g. (61.5%) of **β-hydroxyethyl isopropyl sulfide**, b.p. 89° (19 mm.), n^{25}_D 1.4748.

Anal. Calcd. for $C_5H_{12}OS$: C, 49.95; H, 10.07; S, 26.67. Found: C, 49.73; H, 9.96; S, 26.67.

Isopropyl vinyl sulfide was obtained by dropping 25 g. of the alcohol above onto 10 g. of solid potassium hydroxide heated to 250–300° in a distilling flask. The distillate was washed, dried and redistilled, to yield 11.0 g. (43%), b.p. 104.5–105.5° (745 mm.), n^{25}_D 1.4632.

Anal. Calcd. for $C_5H_{10}S$: C, 58.82; H, 9.80; S, 31.37. Found: C, 58.71; H, 9.73; S, 30.86.

Polymerization of divinyl sulfide by means of benzoyl peroxide was unsuccessful, even after 16 days at 60°. Exposed to sunlight and air for 4 days, Compound I produced a foul-smelling gel. Azobisisobutyronitrile at 60° for 41 hours gave a 50% conversion to a solid white polymer soluble in carbon disulfide.

Anal. Calcd. for C_4H_6S: C, 55.81; H, 7.02; S, 37.17. Found: C, 53.86; H, 6.96; S, 35.40 (corr. for oxygen: C, 55.97; H, 7.23; S, 36.79.).

The viscosity of solutions changed so rapidly as to make it impossible to obtain significant viscosity data.

These experiments, coupled with other observations below on spectra, indicate the importance of avoiding peroxides, due to the ease with which they may oxidize the sulfide to sulfoxide.

Copolymerization of pairs of monomers was carried out at 60° in sealed, nitrogen-flushed Pyrex test-tubes containing a total of 0.08 mole of monomers and 0.00016 mole of catalyst. Polymer was isolated by pouring the contents of the tube into 200 ml. of cold methanol. The dried precipitate was dissolved in a minimum amount of benzene and filtered into filtered cold methanol. The results are listed in Tables I and II.

From the data in Tables I and II, the copolymerization ratios r_1 and r_2 were estimated by the intersection method and

---

(4) W. Steinkoff, J. Herold and J. Stohr, *Ber.*, **53B**, 1017 (1920).

(5) L. A. Burrow and E. E. Reid, THIS JOURNAL, **56**, 1720 (1934).

(6) W. Rough and H. Erickson, *ibid.*, **61**, 915 (1939).

Q and *e* were calculated.[1] The results are summarized in Table III.

Copolymerizations with methyl acrylate proceeded so vigorously and exothermically that no soluble polymers were produced.

Ultraviolet spectra were measured on a Beckmann DU spectrophotometer, as modified by Process and Instruments Co. The results are summarized in Table IV.

Notre Dame, Ind.
Philadelphia, Penna.

[Contribution from the Illinois State Geological Survey]

Aromatic Fluorine Compounds. IX. 2-Fluoropyridines[1,2]

By G. C. Finger and Laurence D. Starr

Received October 13, 1958

The synthesis of 2-fluoro-3-nitropyridine, 2-fluoro-5-nitropyridine and 3-bromo-2-fluoro-5-nitropyridine from the corresponding chloropyridines in yields exceeding 50% has been accomplished in dimethylformamide by replacement of –Cl by –F using potassium fluoride. The 3-bromine as well as the 5-nitro group activates the 2-position as shown by the increased reaction velocity of the 2-chlorine in 3-bromo-2-chloro-5-nitropyridine as compared with 2-chloro-5-nitropyridine. With 2-chloro-4-nitropyridine both groups appear to be replaced, but no 2,4-difluoropyridine could be isolated. A fluoropyridine was not isolated by reaction of potassium fluoride with 2-bromopyridine, 2-bromopyridine-N-oxide, 2-chloropyridine or 2-chloropyridine hydrochloride.

Generally, 2-fluoropyridines are obtained in low yield from aminopyridines by diazotization in hydrofluoric acid[3,4] or by the Schiemann reaction.[5] The work reported here describes the synthesis of substituted 2-fluoropyridines in good yield using the previously reported potassium fluoride exchange technique.[6]

Using this method, 2-chloro-3-nitro- and 2-chloro-5-nitropyridine when heated with potassium fluoride in dimethylformamide (DMF) gave 2-fluoro-3-nitro- and 2-fluoro-5-nitropyridine in 76 and 78% yields, respectively. When 3-bromo-2-chloro-5-nitropyridine was heated with potassium fluoride for one hour at 100°, a 50% yield of 3-bromo-2-fluoro-5-nitropyridine was isolated as the sole product. That 2-chloro-3-fluoro-5-nitropyridine could not be isolated demonstrates preferential activation of the 2-position by the 5-nitro group in this substitution. Additional activation of the 2-position by the adjacent 3-bromine is demonstrated by comparing this example to 2-chloro-5-nitropyridine which, under similar conditions, afforded only a 26% yield of 2-fluoro-5-nitropyridine with a 38% recovery of starting material. Under these conditions no reaction could be detected with 2-chloro-3-nitropyridine.

Activation by the ring nitrogen alone is insufficient, for neither 2-chloro- nor 2-bromopyridine gave 2-fluoropyridine, although with potassium fluoride the latter example gave a good silver halide test[7] in dimethyl sulfoxide (DMSO) with the evolution of dimethyl sulfide. This result alone cannot be accepted as evidence that replacement by fluorine did take place, for it has been shown that alkyl halides and DMSO may form O- or S-alkylated adducts containing ionic halogen,[8,9] and that DMSO can bring about an oxidative displacement of active halogen.[10] Indeed, we have found that when 2-bromopyridine was heated in DMSO in the absence of potassium fluoride, dimethyl sulfide was evolved and, as before, a positive silver halide test was obtained. Attempts to increase the ease of replacement of the 2-halogen by employing 2-chloropyridine hydrochloride or 2-bromopyridine-N-oxide failed.

When 2-chloro-4-nitropyridine was heated with potassium fluoride in DMF, very little chlorine was displaced and some oxides of nitrogen were evolved. In DMSO at 160° the reaction was rapid, accompanied by the formation of chloride ion and evolution of oxides of nitrogen. One possible product arising from the replacement of both the chloro and nitro groups is 2,4-difluoropyridine which could not be isolated. In the absence of potassium fluoride no chlorine was displaced. This would indicate that the failure to isolate the 4-fluoropyridine probably was due to its instability, although again the observed results may have been caused by the action of the solvent (DMSO) in the presence of potassium fluoride.

Experimental[11,12]

2-Fluoro-3-nitropyridine.[13]—To a solution of 12.3 g. of 2-chloro-3-nitropyridine[14] and 30 ml. of DMF at 120° was added 9 g. of anhydrous potassium fluoride. After 6 hours at 150° the black mixture was cooled, poured onto crushed ice, saturated with salt and subjected to steam distillation. The distillate was extracted with ether, and the combined ether extracts after drying were evaporated. The remaining yellow oil was distilled to give 8.4 g. (76% yield) of 2-fluoro-3-nitropyridine, b.p. 109–109.5° (10 mm.), $n^{25}\text{D}$ 1.5278.

Anal. Calcd. for $C_5H_3FN_2O_2$: C, 42.26; H, 2.13. Found: C, 42.34; H, 2.00.

---

[1] Published by permission of the Chief of the Illinois State Geological Survey.

[2] Presented before the Division of Organic Chemistry at the 134th Meeting of the American Chemical Society, Chicago, Ill., September 8, 1958.

[3] A. E. Chichibabin and J. G. Rjazancev, *J. Russ. Phys.-Chem. Soc.*, **47**, 1571 (1915).

[4] W. Gruber, *Can. J. Chem.*, **31**, 1020 (1953).

[5] A. Roe and G. F. Hawkins, This Journal, **69**, 2443 (1947).

[6] G. C. Finger and C. W. Kruse, *ibid.*, **78**, 6034 (1956).

[7] The course of the reaction was conveniently followed by dissolving a small portion of the reaction mixture in water and adding dilute nitric acid and silver nitrate. The precipitated silver halide indicated halogen displacement.

[8] S. G. Smith and S. Winstein, *Tetrahedron*, **3**, 317 (1958).

[9] R. Kuhn, *Angew. Chem.*, **17**, 570 (1957); R. Kuhn and H. Grischmann, *Liebig's Ann.*, **611**, 117 (1958).

[10] Kornblum, *et al.*, This Journal, **79**, 6562 (1957).

[11] All boiling points and melting points are uncorrected.

[12] Analyses by D. R. Dickerson, microanalyst for the Illinois State Geological Survey.

[13] This compound is a lachrymator and severe skin irritant.

[14] A. E. Chichibabin and I. G. Builinkin, *J. Russ. Phys.-Chem. Soc.*, **50**, 471 (1920).