TABLE I

Mannich Base	M.P.[a]	Recryst. Solvent[b]	Yield, %	Carbon[c] Calcd.	Carbon[c] Found	Hydrogen Calcd.	Hydrogen Found	Nitrogen Calcd.	Nitrogen Found
2-Dimethylaminomethyl-4-nitrophenol	168–170	A	48	55.1	55.3	6.2	6.4	14.3	14.4
2-Dimethylaminomethyl-4-nitro-6-methoxyphenol	198–200	B	76	53.1	53.3	6.2	6.2	12.4	12.4
2-Dimethylaminomethyl-4-phenyl-6-chlorophenol	75–76	C	68	69.0	69.0	6.1	5.9	5.3	5.4
2-Dimethylaminomethyl-4-phenylphenol	84.5–86	D	82	79.3	79.0	7.5	7.6	6.2	6.2
2-Nitro-4-dimethylamino-methyl-6-chlorophenol	210	B	67	46.9	46.8	4.8	4.7	12.1	11.9

[a] Melting points are uncorrected and were taken on a Mel-Temp capillary melting point apparatus. [b] Recrystallization solvent; A, water; B, not recrystallized; C, ethanol; D, hexane. [c] We are indebted to Dr. Carol Fitz of Needham, Mass., for the microanalyses.

were taken up in 15 min. The product was worked up as above to give 2.4 g. of white crystals (45%), m.p. 198–200°, reprecipitated twice from methanol–ether.

Anal. Calcd. for $C_7H_{10}ClNO$: C, 52.7; H, 6.3; Cl, 22.2; N, 8.8. Found: C, 52.4; H, 6.3; Cl, 22.0; N, 9.0.

2-Dimethylaminomethyl-4-phenylphenol. A warm solution of 7.84 g. of 2-dimethylaminomethyl-4-phenyl-6-chlorophenol in 150 ml. of 95% ethanol over 3 g. of 10% palladium–on-barium sulfate readily absorbed one equivalent of hydrogen on the Parr shaker. The solution gave a positive test for chloride ion, indicating hydrogenolysis of the chlorine. The filtered solution was evaporated to dryness *in vacuo*, the residue dissolved in water, and neutralized with sodium carbonate solution. The product that separated was filtered, dried, and crystallized from hexane to give 2-dimethylamino-4-phenylphenol (see Table I).

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Reaction of the 2-Cyano-2-propyl Radical with Elemental Sulfur

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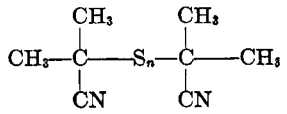
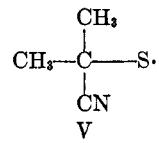
During the course of other work in this laboratory, it became desirable to know the nature and extent of the reaction between elemental sulfur and the 2-cyano-2-propyl radical derived from thermal decomposition of azobisisobutyronitrile (AIBN). The decomposition of AIBN at 80° in benzene containing dissolved sulfur gave a mixture of products I, III, and IV resolved by elution from aluminum oxide with pentane and ether. The new compound III has been characterized by elemental analysis,

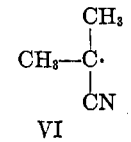


I. $n = 0$
II. $n = 1$
III. $n = 2$
IV. $n = 3$ or more

infrared absorption spectrum, and hydrolysis to the corresponding dicarboxylic acid. Compound III was also prepared for comparison by the reaction of *alpha*-chloroisobutyronitrile and sodium disulfide. The chromatogram shows there is no detectable amount of monosulfide II eluted between the I and III fractions. Zechmeister and Cholnoky have shown for several diverse types of compounds that when a homologous series of adsorbates is eluted from a chromatographic column, the order of elution is strictly that of increasing molecular complexity.[1] Therefore, the nonappearance of monosulfide II between dinitrile I and disulfide III in the chromatogram strongly suggests that none is formed in the reaction of AIBN and sulfur. We may then speculate that the monothio radical V does not exist as an intermediate in the reaction of VI and sulfur, for if it did, we should expect



V



VI

II to be formed along with I and III.[2] It has been widely noted previously that the fragments from the breakup of the S_8 ring contain sulfur in multiples of two atoms.[3]

Hammond, Sen, and Boozer[4] have studied the decomposition of 0.2*M* AIBN in solvents containing similar concentrations of 1-butanethiol. Comparison of their data with the present results indicates that elemental sulfur and 1-butanethiol are approximately equal in efficiency as scavengers for 2-cyano-2-propyl radicals. In both cases only about a 20% yield of I was formed, perhaps by reaction of primary radicals within a solvent cage.

(1) L. Zechmeister and L. Cholnoky, *Principles and Practice of Chromatography*, Wiley, New York, 1941, pp. 24–41.

(2) A system in which equal concentrations of radicals V and VI react in a random manner would give products I, II, and III in the ratio 1:2:1. Since I and III are formed in about the same yields (20% and 16%, respectively) the yield of II should be 30–40% in such a system.

(3) For example, E. H. Farmer and F. W. Shipley, *J. Chem. Soc.*, 1519 (1947); G. F. Bloomfield, *J. Soc. Chem. Ind.*, **67**, 14 (1948).

(4) G. S. Hammond, J. N. Sen, and C. E. Boozer, *J. Am. Chem. Soc.*, **77**, 3244 (1955).

In work to be described elsewhere,[5] the disulfide III has been studied as a free radical initiator and as a vulcanizing agent for natural and synthetic rubber. In contrast with AIBN, which decomposes rapidly between 60 and 100°,[6] compound III appears to be an effective radical source only above 150°.

EXPERIMENTAL[7]

Reaction of AIBN with sulfur. In a 1-l. flask fitted with an oil bath heater and a reflux condenser were placed 16.4 g. (0.100 mole) of AIBN, 25.6 g. (0.100 mole) of sulfur and 500 ml. of reagent grade benzene. Heating the mixture to reflux gave a clear yellow solution. After 2½ hours of reflux a second 16.4-g. portion of AIBN was added and reflux continued for another 16 hr. (about 14 half-lives of AIBN[6]). The reaction mixture was then freed of benzene by distillation and taken up in 150 ml. of methanol. Filtration of the methanol slurry removed 17.3 g. (67.6%) of unreacted sulfur, m.p. 116.5–117.5°. The filtrate was evaporated to dryness to give 30.2 g. of yellow crystalline solid VII, m.p. 35–115°.

Separation of products formed in reaction of AIBN and sulfur. A 3.5 × 17-cm. column was packed with 140 g. of Brockmann grade 1 activated alumina[8] and wet with 105 ml. of 5% reagent ether in reagent pentane. After washing the column with an additional 100 ml. of this solvent, 1.5 g. of VII in 30 ml. of 5% ether in pentane was introduced. The following fractions were then eluted.

Fraction	Pentane Eluent		Residue after Evaporation of Solvent, G.
	Ml.	% Ether	
a	75	5	None
b	75	5	0.05 yellow solid
c	110	5	0.05 yellow solid
d	110	10	None
e	110	10	0.005 oil
f	110	25	0.005 oil
g	110	25	0.025 white solid
h	110	25	0.025 white solid
i	110	50	0.10 white solid
j	150	50	0.10 white solid
k	150	50	0.02 white solid
l	150	50	0.02 lt. yellow oil
m	150	100	0.10 lt. yellow oil
n	150	100	0.10 lt. yellow oil
o	150	100	0.05 white solid
p	150	100	0.02 lt. yellow oil
q	150	100	0.02 lt. yellow oil
r	150	100	0.01 lt. yellow oil
s	300	100	0.01 lt. yellow oil
t	300 Methanol		0.35 yellow oil
u	100 Methanol		None

The various fractions were combined and characterized as follows: *b* and *c*, 0.10 g. (8%) of unchanged sulfur as yellow granules, m.p. 112–115°, lit. value[9] for rhombic form, 112.8°; *g* through *k*, 0.27 g. (20%) of I, tetramethylsuccinonitrile, as white plates, m.p. 158–161°, lit. value[10] 167°; *m*, *n*, *p*, and *q* were seeded by *o* to give a total of 0.31 g. (16%) of III, 2,2′-dithiobisisobutyronitrile, as white granules, m.p. 50–59°; and *r* through *t*, 0.37 g. of higher sulfides IV as yellow oil.

The remainder of the crude reaction product VII was chromatographed on a 5.7 × 100-cm. column packed to a depth of 76 cm. with 1570 g. of Brockmann grade 1 activated alumina. The 6.5 g. of crude 2,2′-dithiobisisobutyronitrile so obtained was recrystallized from 50% ether in pentane to give 5.0 g. of pure III, m.p. 63–64°.

Anal. Calcd. for $C_8H_{12}N_2S_2$: C, 47.96; H, 6.04; N, 13.98; S, 32.02. Found: C, 48.11; H, 5.85; N, 13.87; S, 32.22.

The infrared absorption spectrum of III showed peaks at 2960, 2910 and 2850 cm.$^{-1}$ (aliphatic C—H), 2220 cm.$^{-1}$ (C≡N), 1445 and 1364 cm.$^{-1}$ (aliphatic C—H), 1205 and 1155 cm.$^{-1}$ (isopropyl group), and 770 cm.$^{-1}$ (weak, disulfide).

Hydrolysis of 2,2′-dithiobisisobutyronitrile. Five grams (0.025 mole) of III was heated with stirring for four hours at 100° with 25 ml. of 75% sulfuric acid and 1 g. of sodium chloride. The reaction mixture was cooled to room temperature and poured onto 100 g. of ice. The white precipitate was separated and largely dissolved by 15 ml. of 5% sodium hydroxide. After filtration to remove a small amount of white solid, the clear solution was run into 20 ml. of 20% hydrochloric acid. The white solid was separated, dried and recrystallized from 1:1 acetone-water to give 2.0 g. (34%) of 2,2′-dithiobisisobutyric acid as white crystals, m.p. 157–158°.

Anal. Calcd. for $C_8H_{14}O_4S_2$: C, 40.32; H, 5.92; S, 26.85. Found: C, 40.58; H, 6.13; S, 26.92.

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(5) D. I. Relyea (to U. S. Rubber Co.), U. S. and foreign patents pending.

(6) F. M. Lewis and M. S. Matheson, *J. Am. Chem. Soc.*, **71**, 747 (1949).

(7) All melting points are corrected.

(8) H. Brockmann and F. Volpers, *Ber.*, **80**, 77 (1947).

(9) *Handbook of Chemistry and Physics*, 32nd ed., Chem. Rubber Publ. Co., Cleveland, 1951, p. 578.

(10) A. F. Bickel and W. A. Waters, *Rec. trav. chim.*, **69**, 1490 (1950).

Composition of Peat Humus and Its Derivatives. Oxidative Conversion to Lignin Model Compounds

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The organic chemistry of one of the most ubiquitous natural products, soil humus,[1] remains enigmatic despite its early origin. The biogenesis of humus has been attributed[2–5] to the microbial decomposition of plant and bacterial tissues in the soil. The resulting organic material contains lignin derivatives, proteins, carbohydrates, waxes, organic acids, and other unidentified compounds.

(1) A prospectus of humus research will be presented elsewhere.

(2) S. A. Waksman, *Humus*, Bailliere, Tindall and Cox, London, 1936.

(3) E. J. Russell and E. W. Russel, *Soil Conditions & Plant Growth*, 8th edition, Longmans, Green and Co., New York 1950, Chapter 15.

(4) J. M. Bremner, *J. Soil Sci.*, **5**, 214 (1952).

(5) H. Thiele and H. Kettner, *Kolloid Z.*, **130**, 1310 (1953).