

The optical rotation and ultraviolet absorption data were obtained on a chromatographically pure sample of 3'-deoxyadenosine (III), m.p. 223-225°, obtained by method B below. This sample contained more than 1/4 mole of water, as both the elemental analysis and the observed E values suggested. The observed data were $[\alpha]^{25}_D -42^\circ$ [1% (super-saturated) in water]; $\lambda_{\text{max}}^{\text{H}^1} 258$ (ϵ 13,800), $\lambda_{\text{max}}^{\text{H}^{13}} 260$ (ϵ 14,500), $\lambda_{\text{max}}^{\text{H}^{16}} 261$ (ϵ 14,400). The value in water was lower than that observed for either adenosine³⁵ or 2'-deoxyadenosine⁷ [$\lambda_{\text{max}}^{\text{H}^{16}}$ 260 (ϵ 14,900)] and indicated for that sample of III an actual molecular wt. of 260 instead of 251; there was, therefore, 0.5 mole of water per mole of 3'-deoxyadenosine in that sample.

B. From the Free 3'-Ethylthio Nucleoside (II).—A mixture of the free 3'-ethylthio nucleoside (II) and 40 g. of freshly prepared Raney nickel "C"¹⁸ (prepared by a slight modification³⁶) in 175 ml. of 2-methoxyethanol was refluxed for 6 hr. and then worked up as above to give 1.15 g. of crude product.

This crude material, 1.14 g., was stirred with 20 ml. of

(35) G. H. Beaven, E. R. Holiday and E. A. Johnson in "Nucleic Acids," Vol. I, ed. by E. Chargaff and J. M. Davidson, Academic Press, Inc., New York, N. Y., 1955, p. 510.

(36) The modification consisted of keeping the temperature below 10°, not only during the addition of the nickel alloy to the sodium hydroxide solution but also during the storage overnight and the subsequent rinsing and seemed to give a more active desulfurization catalyst.

water and 5 ml. of chloroform to give a white, crystalline precipitate, which, after filtering, water-washing (4 × 20 ml.) and drying amounted to 0.15 g. of starting material II. By paper chromatography this was found to have about 85% purity, with about 5% of product (III) and 10% of other impurities also present.

The aqueous layer and the water-washes were combined and extracted with chloroform-methanol (4:1) (4 × 50 ml.) and chloroform (4 × 25 ml.). Paper chromatography indicated that at this point the aqueous phase essentially contained only 3'-deoxyadenosine (III). Evaporation of the aqueous solution *in vacuo* gave 0.32 g. of III, m.p. 222-224°, containing about 2-3% of starting material II and no other contaminant. By infrared spectra and paper chromatographic behavior in solvent systems E (R_{Ad} 0.75), F (R_{Ad} 1.28) and G (R_{Ad} 1.14), this sample of III was shown to be identical with that obtained by Procedure A.

Evaporation of the chloroform solutions *in vacuo* gave a total of 434 mg. of a solid residue which was a mixture of 3'-deoxyadenosine (III) and starting material (II). This residue was redissolved in a known volume of 2-methoxyethanol and aliquots were removed for paper chromatography. The results indicated that this mixture consisted of about 75% 3'-deoxyadenosine (III) and 25% starting material (II).

On the basis of these results, the yield of isolated and purified 3'-deoxyadenosine (III) was 23% (corrected for unchanged starting material). The total yield of 3'-deoxyadenosine (III) including that left in the unseparated mixture was 45% (corrected for unchanged starting material).

[CONTRIBUTION NO. 657 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO., WILMINGTON 98, DEL.]

Syntheses by Free-radical Reactions. XIII. Reactions of Thiyl Radicals with Olefins

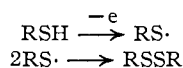
BY E. L. JENNER AND R. V. LINDSEY, JR.

RECEIVED NOVEMBER 25, 1960

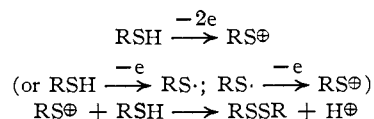
The oxidation of thiols (RSH) in the presence of butadiene (M) has been found to give a number of different types of products: RSSR, RSMH, RSMR, RSMMSR, and RSMOH. The course of the reaction depends principally on the oxidizing agent employed. Under some conditions essentially single products are obtained and the reaction can be controlled to give good yields of the additive dimers, RSMMSR. The implications of this study on the mechanism of the oxidation of thiols to disulfides are considered.

In previous studies,¹ it was found that the generation of stoichiometric quantities of free radicals (R·) in the presence of butadiene (M) gave rise to products containing two radicals combined with two molecules of butadiene, *i.e.*, R-M-M-R. Characterization of these products, called "additive dimers," proved valuable in identifying free radicals generated in reaction systems. We have now examined additive dimerizations employing thiols as free radical sources as a means of (1) synthesizing some novel dithio compounds and (2) providing some information on the mechanism of the oxidation of thiols to disulfides.

The oxidation² of a mercaptan (RSH) to a disulfide (RSSR), which can be accomplished by a variety of oxidizing agents, may involve the combination of two free radicals, *i.e.*



or may occur by an ionic reaction, *e.g.*



In the current study, thiols were oxidized in the presence of unsaturated compounds in an effort to capture and identify free-radical intermediates, if formed. The conditions employed differed from those typically used to effect the addition of thiols to olefins in that we employed oxidizing agents (or free-radical generators) in gross quantities as reactants rather than in catalytic amounts.

In most of this work butadiene was employed as olefin. Ethanethiol, thioacetic acid and mercaptoacetic acid were the thiols studied and hydroxyl radicals (Fenton reagent), ceric salts, ferric chloride, ferric nitrate and potassium ferricyanide were used as oxidizing agents.

It was found that the course of the reaction varied greatly depending principally upon the oxidizing agent employed. Thus, the oxidation of thiols (RSH) in the presence of butadiene as the unsaturated compound (M) gave several types

(1) D. D. Coffman and E. L. Jenner, *J. Am. Chem. Soc.*, **80**, 2872 (1958); D. D. Coffman and H. N. Cripps, *ibid.*, **80**, 2877 and 2880 (1958).

(2) L. Michaelis and M. P. Schubert, *Chem. Revs.*, **22**, 444 (1938); I. Pascal and D. S. Tarbell, *J. Am. Chem. Soc.*, **79**, 6015 (1957); J. J. Bohning and K. Weiss, *ibid.*, **82**, 4724 (1960).

of products: RS-SR, RS-M-H, RS-M-SR, RS-M-M-SR and RS-M-OH.

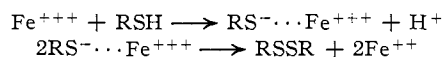
Under some conditions a single product was obtained; under others very complex mixtures were produced. For example, when mercaptoacetic acid (HSCH₂COOH) was treated with either hydroxyl radicals or ceric salt in the presence of butadiene, the product was the additive dimer HOOCCH₂S-C₄H₆-C₄H₆-SCH₂COOH. When, however, ferric nitrate, ferric chloride or potassium ferricyanide was employed, the simple disulfide HOOCCH₂SSCH₂COOH was formed exclusively even though the reaction system was saturated with butadiene. The results obtained with hydroxyl radicals and with ceric ion, evaluated in view of earlier work on additive dimerization,¹ indicate that thiyl radicals, RS·, were formed in these systems. The fact that no butadiene was incorporated with the other oxidizing agents suggests that under these conditions free thiyl radicals were not generated. Therefore, the disulfide (RSSR) must have been produced by a reaction other than the dimerization of thiyl free radicals.

When thiolacetic acid (CH₃COSH) was treated with hydroxyl radicals in the presence of butadiene, an additive dimer, *i.e.*, a diacetyl derivative of an unsaturated C₈-dithiol, was obtained. The same product resulted with ceric ion provided equimolar quantities of ceric ion and thiolacetic acid were used. When an excess of the sulfhydryl compound was used, the 1:1 adduct (butenyl thioacetate) and the 2:1 product (butenylene bis-thioacetate) were obtained in addition to the additive dimer. When ferric chloride was used with an excess of thiolacetic acid, the principal products were butenyl thioacetate and butenylene bis-thioacetate. In contrast, addition of ferric chloride to a solution of the sodium salt of thiolacetic acid in the presence of butadiene gave only acetyl disulfide.

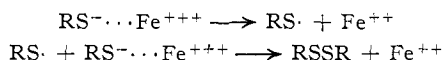
The action of ceric salt on ethanethiol in the presence of butadiene gave as the principal products the additive dimer and a hydroxy sulfide, 1-ethylthio-3-butene-2-ol. The latter contained one butadiene residue, an ethylthiyl group and a hydroxyl group. When the reaction was conducted with a large excess of ethanethiol, the 1:1 adduct, ethyl butenyl sulfide, also was formed. With ferric chloride as oxidizing agent the principal product was the 2:1 adduct corresponding to the addition of two ethylthiyl radicals to a single butadiene. When the oxidation was effected by potassium ferricyanide in an alkaline solution (*pH* > 12), the principal product was simply ethyl disulfide. A small quantity of material which may have incorporated butadiene also was formed. No reaction occurred when potassium ferricyanide was used in an acidic solution.

It will be noted that only in systems employing hydroxyl radicals or ceric ions were additive dimers obtained. This chemistry corresponds most closely to that expected from thiyl free radicals. In sharp contrast, those systems in which only the disulfide was formed and in which there was no evidence for participation of the butadiene would appear to involve reaction intermediates other than free thiyl radicals. It may be that in these cases complexes

between the thiol and the oxidizing metal ion are formed, and that these complexes react bimolecularly to form the disulfide and two reduced metal ions.

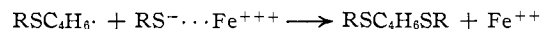
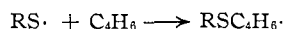


Alternatively, a stable complex of the oxidizing ion and the thiol may be present in the solution in such high concentration that as soon as a thiyl radical is formed it is scavenged by the thiol-metal ion complex so efficiently that reaction between the radical and butadiene does not occur.



A third possibility is simply that the thiyl radical reacts with a second oxidizing ion much more rapidly than it reacts with butadiene.

The preferential formation of products incorporating two thiyl radicals and one butadiene residue is difficult to account for. The formation of 2:1 products has been observed previously in addition of mercaptans to olefins³ and in radical addition reactions involving halogen atoms,⁴ aryl-oxy radicals,⁵ alkylperoxy radicals⁶ and radicals generated by electrolysis.⁷ The formation of products of this type in the current studies might result simply from the radical-radical combination of such species as RS· and RSM·. If this were the case, however, simultaneous formation of the 2:2 product, the additive dimer, would be expected. Since several of these systems, *e.g.*, the oxidation by ferric chloride of ethanethiol and of thiolacetic acid, give the 2:1 compound without producing any additive dimer, it would appear that a more highly selective reaction sequence was involved. It is possible that in these reaction systems there is a high concentration of the complex formed from the thiol and the ferric ion and that these complexes scavenge RSM· radicals as they are formed.



The formation of a hydroxy sulfide III by the action of ceric ion on ethanethiol in the presence of butadiene is of interest. This product is favored by the presence of excess ceric ion and it probably is formed by the oxidation of an intermediate radical by ceric ion. Thus, a thiyl radical may add to butadiene to give the intermediate allylic radical I. This may be oxidized by ceric ion to give the corresponding carbonium ion which is converted to the alcohol. Interestingly, the proposed carbonium ion intermediate could be stabilized by a structure possessing a three-membered sulfonium ring.

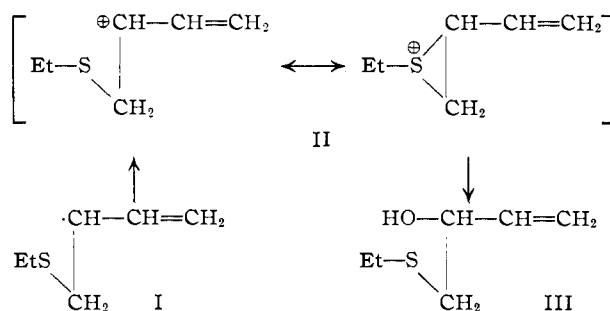
(3) C. S. Marvel and R. R. Chambers, *J. Am. Chem. Soc.*, **70**, 993 (1948).

(4) C. M. Langkammerer, E. L. Jenner, D. D. Coffman and B. W. Howk, *ibid.*, **82**, 1395 (1960).

(5) W. R. Hatchard, R. D. Lipscomb and F. W. Stacey, *ibid.*, **80**, 3636 (1958).

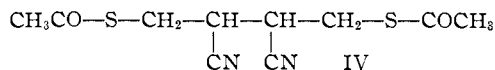
(6) M. S. Kharasch, P. Pauson and W. Nudenberg, *J. Org. Chem.*, **18**, 322 (1953).

(7) R. V. Lindsey, Jr., and M. L. Peterson, *J. Am. Chem. Soc.*, **81**, 2073 (1959).



There is considerable evidence that free radicals can be oxidized by a high-valence metal ion.⁸ Postulation of an oxidation process of this type was made in explaining the formation of amino alcohols from the action of amino radicals on olefins in systems containing vanadium salts.⁹

In addition to the studies with butadiene, the synthesis of the additive dimer from thiolacetic acid and acrylonitrile has been effected using ceric ion as an oxidizing agent. The product is the diacetate of a four-carbon dithiol bearing two cyano groups as substituents. The structural arrangement of these fragments has not been determined. By analogy with the established reactivity of acrylonitrile, the thiyl radical would attach itself to the β -carbon atom of the acrylonitrile to yield a free radical which upon dimerization would give a substituted succinonitrile IV.



Experimental

Action of Ceric Ion on Ethanethiol in the Presence of Butadiene. (a) **Excess Ethanethiol.**—A creased flask equipped with a high-speed glass propeller was charged with 2 l. of *t*-butyl alcohol and 1 l. of water. Gaseous butadiene was introduced below the surface of the liquid at a rapid rate (approx. 2 liters per minute) while 750 ml. of 0.67 *M* ceric bisulfate (0.5 mole of Ce^{4+}) and a solution of 43 g. (0.7 mole) of freshly distilled ethanethiol in 126 ml. of *t*-butyl alcohol was added. One-seventh of the ethanethiol solution was added before the addition of the ceric solution was started and thereafter the two solutions were added equivalently over a 14-minute period while a temperature of 30° was maintained. The reaction mixture was extracted three times with benzene and the benzene extracts were washed with water and dried over magnesium sulfate. The benzene was removed by distillation under reduced pressure and the product was fractionally distilled to obtain 8.0 g., b.p. 35–41° at 1 mm., n_D^{20} 1.4919; 2.8 g. of an intermediate fraction distilling at 60–98° at 1 mm., n_D^{20} 1.5022; 12.6 g. distilling at 105–140° at 1 mm., n_D^{20} 1.5185; and 3.3 g. of non-volatile residue. Steam distillation of the lowest boiling fraction gave a product, n_D^{20} 1.4915, identified as an unsaturated alcohol formed by addition of an ethylthio group and a hydroxyl group to a molecule of butadiene, *i.e.*, $\text{C}_2\text{H}_5\text{S}-\text{C}_4\text{H}_6-\text{OH}$. The infrared spectrum of the alcohol showed the presence of terminal unsaturation (10.1 and 10.8 μ), hydroxyl at 2.95 μ and the essential absence of internal unsaturation (10.35 μ). (The analysis of the fraction before steam distillation corresponded to a composition of 80% of the hydroxy sulfide and 20% of butenyl ethyl sulfide.)

Anal. Calcd. for $\text{C}_6\text{H}_{12}\text{OS}$: C, 54.60; H, 9.15; S, 24.25. Found: C, 54.66; H, 9.39; S, 24.08.

The fraction boiling at 105–140° at 1 mm. was shown by elemental analysis to be the additive dimer,¹⁰ $\text{C}_2\text{H}_5\text{S}-$

(8) E. Collinson and F. S. Dainton, *Nature*, **177**, 1224 (1956); R. M. Haines and W. A. Waters, *J. Chem. Soc.*, 4256 (1955).

(9) C. J. Albisetti, D. D. Coffman, F. W. Hoover, E. L. Jenner and W. E. Mochel, *J. Am. Chem. Soc.*, **81**, 1489 (1959).

$\text{C}_4\text{H}_6-\text{C}_4\text{H}_6-\text{SC}_2\text{H}_5$. The infrared spectrum showed terminal (10.1 and 10.8 μ) and internal (10.35 μ) unsaturation.

Anal. Calcd. for $\text{C}_{12}\text{H}_{22}\text{S}_2$: C, 62.55; H, 9.62; S, 27.83; mol. wt., 230. Found: C, 61.71; H, 9.64; S, 27.00; mol. wt., 220.

(b) **Excess Ceric Ion.**—The experiment was conducted as described above except that 0.5 mole of ethanethiol was used with 0.7 mole of Ce^{4+} . In this case one-seventh of the ceric solution was added to the reaction vessel initially and then the two solutions were added equivalently. Fractional distillation gave 17.9 g. of the alcohol, b.p. 35–41° at 1 mm., n_D^{20} 1.4909; and 10.0 g. of the additive dimer, b.p. 99–115° at 1 mm., n_D^{20} 1.5161. This is substantially the reverse of the ratio of the two products obtained in the previous run.

Action of Ceric Ion on Ethanethiol in the Absence of Butadiene.—This experiment was conducted in the apparatus described above. The flask was charged with 500 ml. of water, 325 ml. of *t*-butyl alcohol, 40 ml. of sulfuric acid and 60 ml. (50 g., 0.81 mole) of ethanethiol. The mixture was cooled to 10° and 600 ml. of 0.414 *M* ceric sulfate in aqueous sulfuric acid (0.248 mole of Ce^{4+}) was added over a 30-minute period. The reaction mixture was light yellow during the reaction period. When the ceric sulfate addition was interrupted temporarily, the yellow color in the mixture faded in approximately 10 seconds. The reaction mixture was extracted three times with 100-ml. portions of 30–60° petroleum ether and the extracts were dried over magnesium sulfate. After removal of the petroleum ether and *t*-butyl alcohol by distillation at atmospheric pressure, the product was distilled through a 12" Vigreux column to obtain 8.0 g. (49%) of ethyl disulfide, b.p. 46–47° at 18 mm., n_D^{20} 1.5042, λ_{max} 2480 ($\log \epsilon$ 2.62) (Vogel and Cowan¹¹ reported b.p. 152°, n_D^{20} 1.5070). No higher boiling (or non-volatile) products were obtained.

Action of Hydroxyl Radicals on Ethanethiol in the Absence of Butadiene.—The reaction vessel was charged initially with 500 ml. of water, 350 ml. of *t*-butyl alcohol, 40 ml. of sulfuric acid and 60 ml. (50 g., 0.81 mole) of ethanethiol. The mixture was cooled to 10° in an ice-bath and the hydroxyl radical generating solutions (A and B) were added simultaneously and equivalently over a 20-minute period: (A) 250 ml. of 1.2 *M* hydrogen peroxide (0.3 mole) and (B) 250 ml. of 1.3 molar ferrous sulfate in aqueous 1.3 *M* sulfuric acid. The reaction mixture was extracted with three 100-ml. portions of 30–60° petroleum ether and the extracts were dried over magnesium sulfate. Following distillation of the alcohol and petroleum ether at atmospheric pressure, the product was distilled through a 12" Vigreux column to obtain 16.9 g. of ethyl disulfide, b.p. 95° at 42 mm., n_D^{20} 1.5044. No higher boiling material was formed. The ethyl disulfide was obtained in 48% yield calculated on the assumption that the ferric ions produced by the hydrogen peroxide-ferrous salt reaction can also oxidize the mercaptan. If it is assumed that oxidation of the mercaptan can be effected by hydroxyl radical exclusively, the yield of disulfide becomes 95%.

Action of Ferric Chloride on Ethanethiol in the Presence of Butadiene.—As described above, solutions of ferric chloride (270 g., 1 mole, of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in 360 ml. of H_2O) and ethanethiol (62 g., 1 mole, in 420 ml. of *t*-butyl alcohol) were added simultaneously to a solution of 1500 ml. of *t*-butyl alcohol in 1000 ml. of water through which a vigorous stream of butadiene was passed. The addition required 20 minutes during which the temperature was held at 20°. The reaction mixture was extracted with benzene and the extracts were dried over magnesium sulfate and distilled to obtain, after removal of the benzene, 2.0 g., b.p. 40–49° at 2 mm., n_D^{20} 1.5035; 8.0 g., b.p. 70–78° at 2 mm., n_D^{20} 1.5161; and a 4-g. non-volatile residue. Analysis of the higher-boiling fraction, which comprised the majority of the product, indicated it to be the adduct corresponding to the addition of two ethylthio groups to a *single* butadiene molecule. The infrared spectrum of this material showed strong absorption for carbon-carbon double bonds, principally internal, and also the presence of hydroxyl-containing impurities (correlates with low sulfur analysis).

Anal. Calcd. for $\text{C}_8\text{H}_{16}\text{S}_2$: C, 54.49; H, 9.15; S, 36.36. Found: C, 54.32; H, 9.20; S, 34.23.

(10) E. L. Jenner, U. S. Patent 2,842,582, July 8, 1958.

(11) A. I. Vogel and D. M. Cowan, *J. Chem. Soc.*, 18 (1943).

Action of Alkaline Ferricyanide on Ethanethiol in the Presence of Butadiene.—The reaction was carried out by the general procedure described for the experiment employing ceric salt. Solutions containing (a) 1 mole of potassium ferricyanide and 1.5 moles of sodium hydroxide in 900 ml. of water and (b) 1 mole of ethanethiol in 420 ml. of *t*-butyl alcohol were added simultaneously to a solution of sodium hydroxide (20 g.) in 1500 ml. of *t*-butyl alcohol and 1000 ml. of water. The mixture was maintained at 30° and a rapid stream of butadiene was introduced during the 17 minutes required for the addition. The final pH of the reaction mixture was 12. The mixture was extracted with ether and the products were distilled to obtain 22 g. of product, b.p. 60° at 30 mm., n_D^{25} 1.4782, identified as ethyl disulfide by its elemental analysis and by comparison of its infrared spectrum with that of an authentic sample.

A 6-g. distillation residue was obtained which had an elemental composition suggesting the incorporation of butadiene.

Anal. Found: C, 55.79; H, 9.25; S, 30.29.

Action of Ceric Ion on Thiolacetic Acid in the Presence of Butadiene.—The reaction vessel (employed above for the studies with ethanethiol) was charged with 1500 ml. of *t*-butyl alcohol and 1000 ml. of water. The temperature was held at 30°, butadiene was introduced at a rapid rate, and solutions of ceric perchlorate (1000 ml. of a 0.5 *M* solution in 6 *M* HClO₄) and of thiolacetic acid (38 g., 0.5 mole) in *t*-butyl alcohol (460 ml.) were added simultaneously and equivalently over a 30-minute period. The reaction mixture was extracted with benzene, the extracts were dried over anhydrous magnesium sulfate, and the benzene was distilled at reduced pressure. Fractional distillation of the product yielded 38.5 g. (59% yield) of the additive dimer, the diacetyl derivative of an unsaturated 8-carbon dithiol, b.p. 136–155° at 1 mm., n_D^{25} 1.5308. The structure of the product was supported by its infrared spectrum which showed thioester at 5.9 μ and vinyl unsaturation at 10.05 and 10.85 μ .

Anal. Calcd. for C₁₂H₁₈S₂O₂: C, 55.78; H, 7.02; S, 24.82. Found: C, 55.82; H, 7.00; S, 25.09.

An experiment was conducted with a 4:1 molar ratio of thiolacetic acid to ceric ion. In contrast to the experiment just described, this technique yielded a complex mixture which apparently contained 1:1 adduct (butenyl thioacetate), 2:1 adduct (butenylene bis-thioacetate) and the additive dimer.

Action of Hydroxyl Radicals on Thiolacetic Acid in the Presence of Butadiene.—The vessel was charged initially with 1500 ml. of water, 1000 ml. of *t*-butyl alcohol and 25 ml. of sulfuric acid. Butadiene was introduced in a rapid stream and the following three solutions were added simultaneously and equivalently over a 15-minute period while the mixture was maintained at 0°: (a) 278 g. (1 mole) of ferrous sulfate heptahydrate and 55 ml. (1 mole) of sulfuric acid in 575 ml. of water; (b) 150 ml. of 6.67 *M* aqueous hydrogen peroxide (1 mole); and (c) 76 g. (1 mole) of thiolacetic acid dissolved in 80 ml. of *t*-butyl alcohol. The reaction mixture was extracted twice with ether, the combined extracts were dried with anhydrous magnesium sulfate, and the ether was distilled. The product was fractionally distilled under reduced pressure to obtain a foreshot of 24.2 g., b.p. 80–130° at ca. 1 mm., n_D^{25} 1.5120, and the additive dimer, 56.3 g., b.p. 130–145° at ca. 1 mm., n_D^{25} 1.5251–1.5302. There was a non-volatile residue of 13 g. The additive dimer, which was characterized by elemental analyses, was the same diacetyl derivative of an unsaturated 8-carbon dithiol that was obtained in the first experiment described above employing a ceric salt.

Action of Ferric Chloride on Thiolacetic Acid in the Presence of Butadiene.—The reaction vessel was charged with 1500 ml. of *t*-butyl alcohol, 1000 ml. of water and 152 g. (2 moles) of thiolacetic acid. Butadiene was introduced at a rapid rate for 30 minutes while a solution containing 0.5 mole of ferric chloride (135 g., FeCl₃·6H₂O) in 400 ml. of water was added. The addition was conducted at 30°. The mixture was extracted three times with benzene and the combined extracts were dried over anhydrous magnesium sulfate. After distillation of the benzene, the product was distilled at reduced pressure. The fractions obtained appear to be mixtures. The neutral equivalents of fractions 1 and 2 (208 and 314, respectively) indicate

Fraction	Wt., g.	°C.	B.p. Mm.	n_D^{25}	C	H	S
1	38.5	42–58	4	1.5091	46.45	6.38	32.39
2	8.3	63–104	3	1.5371	43.32	5.79	35.19
3	8.0	112–133	3	1.5528	43.40	5.80	35.13
Residue	2.0						

the presence of large quantities of thiolacetic acid and/or acetyl disulfide. The analysis of fraction 1 corresponds to an equimolar mixture of thiolacetic acid and butenyl thioacetate, the 1:1 adduct. The analytical data for fraction 2 are compatible with its being a mixture of 25% thiolacetic acid (or acetyl disulfide) and 75% bis-thioacetate, the product containing two thioacetate groups and one butadiene residue. These data establish the fact that under these conditions incorporation of the butadiene is an important process but that the products are not additive dimers.

When ferric chloride (1 mole) and an aqueous solution of the sodium salt of thiolacetic acid (1 mole) were added to an aqueous solution of *t*-butyl alcohol which was saturated with butadiene, there was no evidence of reactions involving butadiene. The sole product was acetyl disulfide, b.p. 40–47° at 1.5 mm., m.p. 18°, n_D^{25} 1.5392 (Kekule and Linnemann¹² reported m.p. 20° and Mikhailov and Blokhina¹³ reported b.p. 85–86° at 6 mm.)

Action of Hydroxyl Radicals on Thioglycolic Acid in the Presence of Butadiene.—The reaction vessel was charged with 1500 ml. of water, 1000 ml. of *t*-butyl alcohol and 25 ml. of sulfuric acid, and held at 5° while a rapid stream of butadiene was introduced. Solutions of (a) 278 g. of ferrous sulfate heptahydrate (1 mole) and 55 ml. of sulfuric acid (1 mole) in 575 ml. of water, (b) 150 ml. of 6.67 *M* hydrogen peroxide (1 mole), and (c) 92 g. (1 mole) of thioglycolic acid in 80 ml. of water were added over a 15-minute period. The color of the reaction mixture changed back and forth from blue to yellow to green as the reaction proceeded. The mixture was extracted twice with ether, and the extracts were dried over anhydrous magnesium sulfate. The ether was distilled, and the residue was taken to a temperature of 144° at a pressure of 2 mm. The additive dimer, a C₁₂-dithia diacid, obtained as a distillation residue, was a dark viscous liquid, 114 g. (79% yield). The infrared spectrum showed carboxyl hydrogen (3.3, 3.75 and 3.9 μ), carboxyl carbonyl (5.8 μ) and internal unsaturation (10.3 μ).

Anal. Calcd. for (C₄H₆SCH₂COOH)₂: C, 49.63; H, 6.25; S, 22.08; neut. equiv., 145. Found: C, 48.53; H, 6.50; S, 22.79; neut. equiv., 161.

Action of Ceric Ion on Thioglycolic Acid in the Presence of Butadiene.—The reaction vessel was charged with 1000 ml. of water, 1500 ml. of *t*-butyl alcohol and 25 ml. of sulfuric acid. The solution was held at 30–35° and a rapid stream of butadiene was introduced during the 36 minutes required for the addition of 1000 ml. of 0.39 *M* ceric sulfate. A solution of 46 g. (0.5 mole) of thioglycolic acid in 215 ml. of water was added during the first half of the addition of the ceric sulfate. The mixture was extracted twice with ether and the extracts were dried over anhydrous magnesium sulfate. Distillation to a temperature of 100° at 1 mm. left the C₁₂-dithia diacid as a dark viscous residue, 41.2 g. (71% yield).

A portion of the product was dissolved in aqueous alkali and the solution was extracted three times with ether. The aqueous alkali solution then was acidified with sulfuric acid, and the liberated acid was extracted twice with ether. The ether extract was dried and the ether distilled. The product thus purified partially crystallized upon standing.

Anal. Calcd. for (C₄H₆SCH₂COOH)₂: C, 49.63; H, 6.25; S, 22.08; neut. equiv., 145. Found: C, 51.08; H, 6.57; S, 21.71; neut. equiv., 155.

Action of Ferric Nitrate, Ferric Chloride and Potassium Ferricyanide on Thioglycolic Acid in the Presence of Butadiene.—Three experiments were conducted using the indicated oxidizing agents by the general procedures described above. In each case the system was saturated with butadiene throughout the experiment. Products were isolated by extraction followed by distillation of the ether employed as solvent. In each case the disulfide of thioglycolic acid

(12) A. Kekule and E. Linnemann, *Ann.*, **123**, 280 (1862).

(13) B. M. Mikhailov and A. N. Blokhina, *Doklady Acad. Nauk. U.S.S.R.*, **80**, 375 (1951).

was obtained and characterized by its melting point and neutral equivalent. No products incorporating butadiene were found.

Action of Ceric Ion on Thiolacetic Acid in the Presence of Acrylonitrile.—The reaction vessel was charged with 1500 ml. of water, 1000 ml. of *t*-butyl alcohol and 25 ml. of sulfuric acid. The mixture was maintained at 30° and blanketed with nitrogen during the 10-minute period in which the following three solutions were added simultaneously and equivalently: (A) 26.5 g. (0.5 mole) of acrylonitrile in 117 ml. of *t*-butyl alcohol, (B) 38 g. (0.5 mole) of thiolacetic acid in 114 ml. of *t*-butyl alcohol, and (C) 750 ml. of a solution containing 0.5 mole of ceric sulfate. The mixture was extracted four times with ether, the ex-

tracts were dried over anhydrous magnesium sulfate, and the ether was distilled to a temperature of 100° at 1 mm. The additive dimer, a diacetyl derivative of a four-carbon dicyanodithiol, was obtained as a dark viscous residue, 40.5 g. (62% yield).

Anal. Calcd. for C₁₀H₁₂S₂O₂N₂: C, 46.85; H, 4.72; S, 25.01; N, 10.93. Found: C, 46.03; H, 5.18; S, 25.23; N, 9.95.

Upon standing, this product partially crystallized. The mixture of crystals and liquid was treated with cold methanol to leave a white crystalline product, m.p. 116–118°.

Anal. Found: C, 47.21; H, 4.89; S, 24.97; N, 10.82; mol. wt., 270 (calcd. mol. wt., 256).

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

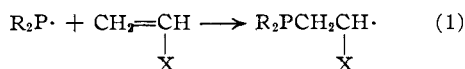
Reversibility in the Reaction of Phosphinyl Radicals with Olefins

By JOSEPH PELLON

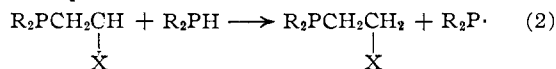
RECEIVED DECEMBER 2, 1960

cis-Butene-2 is isomerized to *trans*-butene-2 during the course of the reaction of the *cis*-butene with various phosphines [C₆H₅PH₂, (C₄H₉)₂PH, CNCH₂CH₂PH₂] in the presence of a free radical initiator. The reversibility of a phosphinyl radical addition to a double bond is thereby demonstrated. The similarity between phosphines and thiols in terms of radical initiated addition to olefins is discussed.

The free radical addition of phosphines to olefins is presumed to involve the propagating reactions of addition



and displacement



A previous study in these laboratories¹ dealt with structural effects in the displacement step (2) and indicated a close similarity between phosphines and thiols in the hydrogen abstraction reaction. It has been shown by Sivertz, *et al.*,² that the addition step indicated in reaction 1 can be reversible when thiyl radicals are involved. Reversible thiyl radical addition was also demonstrated recently by Walling and Heimreich³ by the isomerization of *cis*- or *trans*-butene-2 during the reaction. This paper describes a similar investigation of phosphinyl radicals.

Experimental

Phenylphosphine and 2-cyanoethylphosphine were available in these laboratories,⁴ while di-*n*-butylphosphine was kindly supplied by Westvaco. All were fractionally distilled and a center cut used in this study. Phillips 66 research grade *cis*- and *trans*-butene-2, Nujol (Plough Inc.) and Eastman Kodak Co. azobisisobutyronitrile (AIBN) were used as received.

The reactions were carried out in 20-ml. capacity glass vials having constricted necks for sealing. Measured amounts of AIBN, Nujol and the phosphine (under N₂) were placed in a number of vials which were then immersed in liquid nitrogen while the *cis*-butene-2 (at 0°) was distilled into each vial. The samples, which were then deaerated

by the usual cycle of freezing, evacuating and thawing, were sealed under vacuum and placed in a constant temperature bath at 70°. At a given interval each sample was removed from the bath, butene-2 was isolated and measured volumetrically, and the *cis* to *trans* ratio of the isolated butene-2 determined by infrared analysis. The procedure used in the isolation and the analysis is given below.

On removal from the constant temperature bath, the sample was frozen by immersing it in liquid nitrogen. The vial was then opened and attached to a distillation train. The receiver, consisting of a 10-ml. graduated cold trap, and a second protective cold trap were immersed in liquid nitrogen. Butene-2 was distilled from the sample vial to the graduated receiver in two stages. In the first stage the system was kept at 160 mm. pressure while the sample was allowed to warm up at its own rate (from the temperature of liquid nitrogen) for 10 minutes. Following this the pressure was reduced to 90 mm. and the sample was shaken and warmed gently with the hands until the evolution of butene-2 had ceased. In some cases traces of butene-2 were isolated in a second cold trap. This material was distilled back into the graduated receiver. After recording the volume (at 0°) of butene-2 isolated, 40 mm. of this sample was introduced into an infrared gas cell.

Analysis of the *cis* and *trans* content in the butene-2 sample was made from absorbance measurements⁵ at 675 (*cis*) and 962 cm.⁻¹ (*trans*) on a Beckman IR-4 spectrometer using a calibration curve. A NaCl window, 100-mm. path length gas cell was used. The evacuated cell showed no absorption.

Results and Discussion

By analogy to the thiol system³ the expected scheme for the free radical initiated reaction between *cis*- and *trans*-butene-2 and a phosphine can be written as shown in the equilibrium diagram, where k_{a1} and k_{-a1} , k_{a2} k_{-a2} are rate constants referring, respectively, to the reversible addition of the phosphinyl radical to *cis*- or *trans*-butene-2; (C·) is the composite radical resulting from the addition process, having lost its geometric singularity by rapid equilibration; and k_d the rate constant for the displacement reaction of the composite radical with the phosphine to give the propagating phosphinyl radical and the product. According to

(5) W. F. Anderson, J. A. Bell, J. M. Diamond and K. R. Wilson, *ibid.*, **80**, 2384 (1958).

(1) J. Pellon, *J. Polymer Sci.*, **43**, 537 (1960).

(2) C. Sivertz, W. Andrews, W. Elsdon and K. Graham, *ibid.*, **19**, 587 (1956).

(3) C. Walling and W. Heimreich, *J. Am. Chem. Soc.*, **81**, 1144 (1959).

(4) M. M. Rauhut, I. Hechenblekner, H. A. Currier, F. C. Schaefer and V. P. Wystrach, *ibid.*, **81**, 1103 (1959).