added, with stirring, 2.45 g. (9.63 mmoles) of phenylacetic anhydride[5] in 5.0 ml. of benzene. The temperature rose slightly during the addition and the solution was then refluxed for 1 hr., cooled, and extracted with 5% aqueous KOH. The benzene layer was washed with water, dried, and evaporated, leaving 537 mg. (34%) of a viscous yellow oil which solidified upon chilling: λ_{max}^{KBr} 2.94 and 6.08 μ. A t.l.c. plate showed two spots, the larger one due to **3** having the higher R_f value, and the smaller having the same R_f as **2**.

1-Methyl-1-phenylacetyl-*p*-nitrobenzalhydrazone (4).—To a solution of 78 mg. (0.48 mmole) of 1-methyl-1-phenylacetyl-hydrazine in 0.3 ml. of ethanol was added a solution of 76 mg. (0.50 mmole) of *p*-nitrobenzaldehyde in 0.5 ml. of ethanol. The solution was refluxed for 10 min. on a steam bath. Upon cooling a precipitate separated which was filtered and washed with ethanol, yielding 96 mg. (68%) of **4**, m.p. 171–172°. Recrystallization from acetone–ethanol gave pale yellow needles: m.p. 172–173°; λ_{max}^{KBr} 5.94, 6.33, and 6.63 μ.

Anal. Calcd. for $C_{16}H_{15}N_3O_3$ (297.30): C, 64.63; H, 5.09; N, 14.14. Found: C, 64.61; H, 5.09; N, 14.17.

1-Methyl-1,2-diphenylacetylhydrazine (5).—To a stirred solution of 866 mg. (18.8 mmoles) of methylhydrazine in 1.6 ml. of water at 10° was added 2.90 g. (18.8 mmoles) of phenylacetyl chloride followed by a solution of 1.29 g. of K_2CO_3 in 1.5 ml. of water. After 1 hr. the mixture was extracted three times with ethyl acetate and the ethyl acetate solution was dried and evaporated to a pale yellow oil, which crystallized after standing for 3 days; 1.35 g. (49%), of white crystals, m.p. 75–83°, was obtained. Recrystallization from ethanol–ether gave white crystals: m.p. 85–86°; λ_{max}^{KBr} 3.02 and 5.94 μ; n.m.r., 182 (s, 3) 208 (s, 2), 212 (s, 2), 437 (multiplet, 10), and 467 c.p.s. (1, exchangeable with D_2O in presence of acid).

Anal. Calcd. for $C_{17}H_{18}N_2O_2$: C, 72.32; H, 6.43. Found: C, 72.46; H, 6.60.

Treatment of crude **3** with phenylacetyl chloride under similar conditions gave **5** in 79% yield.

(5) I. M. Heilbron, D. H. Hey, and B. Lythgoe, *J. Chem. Soc.*, 297 (1936).

The Structure of Alloocimene Dioxide[1]

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In 1950, Desalbres[2] described a product, $C_{10}H_{16}O_2$, obtained from the spontaneous depolymerization of the insoluble gummy product resulting from autoxidation of alloocimene (I). This work was repeated in 1953 by

Fig. 1.—N.m.r. spectra at 60 Mc./sec. relative to tetramethylsilane: A, IIa; B, IIb.

Dranishnikov,[3] who further showed that the monomeric product reacted as a diepoxide, giving a crystalline tetrol, $C_{10}H_{16}(OH)_4$, and a dihydroxy dimethyl ether, $C_{10}H_{16}(OH)_2(OCH_3)_2$ (V), by reaction with water and methanol, respectively, in the presence of catalytic amounts of acid.

Later, each of these authors proposed a different structure for the monomeric dioxide, with Desalbres[4]

favoring the 2,3,6,7-diepoxide II based on conversion to a known mixture of C_{10} methyl ketones (VI), while Dranishnikov[5] felt that the 2,3,4,5-diepoxide structure (III) was necessary to explain the results of his oxidation experiments. Previous work in our laboratory[6] suggested that the monomer as normally prepared might contain significant amounts of the cyclic peroxide IV.

In view of these conflicting results, we have repeated the work of Desalbres, *et al.*, and in addition have obtained further evidence in support of structure II,

(1) Presented at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963.

(2) L. Desalbres, *Bull. soc. chim. France*, 1245 (1950).

(3) G. L. Dranishnikov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 470 (1953).

(4) Yves-Rene Naves, L. Desalbres, and P. Ardizio, *Bull. soc. chim. France*, 1768 (1956).

(5) G. L. Dranishnikov, *Izv. Vysshikh Uchebn. Zavendenii, Lesn. Zh.*, **3**, 127 (1960).

(6) J. H. Stump, Jr., and O. G. Wilson, U. S. Patent 3,038,906 (June 12, 1962).

Fig. 2.—N.m.r. spectrum of VII at 63 Mc./sec. in carbon tetrachloride relative to tetramethylsilane.

2,3,6,7-diepoxy-2,6-dimethyl-4-octene, which for convenience we designate alloocimene dioxide (AOD).

Redistilled AOD, prepared by a recently described method,[6] gave two incompletely resolved peaks when examined by gas chromatography. Careful fractionation of the mixture at 20–30-plate efficiency yielded 5% each of the two components, IIa and IIb, each in about 95% purity.

The n.m.r. spectra of IIa and IIb (Fig. 1) each have three well-defined groups of signals centered near 1.2, 3.0, and 5.6 p.p.m. [relative to $Si(CH_3)_4$] in the ratio of 12:2:2. This distribution of methyl, oxirane, and vinyl protons is in agreement with structure II and would seem to exclude both III and IV.

IIa   IIb
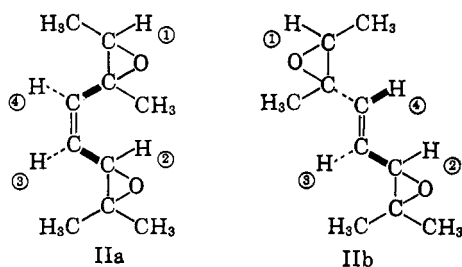
Examination of the oxirane proton region (ca. 3.0 p.p.m.) discloses two distinct single-proton signals. One, at 2.92 in IIa and 2.81 in IIb, is a 1:3:3:1 quartet typical of the grouping $H-C-CH_3$ and may therefore be ascribed to proton 1. The other, at 3.18 in IIa and 3.12 in IIb, due to proton 2, is spin coupled ($J = 4$–6 c.p.s.) with the adjacent vinyl proton 3 in each isomer. In the case of IIb each member of the resulting doublet is further split ($J = 2$ c.p.s.). One explanation of this secondary splitting is that the IIa and IIb differ in their geometry around the central double bond as shown and that the trans structure permits a long-range coupling of protons 2 and 4. It may be argued that the structures for IIa and IIb might be reversed and that the observed small coupling is due to a

relationship between protons 2 and 4. In any case, the difference between the two isomers must involve the environment near proton 2 and an olefinic cis–trans relationship appears to best fulfill this requirement.

To aid in the interpretation of the infrared spectra of IIa and IIb, the dimethoxy compound V was prepared

by a method in which a strongly acidic resin catalyst was substituted for the sulfuric acid of Dranishnikov.[2]

The differences in the infrared spectra of IIa and IIb are slight and involve absorption bands of weak to medium intensity. A band at 990 cm.$^{-1}$ in IIb, not present in IIa, agrees well with expected trans olefin absorption. Bands which disappear on reaction with methanol to give V and may be presumed to be due to the intact oxirane ring are at 1270 and 805 cm.$^{-1}$ in IIa and at 1340, 840, and 780 cm.$^{-1}$ in IIb.

The two oxirane rings in II have reactivities sufficiently different that stepwise ring opening by aqueous dimethylamine is possible and by proper choice of reaction conditions either the mono VII or the bis VIII dimethylamino derivative may be prepared in good yield.
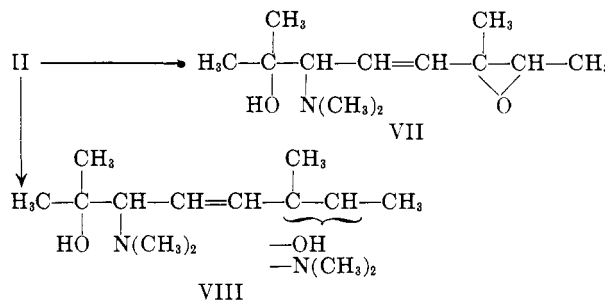
The structure shown for VII is assigned on the basis of the following interpretation of its n.m.r. spectrum (Fig. 2). In comparison with Fig. 1, the signal due to proton 2 (3.12–3.18 p.p.m.) in II has shifted to higher field at ca. 2.6 p.p.m. This is the direction and magnitude of the shift to be expected[7] for a proton α to a dialkylamino group vs. an oxirane proton. Had this proton become α to a hydroxyl group, as required by opening of the ring in the opposite direction, its signal should be found at considerably lower field.

Gas Chromatography of Alloocimene Dioxide.—Material prepared by a recently described method[6] was examined by gas chromatography and found to consist of 15% (area) of a number of low-boiling components, the remainder giving two partially separated peaks of about equal areas. In the experiments described below, redistilled material, from which the low-boiling components had been removed, was used.

Alloocimene Dioxide Isomers (IIa and IIb).—Alloocimene dioxide[6] (4 l., n^{20}D 1.46995, d^{20} 0.9448) was distilled through a 1.5 in. × 4 ft. column, containing stainless steel protruded packing, at 5-mm. pressure and a reflux ratio of 4:1. Each fraction (200 ml.) was analyzed by gas chromatography, the final fraction (no. 18), b.p. 79° (5 mm.), n^{20}D 1.4638°, d^{20} 0.9539, being 95% IIb, $\bar{\nu}_{max}^{neat}$ 3050 (w), 3000, 2970, 2920 (s), 2880 (m), 1810 (w), 1710 (w), 1665 (w), 1460 (s), 1425 (m), 1380, 1375 (s), 1320 (m), 1270 (m), 1260 (m), 1255 (m), 1205 (w), 1160 (m), 1120 (m), 1075 (m), 1040–1030 (w), 990 (shoulder), 968 (s), 890 (m), 865 (s), 820 (m), 805 (w), 760 (m), 725 (w), 705 (m), 680 (m), 630 (w) cm.$^{-1}$.

Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.42; H, 9.52. Found: C, 71.67; H, 9.69.

Redistillation of fractions 5–8 through a 1.5 in. × 2 ft. column, with the same type packing, at 5 mm. gave a 200-ml. center cut, b.p. 76–77°, n^{20}D 1.4616°, d^{20} 0.9519, 95% IIa by g.l.p.c., $\bar{\nu}_{max}^{neat}$ 3500 (w), 3050–2960–2930–2880 (s), 1710 (w), 1630, 1675

(7) L. M. Jackman, "Nuclear Magnetic Resonance Spectroscopy," Pergamon Press Inc., New York, N. Y., 1960, pp. 55–56.

(8) Gas chromatography was carried out using a Burrell Kromo-Tog Model K2 with a 2.5-m. polyethylene glycol on Chromosorb W column and helium as carrier gas.

(9) Infrared spectra were determined with a Perkin-Elmer Model 237 double-grating spectrophotometer.

(w), 1450 (s), 1425 (m), 1370 (s), 1340–1320 (m), 1275 (w), 1255 (m), 1150 (m), 1125 (m), 1075 (m), 1050 (w), 1040 (w), 975 (s), 890 (m), 870 (s), 840 (m), 820 (m), 780 (w), 760 (w), 705 (w), 680 (m) cm.$^{-1}$.

Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.42; H, 9.52. Found: C, 71.58; H, 9.61.

Oxirane Determination.[10]—To 0.3116 g. of IIa was added 25.0 ml. of 0.2 *N* dry hydrogen chloride in ether. After 2 hr., 50 ml. of neutral ethanol was added and the excess hydrogen chloride was titrated with 0.100 *N* aqueous potassium hydroxide using a Beckman Model B pH meter. A sharp break occurred in the pH *vs.* titrant volume curve at pH 3.2 to 8.2 (midpoint 6.2) corresponding to 2.48 mequiv. of oxirane (1.39 oxirane rings/$C_{10}H_{16}O_2$). Further titration of the sample gave a second pH break at 8 to 10 and corresponded to titration of the total amount of hydrogen chloride introduced. A similar titration of IIb showed 1.26 oxirane rings.

Reaction with Methanol.—To a stirred mixture of 288 g. (9.0 moles) of methanol and 8.5 g. of Amberlyst-15 acidic resin catalyst (Rohm and Haas) was added 190 g. (1.13 moles) of distilled alloocimene dioxide (mixed isomers) during 35 min. at 25–30° with ice bath cooling. After an additional 45 min. at room temperature, the catalyst was filtered off, and washed with two 50-ml. portions of methanol, and the combined filtrate was vacuum stripped to remove the solvent. The residue was pot distilled from 10 g. of potassium hydroxide, giving the dimethoxy product V as a single 186-g. cut, b.p. 137–141° at 5 mm., 77% pure by g.c. Redistillation gave 98% pure V, n^{20}D 1.4667°, d^{20} 1.0215 showing $\bar{\nu}_{max}^{neat}$ 3450 (s), 3000–2950–2900 (s), 2800 (m) 2750 (m), 1450–1460 (m, doublet,) 1380 (m), 1290 (w), 1230 (w), 1165 (m), 1105 (s), 1095 (vs) 1040 (w), 990 (m), 952 (m), 920 (w), 875 (w), 828 (w), 750 (w) cm.$^{-1}$.

Anal. Calcd. for $C_{12}H_{24}O_4$: C, 62.07; H, 10.34. Found: C, 61.92; H, 10.50.

Reaction with Dimethylamine. Monodimethylamino Derivative VII.—To 630 g. (3.75 moles) of alloocimene dioxide (mixed isomers) was added with stirring 539 g. (3.0 moles) of 25% aqueous dimethylamine over a 2.75-hr. period at 45°, slight intermittent heating being required to maintain this temperature. The mixture was stirred an additional 2 hr. at 45°, with increasingly more heat being required. The organic layer (739 g.) was separated and distilled at 3 mm. through a 1.5 × 24 in. column containing stainless steel protruded packing. After a small forerun consisting mainly of water, 274 g. of recovered alloocimene dioxide, b.p. 60–85°, was collected. This was followed by a 276-g. product cut, b.p. 112–123° (61% yield based on unrecovered AOD). The product cut was pot distilled; a center cut, b.p. 114–115° at 5 mm., n^{20}D 1.4674, d^{20} 0.9520, taken for analysis, showed $\bar{\nu}_{max}^{neat}$ 3400 (s), 2950–2900–2850–2800–2750 (s), 1650 (w), 1450 (s), 1365 (s), 1320 (m), 1250 (m), 1205 (w), 1160 (m), 1110 (m), 1060 (m), 1020 (m), 970 (s), 925 (w), 910 (w), 868 (m), 820 (w), 750 (w), 700 (w), 680 (w) cm.$^{-1}$.

Anal. Calcd. for $C_{12}H_{23}NO_2$: C, 67.60; H, 10.79; N, 6.57. Found: C, 67.04; H, 10.77; N, 5.87.

Bisdimethylamino Derivative VIII.—A mixture of 312 g. (1.85 moles) of alloocimene dioxide and 2000 g. (11.1 moles) of 25% aqueous dimethylamine was stirred at room temperature. During the first 2 hr. the temperature gradually rose to 45° and the originally two-phase system became homogeneous. After 3 hr. more, during which time the solution cooled back to 30°, the bulk of the water and excess amine was removed by distillation at atmospheric pressure to a pot temperature of 130° and the remainder stripped away under vacuum. Pot distillation of the residue gave a single product cut (389 g., 82% yield), b.p. 138–144° at 5 mm. Redistillation gave an analytical sample, b.p. 150–153° at 8 mm., n^{20}D 1.4804°, d^{20} 0.9653, which showed $\bar{\nu}_{max}^{neat}$ 3400 (s), 2980–2950–2850–2810–2780 (s), 1650 (w), 1450 (s), 1360 (s), 1300 (w), 1250 (w), 1170 (m), 1150 (m), 1100 (w), 1045 (s), 1015 (m), 990 (m), 970–960 (m), 910 (w), 835 (m), 715 (w) cm.$^{-1}$.

Anal. Calcd. for $C_{14}H_{30}N_2O_2$: C, 65.11; H, 11.62; N, 10.85. Found: C, 65.16; H, 11.53; N, 10.87.

(10) D. Swern, T. W. Findley, G. N. Billen, and J. T. Scanlan, *Anal. Chem.*, **19**, 414 (1947).
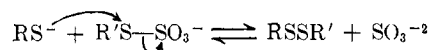
Unsymmetrical Disulfides from an Amino Bunte Salt

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The reaction of Bunte salts (alkyl thiosulfates) with mercaptans has been used with varying success in the synthesis of unsymmetrical disulfides.[1-4] The reaction apparently proceeds *via* an SN2 attack of mercaptide ion on the sulfur atom attached to the alkyl group in the Bunte salt.[5] There is no instance reported in the

$$RS^- + R'S-SO_3^- \rightleftharpoons RSSR' + SO_3^{-2}$$

literature, however, in which a Bunte salt bearing an amino group was used for the synthesis of a mixed disulfide. It was of interest, therefore, to see if 2-aminoethanethiosulfuric acid could be used to prepare an unsymmetrical disulfide containing the cysteamine (mercaptoethylamine) moiety.

Using the method of Swan,[3] 2-aminoethanethiosulfuric acid was combined with 1 equiv. of a mercaptan in both aqueous and aqueous ethanolic media. A stream of nitrogen was bubbled into the solution to remove the sulfur dioxide anticipated as a by-product. The reac-

$$H_2NCH_2CH_2SSO_3H + RSH \longrightarrow$$
$$H_2NCH_2CH_2SSR + SO_2 + H_2O$$

tion failed to proceed at room temperature. On prolonged heating a very slight evolution of sulfur dioxide was detected, but nearly all the starting Bunte salt was recovered unchanged on work-up of the reaction mixture.

The reaction of sodium 2-aminoethanethiosulfate with a sodium mercaptide in water by the method of Footner and Smiles[1] proceeded with a slow uptake of the thiol. The use of methanol as the solvent for the above reaction markedly increased the rate of the reaction. A prompt precipitation of sodium sulfite occurred and the mercaptan was consumed in less than 5 min. The insolubility of sodium sulfite in methanol presumably served to drive the reaction to completion. Performance of the reaction at 0°, rather than at room or elevated temperatures, improved yields. Reactions run at −10° or below were too slow to be useful. The mixed disulfides were isolated and purified as hydrochloride salts (Table I).

$$RS^- + H_2NCH_2CH_2SSO_3^- \rightleftharpoons H_2NCH_2CH_2SSR + SO_3^{-2}$$

Yields of unsymmetrical disulfides were rarely greater than 60% due to the formation of considerable quantities of symmetrical disulfides. The ease with which mixed disulfides disproporionate into symmetrical disulfides has been observed by Schöberl and Bauer.[2]

(1) H. B. Footner and S. Smiles, *J. Chem. Soc.*, **127**, 2887 (1925).
(2) A. Schöberl and G. Bauer, *Angew. Chem.*, **69**, 478 (1957).
(3) J. M. Swan, *Nature*, **180**, 643 (1957).
(4) B. Milligan and J. M. Swan, *J. Chem. Soc.*, 6008 (1963).
(5) O. Foss, "Organic Sulfur Compounds," Vol. I, N. Kharasch, Ed., Pergamon Press, Inc., New York, N. Y., 1961, p. 83.