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Writings

The Osmium Tetroxide
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Unsaturated Fatty Acids ca. 1948

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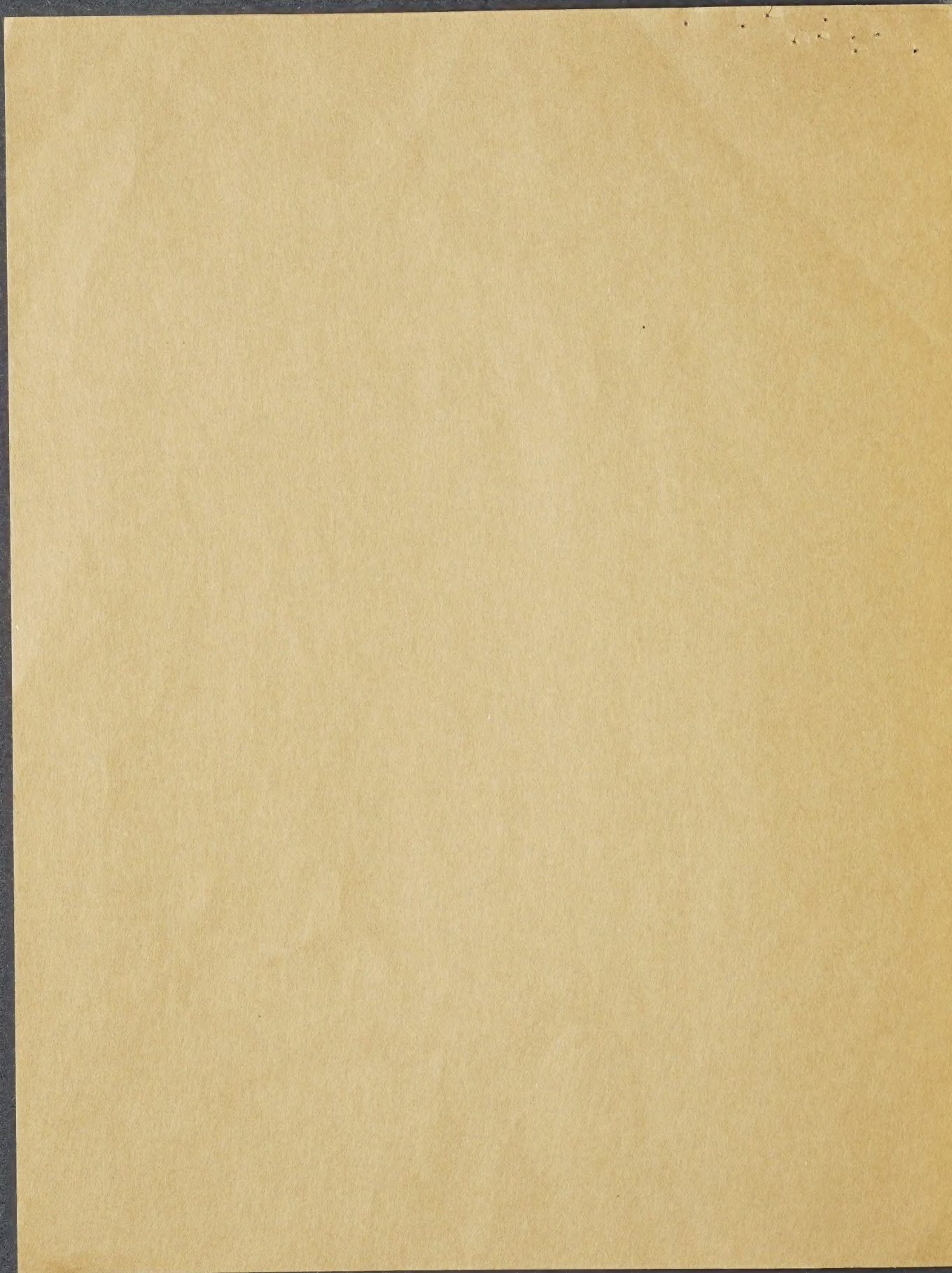
BOX 9

FILE 26

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The Osmium Tetroxide Oxidation of Some Long-Chain Unsaturated Fatty Acids

By Alfred R. Bader



The Osmium Tetroxide Oxidation of Some Long-Chain Unsaturated Fatty Acids

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As a means of extending the evidence of the configurations of the products of oxidation of oleic, elaidic, linoleic, erucic, and brassidic acid with permanganate and peracids, a study has been made of their oxidation by osmium tetroxide. Since this reacts through a cyclic ester intermediate,¹ a *cis*-ethylene must give an *erythro* diol and a *trans* ethylene a *threo* diol. In each case the oxidation products obtained were the ones obtained also in the alkaline permanganate oxidation of the same acids. Hence the 9,10-dihydroxystearic acid melting at 132° and the 13,14-dihydroxybehenic acid melting at 132° are the *erythro*-diols, the two isomers melting at 95° and 101°, respectively, are the *threo*-diols and the eight diastereoisomers of 9,10,12,13-tetrahydroxystearic acid have the configurations assigned them by McKay and Bader.²

This is in accord with the work of Wittcoff and co-workers^{3,4} who pointed out that the criteria (*viz.*, formation of boric acid complexes, rate of oxidation with lead tetraacetate and periodate, and rate of formation of isopropylidene compounds) which characterize *cis*-glycols in cyclic structures also characterize *threo*- rather than *erythro*-diols in straight chain compounds.

Swern⁵ has criticized McKay and Bader² for their supposed assumption that alkaline permanganate oxidation proceeds by "*trans* hydroxylation"; this criticism is due to the use² of the confusing designation "*trans*" glycol to describe a compound of the *erythro* series. "*trans*" was used² for *erythro* and "*cis*" for *threo*, because the vicinal hydroxyl groups in *threo* diols possess a closer spatial relationship than those in *erythro*

diols.⁴ The present work supports the actual conclusions reached^{2,3,4,5} which are the opposite of those of Hilditch and co-workers^{6,7,8} and of Dorée and Pepper.⁹ They assumed that the alkalinity of the permanganate solutions causes inversion, but in the osmium tetroxide reaction the medium is acidic throughout and yet the same products are obtained.

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Experimental

Oleic,¹⁰ elaidic,¹¹ linoleic,¹² erucic⁹ and brassidic⁹ acids were prepared by the standard procedures. One gram lots of each were oxidized with osmium tetroxide by the method of Butenandt.¹³ In each case there were obtained in about 60% yield the *hydroxyacids* obtained also in the alkaline potassium permanganate oxidation of the same acids. Their identity was established by melting point and mixed melting point. The mixture of stereoisomers melting at 156° obtained in the oxidation of linoleic acid was separated into the two isomers melting at 173° and 164°, respectively, by the method of Riemenschneider and co-workers.¹⁴ The experimental data are summarized in Table I.

TABLE I

Compound oxidized	Crude product		Pure product		
	Wt. g.	M. p., °C.	Wt. g.	M. p., °C.	Mixed m. p., °C.
Oleic acid	0.86	126-129	0.67	132	132
Elaidic acid	.82	88-91	.62	94-95	94-95
Erucic acid	.90	124-127	.70	132	131-132
Brassidic acid	.79	94-96	.59	101	101
Linoleic acid	.80	156-157	.28	172-173	172-173
			.17	164	164

(7) Hilditch and Lea, *ibid.*, 1576 (1928).

(8) Atherton and Hilditch, *ibid.*, 204 (1943).

(9) Dorée and Pepper, *ibid.*, 477 (1942).

(10) Lapworth, Pearson and Mottram, *Biochem. J.*, **19**, 7 (1925).

(11) Bertram, *Chem. Weekblad*, **33**, 3 (1936).

(12) McCutcheon, "Organic Syntheses," **22**, 75 (1942).

(13) Butenandt, Schmidt-Thomé and Paul, *Ber.*, **72**, 1116 (1939).

(14) Riemenschneider, Wheeler and Sando, *J. Biol. Chem.*, **127**, 391 (1939).

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(1) Criegee, *Ann.*, **522**, 75 (1936).

(2) McKay and Bader, *J. Org. Chem.*, **13**, 75 (1948).

(3) Wittcoff and Miller, *This Journal*, **69**, 3138 (1947).

(4) Wittcoff, Moe and Iwen, *ibid.*, **70**, 742 (1948).

(5) Swern, *ibid.*, **70**, 1239 (1948).

(6) Hilditch, *J. Chem. Soc.*, 1828 (1926).

