



ring, indicated that the three-carbon chain of propiophenone remained intact during pyrolysis. Labeling of one of the N-methyl groups of **9** with  $^{14}\text{C}$ , followed by pyrolysis, gave **12**, in which one-third of the original activity was retained. Thus, the  $\gamma$  carbon (4C) of the pyridine nucleus must be derived from the trimethylamine moiety of the quaternary fluoroborate.

Phenylazirine, which has been isolated during studies of the Neber rearrangement,<sup>4</sup> was not detected nor was its expected dimerization product, 2,5-diphenylpyrazine.<sup>10</sup> Products arising from C-N skeletal rearrangement were not detected, which implies that either the incipient intermediate **2** does not form or, if formed, it does not undergo rearrangement under the conditions used.

Investigations of the synthetic utility and mechanism of these pyrolysis reactions are being continued.

**Acknowledgment.** Mass spectroscopic analyses were performed by Nathan M. Ingber in the laboratories of The Standard Oil Co., Cleveland, Ohio.

(10) L. Horner, A. Christmann, and A. Gross, *Ber.*, **96**, 399 (1963).

(11) To whom inquiries should be addressed.

(12) NASA Trainee, 1965-1966.

D. L. Fishel,<sup>11</sup> George R. Newkome<sup>12</sup>

Department of Chemistry, Kent State University  
Kent, Ohio 44240

Received February 8, 1966

## An Unequivocal Ozonide Stereoisomer Assignment

Sir:

The formation of both *cis*- and *trans*-ozonides upon ozonolysis of olefinic materials has now been reported by a number of workers.<sup>1-8</sup> In those cases where individual ozonide stereoisomer assignments have been reported they have been based upon some combination of infrared, nmr, glpc, and chemical reactivity data. Such a combination of data has permitted some reasonable stereoisomer designations to be made. However, it should be noted that in many cases the significant finding is a dependence of ozonide<sup>1,2,5-7,9</sup> or cross-ozonide<sup>9</sup> *cis*:*trans* ratio on olefin geometry rather than the specific assignments made. Such assignments are, nevertheless, equivocal, and a more exact method becomes essential in several important cases.

The surprising results reported by Schröder, for example, that *trans*-di-*t*-butylethylene gives 100% *trans*-ozonide while the *cis* isomer gives a 70:30 (*cis*:*trans*) ratio, are based, in part, on the difference in rate of reduction of the ozonides with lithium aluminum hydride, the reasonable assumption being made that the *cis* isomer is more rapidly reduced. A similar difference in rate of reaction of ozonides, this time with triphenylphosphine, was used by Lorenz and

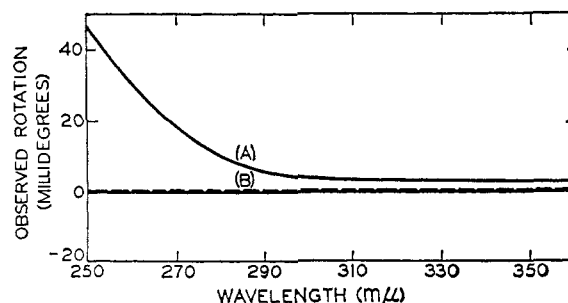


Figure 1. Optical rotatory dispersion curves of the isomeric ozonides of 2,5-dimethylhexene-3 after reaction with brucine. Isomer A is necessarily assigned the *trans* configuration, and B the *cis* configuration.

Parks<sup>7</sup> to distinguish between the diisopropyl ozonide isomers. Again the underlying assumption is that the *cis*-ozonide will react faster. In the diisopropyl ozonide case the assignment based on chemical reactivity correlated with the glpc data.<sup>7</sup> In the case of the butene-2 ozonides, however, the isomer with the longer glpc retention time, *i.e.*, the alleged *cis* isomer, reacted more slowly with triphenylphosphine. Existing stereoisomer assignments must be regarded as tentative, therefore, with a consequent reduction in their value to the ozonolysis mechanism problem.

With increasing attention being given to the use of ozonide *cis*:*trans* ratios as a means of investigating the mechanism of ozonolysis,<sup>9,10</sup> it has become necessary to be able to make this stereochemical assignment on an unequivocal basis. We wish to report an unequivocal assignment of ozonide stereoisomers. The method takes advantage of the fact that the *trans* isomer of a symmetrical ozonide must be a *dl* pair.

Based on our earlier observations<sup>11</sup> that ozonides react rapidly with amines, we have treated each isomer of 2,5-dimethylhexene-3 ozonide (diisopropyl ozonide, I)<sup>12</sup> with less than the anticipated<sup>13</sup> stoichiometric amount of brucine in an attempt at kinetic resolution of the true *trans* isomer. In a typical reaction 100 mg of ozonide was treated with 70 mg of brucine in dichloromethane at  $-70^\circ$  for *ca.* 10 min. The reaction mixture was allowed to warm to room temperature and stand for 16 hr. Pentane was then added and the precipitated material filtered off. The unreacted ozonides were isolated from their mother liquors by glpc, identified by comparison with authentic samples, and investigated for optical activity. In order to magnify any optical activity developed we have run ORD curves<sup>14</sup> on both of the recovered ozonides. The results from a typical run are shown in Figure 1. One of the ozonide isomers (isomer A) develops a strong rotation with the beginning of a positive Cotton effect lobe while the other (isomer B) has no rotation. Isomer A is, therefore, unequivocally assigned the

(1) G. Schröder, *Chem. Ber.*, **95**, 733 (1962).

(2) R. Criegee, S. S. Bath, and B. V. Bornhaupt, *ibid.*, **93**, 2891 (1960).

(3) O. S. Privett and E. C. Nickell, *J. Lipid Res.*, **4**, 208 (1963).

(4) G. Riezebos, J. C. Grimmelikhuisen, and D. A. Van Dorp, *Rec. Trav. Chim.*, **82**, 1234 (1963).

(5) P. Kolsaker, *Acta Chem. Scand.*, **19**, 223 (1965).

(6) F. L. Greenwood and B. J. Haske, *Tetrahedron Letters*, 631 (1965).

(7) O. Lorenz and C. R. Parks, *J. Org. Chem.*, **30**, 1976 (1965).

(8) L. D. Loan, R. W. Murray, and P. R. Story, *J. Am. Chem. Soc.*, **87**, 737 (1965).

(9) R. W. Murray, R. D. Youssefyeh, and P. R. Story, *ibid.*, **88**, 3143 (1966).

(10) P. R. Story, R. W. Murray, and R. D. Youssefyeh, *ibid.*, **88**, 3144 (1966).

(11) R. W. Murray, P. R. Story, L. D. Loan, and R. D. Youssefyeh, unpublished results.

(12) For details of the ozonolysis and isomer separation procedures see ref 9.

(13) The mechanism of the reaction between ozonides and amines is still not completely clear. Work on this aspect of the problem is in progress.

(14) The ORD spectra were measured on a Durrum-Jasco Model ORD/UV-5 spectrophotometer and ORD recorder using a 0.5 M solution of ozonide in hexane.