

assignment of this rests on analogy to the previous case.

*In vitro* biological data on the 6-deoxy epimers (Ia, Ib) as well as on known 6-deoxy-6-demethyl-tetracycline<sup>1,2,4</sup> (Ic, a compound with no asymmetry at C.6) are presented in Table I.<sup>15</sup> The

TABLE I

Compound	Bioassay <sup>a</sup> vs. <i>K. Pneumoniae</i> <sup>b</sup>
6-Dimethyl-6-deoxytetracycline (Ic)	900
$\alpha$ -6-Deoxytetracycline (Ia)	700
$\alpha$ -6-Deoxy-5-hydroxytetracycline (Ib)	1400
$\beta$ -6-Deoxytetracycline (Ia)	500
$\beta$ -6-Deoxy-5-hydroxytetracycline (Ib)	400

<sup>a</sup> Expressed in oxytetracycline units/mg. Cf. R. C. Kersey, *J. Am. Pharm. Assoc.*, **39**, 252 (1950). In this assay 5-hydroxytetracycline is taken as the standard at 1000 units/mg. <sup>b</sup> Similar relative activities have been noted with other microorganisms.

reduced activity in the  $\beta$ -series may well be the result of conformational distortion.

(15) We are indebted to Mr. J. J. Smith and his associates for these data.

M. SCHACH VON WITTENAU  
 MEDICAL RESEARCH LABORATORIES JOHN J. BEEREBOOM  
 CHAS. PFIZER & Co., INC. ROBERT K. BLACKWOOD  
 GROTON, CONNECTICUT CHARLES R. STEPHENS  
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#### HOT RADICAL EFFECTS IN AN INTRAMOLECULAR INSERTION REACTION

Sir:

Thermal decomposition of *p*-toluenesulfonylhydrazones of aldehydes and ketones in basic media gives rise to diazocompounds, which in aprotic solvents themselves undergo decomposition by a carbenoid process.<sup>1</sup> The decomposition of the tosylhydrazone of 2-butanone<sup>2</sup> in diethylcarbitol in the presence of sodium methoxide yields *cis*- and *trans*-butene-2, butene-1 and a trace of methylcyclopropane (see table). These compounds presumably are formed from methylethylcarbene by reactions that can be considered as intramolecular insertion reactions formally similar to the intermolecular insertion reactions of methylene itself.<sup>3</sup>

We wish to report that the thermal decomposition of methylethyldiazirine in the gas phase at  $\sim 160^\circ$  also results in the formation of these hydrocarbons in ratios virtually identical with those reported by Friedman and Shechter.<sup>2</sup> There can be little doubt that this reaction proceeds *via* the formation of the carbene which supports a similar mechanism for the decomposition of the tosylhydrazones. Photolysis of methylethyldiazirine (3130 Å. radiation) also results in the formation of the same C<sub>4</sub>H<sub>8</sub> hydrocarbons but in quite different ratios.

In the photolyses the relative yields of the products were independent of the pressure of the diazine in the range 50 to 200 mm. To eliminate the possibility of secondary isomerization of the

(1) J. W. Powell and M. C. Whiting, *Tetrahedron*, **7**, 305 (1959).

(2) L. Friedman and H. Shechter, *J. Am. Chem. Soc.*, **81**, 5512 (1959).

(3) W. E. Doering, R. G. Buttery, R. G. Laughlin and N. Chaudhuri, *ibid.*, **78**, 3224 (1956).

TABLE I

% Composition	1 <sup>a</sup>	2 <sup>b</sup>	3 <sup>c</sup>
Butene-1	5	3.6	23.4
<i>trans</i> -Butene-2	67	66.5	38.6
<i>cis</i> -Butene-2	28	29.5	35.6
Methylcyclopropane	0.5	0.4	2.4

<sup>a</sup> Friedman and Shechter (ref. 2). <sup>b</sup> This work, pyrolysis at  $\sim 160^\circ$ . <sup>c</sup> This work, photolysis (3130 Å.).

initially formed excited olefins, photolyses were carried out in the presence of added nitrogen, at pressures up to 2 atmospheres, without changing the ratios of the products. Thus the compositions shown in the table represent the *initial* rearrangement ratios from the photolytically produced carbene. Below 50 mm. some small variations in the product ratios were observed, which could be rationalized in terms of the secondary isomerization of the methylcyclopropane (initially formed with excess energy) to butenes. At 4 mm. the yield of methylcyclopropane had fallen to 1.0%, the yield of *trans*-butene-2 had risen to 42% and a trace of isobutene was detected.

The relatively high proportion of butene-1 and methylcyclopropane, and the near equivalence of the amounts of *cis*- and *trans*-butene-2 in the photolytic decomposition are in striking contrast to those from the pyrolyses. These differences are most reasonably explained by postulating that the carbene produced photochemically is vibrationally excited. The results, therefore, indicate a hot radical effect in intramolecular insertion reactions of carbenes previously only noted in intermolecular reactions.<sup>4</sup>

(4) H. M. Frey, *ibid.*, **80**, 5005 (1958).

DEPARTMENT OF CHEMISTRY  
 THE UNIVERSITY  
 SOUTHAMPTON, ENGLAND

H. M. FREY  
 I. D. R. STEVENS

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#### AN ISOTOPE EFFECT DURING THE COUNTERCURRENT DISTRIBUTION OF ARABINOSE-1-C<sup>14</sup>

Sir:

Insofar as we know, the literature lacks any reference to an isotope effect influenced by the position of C<sup>14</sup> in a sugar—or other solute—undergoing countercurrent distribution. For this reason, we wish to report the data below.

D-Arabinose-1-C<sup>14</sup> (*K* = 0.11) moved more slowly than unlabeled D-arabinose (Fig. 1) during countercurrent distribution in cyclohexane-95% ethanol with the result that specific activity decreased with increasing number of the tubes of the train constituting the sugar zone. D-Arabinose-1-C<sup>14</sup> and unlabeled L-arabinose also were partly resolved (Fig. 2); similarly L-arabinose-1-C<sup>14</sup> and unlabeled D-arabinose were partly separated. In all cases, such plots of log specific activity against fraction number for tubes containing this pentose were linear and were never parallel to the abscissa, an index of resolution.<sup>1</sup> When radioactivity resided on carbon 5, the mobilities of the radioactive and unlabeled D-arabinose were indistinguishable, after 350 or 800 transfers. Neither D-xylose-1-C<sup>14</sup> (*K* = 0.26) nor D-ribose-1-C<sup>14</sup> (*K*

(1) K. A. Piez and H. Eagle, *J. Am. Chem. Soc.*, **78**, 5284 (1956).