

Figure 1.

bicyclo[2.2.1]heptene, 3069, 1568, and 706  $\text{cm}^{-1}$ .<sup>5</sup> The nuclear magnetic resonance spectrum (measured in  $\text{CDCl}_3$  at 60 Mc.) contains only two sharp bands, at  $\tau$  4.32 (olefinic H) and 6.23 (paraffinic H); again the olefinic hydrogen resonance is closely comparable with that observed in cyclopentene ( $\tau$  4.40).<sup>6</sup> The ultraviolet spectrum (measured in isooctane, Fig. 2) possesses

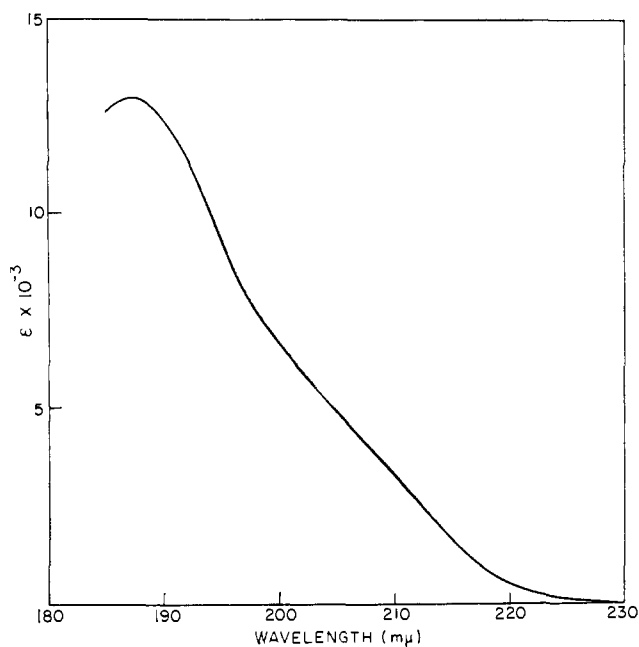


Figure 2.

a single maximum at 187  $\text{m}\mu$  ( $\epsilon$  13,000), very close to that of cyclopentene (188  $\text{m}\mu$ <sup>6,7</sup>), but a broad long wavelength shoulder is present, of sufficient intensity to accommodate one or more new transitions, which might be associated with cooperative electronic excited states.<sup>8</sup>

While our measurements must be interpreted with the reserve which respect for the long arm of coincidence should always engender, they provide at present no evidence of delocalization among the  $\pi$ -electron systems of the double bonds of triquinacene in the ground state.

(5) P. Fuchs, Ph.D. Dissertation, Harvard University, 1955; cf. also R. C. Lord and R. W. Walker, *J. Am. Chem. Soc.*, **76**, 2518 (1954), K. W. F. Kohlrausch, and R. Seka, *Ber.*, **69**, 729 (1936), and K. W. F. Kohlrausch, R. Seka, and O. Tramposch, *ibid.*, **75**, 1385 (1942).

(6) K. B. Wiberg and B. J. Nist, *J. Am. Chem. Soc.*, **83**, 1226 (1961).

(7) L. W. Pickett, M. Munz, and E. M. McPherson, *ibid.*, **73**, 4862 (1951).

(8) The spectra of cyclopentene<sup>6,7</sup> and cyclohexene [ $\lambda_{\text{max}}$  183  $\text{m}\mu$ : W. Potts, *J. Chem. Phys.*, **23**, 65 (1955)], but not that of bicyclo[2.2.1]heptene [ $\lambda_{\text{max}}$  196  $\text{m}\mu$ : our measurement], possess broad long wavelength shoulders, much less intense than that of triquinacene, which have been attributed to vibronic excitations (Potts).

The chemistry of triquinacene is under active investigation.

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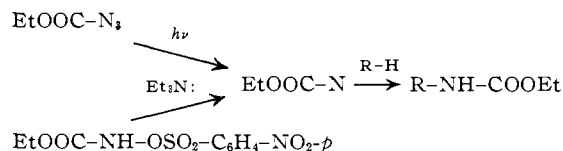
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### Carbathoxynitrene. Selectivity of the C-H Insertion

Sir:

Carbathoxynitrene has been generated by the photolytic decomposition of ethyl azidoformate<sup>1</sup> and by  $\alpha$ -elimination from *N-p*-nitrobenzenesulfonyurethan.<sup>2</sup> It reacts with C-H bonds to form *N*-alkylurethans.



This reaction seems to be analogous to the C-H insertion of carbenes. Most carbenes discriminate but little between different types of C-H bonds, possibly because of a very low energy of activation for the insertion process.<sup>3</sup> Carbomethoxycarbene, the closest carbon analog to carbathoxynitrene, reacts with tertiary C-H bonds only three times faster than with primary ones.<sup>4</sup>

Being interested in the nature of nitrenes and in comparing them with carbenes, we have generated carbathoxynitrene by azide photolysis and by  $\alpha$ -elimination both in pure 2-methylbutane and in a mixture of 44.5% 2-methylbutane and 55.5% dichloromethane. The product mixtures were analyzed by vapor phase chromatography, using a 5-m. column of 20% cyanosilicon XF 1150 on chromosorb, at 125°. The peaks were identified by comparing their retention times, and infrared and n.m.r. spectra with those of the four authentic isoamylurethans, prepared from the known amines and ethyl chloroformate. The peak areas were determined with a planimeter. The two insertion products into primary C-H bonds (in the methyl groups C-1, C-4, and C-5) could not be separated by the column mentioned above, but by a 20% Ucon Polar column. The reactivities of these two types of methyl groups are nearly the same (C-1:C-4 = 1:1.18  $\pm$  10%). The results are given in Table I.

TABLE I

REACTIVITIES OF THE C-H GROUPS IN 2-METHYLBUTANE TOWARD CARBATHOXYNITRENE (CORRECTED FOR THE NUMBER OF HYDROGENS)

	In pure 2-methylbutane			In 44.5% 2-methylbutane-55.5% dichloromethane		
	Type of C-H bond			Type of C-H bond		
	3°	2°	1°	3°	2°	1°
Carbathoxynitrene by $\alpha$ -elimination	27	11	1	25	8	1
Azide dec.	34	9	1	36	10	1
Relative error	$\pm 5\%$	$\pm 10\%$		$\pm 5\%$	$\pm 10\%$	

(1) W. Lwowski and T. W. Mattingly, *Tetrahedron Letters*, 277 (1962).

(2) W. Lwowski, T. J. Maricich, and T. W. Mattingly, *J. Am. Chem. Soc.*, **85**, 1200 (1963).

(3) W. von E. Doering, R. G. Buttery, R. G. Laughlin, and N. Chaudhuri, *ibid.*, **78**, 3226 (1956).

(4) W. von E. Doering and L. H. Knox, *ibid.*, **83**, 1989 (1961).

The data show that (1) carbethoxynitrene is about ten times as selective as the corresponding carbene, (2) the selectivity depends little on the solvent, and (3) the nitrenes generated by photolysis and by  $\alpha$ -elimination have nearly the same selectivity. This is best explained by assuming that the carbethoxynitrene in solution is energetically in equilibrium with its environment and does not contain excess vibrational energy.

From our work with cyclohexene<sup>5</sup> we can estimate that the double bond in cyclohexene reacts about 36 times faster than do the CH<sub>2</sub> groups in positions 4 and 5 (the nonallylic CH<sub>2</sub> groups of cyclohexene). We might, somewhat arbitrarily, equate the reactivities of these CH<sub>2</sub> groups with that in 2-methylbutane. The cyclohexene double bond then would be estimated to react 360 times faster than the primary C-H bond in the methyl groups in 2-methylbutane. This corresponds to a difference in free energies of activation of about 3.5 kcal./mole.

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(5) W. Lwowski and T. W. Mattingly, Jr., to be published.

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### The Hydrolysis of Sodium Tetrahydroborate. Identification of an Intermediate

Sir:

The kinetics of the general acid catalyzed hydrolysis of sodium tetrahydroborate (NaBH<sub>4</sub>, sodium hydroborate, sodium borohydride), has been recently reported by Davis, Bromels, and Kibby,<sup>1</sup> by Stockmayer, Miller, and Zeto,<sup>2</sup> and by Mesmer and Jolly,<sup>3</sup> in whose work earlier literature is cited. In a polarographic study, Marshall and Widing<sup>4</sup> found the anodic wave of the BH<sub>4</sub><sup>-</sup> ion at an  $E_{1/2}$  of  $-0.15$  v. vs. s.c.e., and another much smaller wave at an  $E_{1/2}$  of  $-0.64$  v. vs. s.c.e. Pecsok<sup>5</sup> studied the former wave and used it in his polarographic determination of the rate of hydrolysis of NaBH<sub>4</sub>. Mochalov and Gil'manshin<sup>6</sup> reported that the small wave decreased in height as the NaBH<sub>4</sub> solution decomposed and was larger at lower pH values. They attributed it to the oxidation of an intermediate in the hydrolysis process. We have found that the height of this small wave first increases and then decreases after a solution is prepared and have postulated that it stems from an intermediate in a stepwise hydrolysis process, whose kinetics can be described by a sequential first-order scheme. Polarographic limiting currents, resulting from the oxidation of BH<sub>4</sub><sup>-</sup> at  $-0.01$  v. and

(1) R. E. Davis, E. Bromels, and C. L. Kibby, *J. Am. Chem. Soc.*, **84**, 885 (1962).

(2) W. H. Stockmayer, R. R. Miller, and R. J. Zeto, *J. Phys. Chem.*, **65**, 1076 (1961).

(3) R. E. Mesmer and W. L. Jolly, *Inorg. Chem.*, **1**, 608 (1962).

(4) E. D. Marshall and R. A. Widing, "Polarography of Sodium Borohydride," Atomic Energy Commission Document No. 2914 (1950).

(5) R. L. Pecsok, *J. Am. Chem. Soc.*, **75**, 2862 (1953).

(6) K. N. Mochalov and G. G. Gil'manshin, *Dokl. Akad. Nauk SSSR*, **132**, 134 (1960); *Proc. Acad. Sci. USSR, Chem. Sect.*, **132**, 467 (1960).

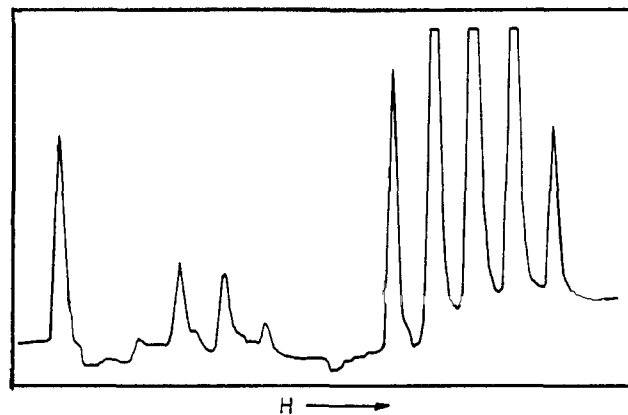


Fig. 1.—B<sup>11</sup> n.m.r. spectrum of base-stabilized, partially hydrolyzed NaBH<sub>4</sub> solution.

the oxidation of the postulated intermediate at  $-0.5$  v., fit such a scheme. Thus, the intermediate is formed by the pseudo-first-order reaction of BH<sub>4</sub><sup>-</sup>, and it is consumed in a second, faster process, which is first order in concentration of the intermediate. Rate constants for these processes have been calculated and will be presented in detail elsewhere<sup>7</sup>; here we report the results of confirmatory experiments, bearing on the identity of this intermediate, which have been performed on solutions, which, according to the kinetic results, have the maximum concentration of the intermediate.

Samples of partially hydrolyzed NaBH<sub>4</sub> solutions, which contained the highest possible concentration of intermediate, were prepared by allowing a fresh solution of NaBH<sub>4</sub> to hydrolyze briefly and then quickly adding base to make the pH 12.5 or greater. A typical procedure, used for preparing samples for n.m.r. work, follows. To 20 ml. of a solution 8 M in NaBH<sub>4</sub> (98% as received from Metal Hydrides, Inc.) and 0.05 M in NaOH, 6 M HCl was rapidly added at  $25 \pm 0.1^\circ$  until the pH dropped to 8.8. After keeping the solution at this pH for 1 min., the pH was raised to 12.5 or greater by the addition of 19.8 M NaOH. The polarographic limiting current at  $-0.5$  v. vs. s.c.e. indicated a concentration of the intermediate of about 0.16 M in the sample. The half-life of the intermediate in such a solution, determined by observation of the decay of the polarographic limiting current, was 3.7 hr. Polarograms of the solutions exhibited only the two known waves ( $E_{1/2} = -0.15$  and  $-0.64$  v. vs. s.c.e.).

It should be noted that the amount of intermediate available for study in the final solution was but a few per cent of the BH<sub>4</sub><sup>-</sup> present. This situation did not affect the n.m.r. spectroscopy, since the concentration of the intermediate was within the limits of detection of the spectrometer, but it did limit the chemical and electrochemical tests which could be done.

Boron-11 n.m.r. spectra were recorded on a Varian HR-60 spectrometer equipped with a 19.3-Mc. oscillator. A 15-mm. sample tube was used. The B<sup>11</sup> spectrum of a base-stabilized, partially hydrolyzed NaBH<sub>4</sub> solution is shown in Fig. 1. The spectrum consists of the borate singlet at low field, a quartet, and a quintet at high field. The quintet is the familiar BH<sub>4</sub><sup>-</sup> spectrum, first studied by Ogg.<sup>8</sup> The quartet of

(7) J. A. Gardiner, "The Hydrolysis of Sodium Hydroborate," Ph.D. Dissertation, Graduate School of The Ohio State University, 1964.

(8) R. A. Ogg, *J. Chem. Phys.*, **22**, 1933 (1954).