Anal. Calcd. for $C_{39}H_{36}B_3N_3$: C, 80.81; H, 6.21; B, 5.61; N, 7.21. Found: C, 78.11; H, 6.41; B, 5.81; N, 7.31.

Preparation of B-Tris(diphenylyl)-N-triphenylborazine (II).—Following the general procedure described above, 44 g. of B-trichloro-N-triphenylborazine[7] reacted with 450 ml. of 0.725 *M* diphenyllithium in ethyl ether to give 38.2 g. of crude product (47% yield), m.p. 292–298°. The product was purified by several recrystallizations from a 1:6 by volume mixture of benzene and petroleum ether (b.p. 35–55°), saturating at reflux temperature and slowly cooling to −30°.. The purified product was in the form of white needles, m.p. 222–223°.

Anal. Calcd. for $C_{54}H_{42}B_3N_3$: C, 84.7; H, 5.5; B, 4.2; N, 5.5. Found: C, 84.8; H, 5.6; B, 4.7; N, 5.4.

Preparation of B-Tris(α-naphthyl)-N-trimethylborazine (III).—B-Trichloro-N-trimethylborazine (22.5 g.) reacted with 215 ml. of 1.41 *M* α-naphthylmagnesium bromide in ethyl ether. The combined crude products from three crystallizations from benzene totaled 28.1 g. (66% yield), m.p. 290–292°. Recrystallizations from a 1:5 by volume mixture of benzene and petroleum ether gave white crystals, m.p. 291–292.

Anal. Calcd. for $C_{33}H_{30}B_3N_3$: C, 79.1; H, 6.0; B, 6.5; N, 8.4. Found: C, 80.6; H, 5.9; B, 6.1; N, 7.7.

Preparation of B-Tris(p-terphenylyl)-N-trimethylborazine (IV).—Attempts to prepare *p*-terphenyllithium by direct reaction of *p*-terphenyl bromide with lithium gave very low yields. Better results were obtained when the *p*-terphenyllithium was prepared by a displacement reaction between *n*-butyllithium and *p*-terphenyl bromide.

B-Trichloro-N-trimethylborazine (22.7 g.) reacted as above with 0.3 mole of *p*-terphenyllithium. An 11-g. yield of crude product was obtained (15% yield based on *p*-terphenyl bromide), m.p. 245–250°. Recrystallizations from a 1:4 by volume mixture of benzene and petroleum ether gave a product, m.p. 255–256°.

Anal. Calcd. for $C_{57}H_{48}B_3N_3$: C, 84.8; H, 6.0; B, 4.0; N, 5.2. Found: C, 82.8; H, 5.9; B, 3.9; N, 5.0.

Hydrolysis Studies.—For the qualitative hydrolysis experiments, weighed samples (50–100 mg.) were treated with 20 ml. of water in a small flask at room temperature and in one case at reflux temperature. After various time intervals, the suspensions were filtered through sintered glass crucibles and the insoluble materials dried under vacuum, weighed, and their identity checked by melting point. The filtrates were analyzed for boron. The results of these experiments are given in Table I. In addition, samples of I and II were treated for several hours with hot concentrated KOH and hydrolysis was found to be complete. Similar treatment of III resulted in only 30% hydrolysis.

TABLE I

HYDROLYSIS OF SUBSTITUTED BORAZINES

Compound	Time, hr.	% recovery	B analysis of filtrate	M.p., °C., of recovered solid
I	0.5	52	Pos.	199–202
II	0.5	95	Neg.	Unchanged
II	0.5[a]	91	Pos.	Unchanged
III	24	95	Neg.	Unchanged

[a] At reflux temperature.

The data obtained on the rates of hydrolysis of I and II in dioxane–water solutions are listed in Table II. Less complete studies on the hydrolysis of III under comparable conditions indicated that the rate of hydrolysis of III was roughly comparable to that of II.

TABLE II

RATES OF HYDROLYSIS IN DIOXANE–WATER SOLUTIONS AT 25°

Compound I		Compound II	
Time, min.	% hydrolysis	Time, min.	% hydrolysis
2	82	3	11
8	87	5	13
27	90	15	16
157	93	53	20
1013	97	83	22
		1112	34

Decarboxylative Deamination of Amino Acids

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Reactions of aliphatic α-amino acids with isoamyl nitrite (γ-methylbutyl nitrite) in various solvents have been studied and the volatile hydrocarbon products have been analyzed by v.p.c. (Table I). In addition to these volatile hydrocarbon components, nitrogen, carbon dioxide, nitrous oxide, and nitric oxide are products of the reactions. The yield of nitrogen is apparently quantitative based on initial amino acid, but, since these inorganic gases also arise from thermal decomposition of isoamyl nitrite,[1] their yields are not necessarily meaningful. The hydrocarbon fraction constitutes less than 1% of the total amino acid consumed in the reaction. Preliminary studies of the nonvolatile products indicate that several products are formed (see Experimental). These have not been characterized. Control reactions have definitely established that the volatile hydrocarbon products do not arise from thermal decomposition of isoamyl nitrite, nor are they formed when isoamyl nitrite is not present in the reaction mixture.

TABLE I

VOLATILE HYDROCARBON PRODUCTS FROM REACTION OF ISOAMYL NITRITE AND α-AMINO ACIDS[a]

Hydrocarbons[d]	Valine–dioxane	Valine–DMF[b]	Valine–EtOH–H_2O[c]	α-Amino-butyric acid–dioxane	Alanine–DMF[b]
Methane	—[e]	—	—	2	3
Ethylene	—	—	3	3	94
Ethane	—	—	—	—	—
Propylene	5	1	—	87	3
Propane	—	—	—	—	0
Cyclopropane	—	0	—	5	—
Isobutane	—	—	—	—	0
Isobutene[f] 1-butene	76	88	82	2	*g*
trans-2-Butene	6	6	15	1	*g*
Methylcyclopropane	12	2	0	0	*g*
cis-2-Butene	≈1	3	0	0	*g*

[a] At 63°; values for products given in per cent. [b] Dimethylformamide. [c] 70% ethyl alcohol–water; room temperature. [d] Given in per cent of the total volatile ($<C_5$) hydrocarbon fraction ($<1\%$ of initial amino acid). [e] — indicates trace amount observed. [f] Not separated under the experimental conditions (see Experimental). [g] The presence of these components was not checked.

This study was originally undertaken to ascertain whether diazotization of α-amino acids under aprotic conditions[2] would lead to the formation of carbenoid species by simultaneous or stepwise loss of nitrogen and carbon dioxide from I. The extremely low yields (*vide supra*) of hydrocarbon products in these reactions, which might be derived from such a reaction, certainly negate any preparatory value.

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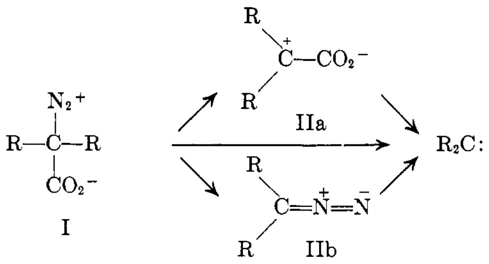
(1) D. H. Szulczewski and T. Higuchi, *Anal. Chem.*, **29**, 1541 (1957); see also N. Kornblum and E. P. Oliveto, *J. Am. Chem. Soc.*, **71**, 226 (1949).

(2) L. Friedman and F. M. Logullo, *ibid.*, **85**, 1549 (1963).



Although, the formation of cyclopropanes in these reactions might be due to carbene intermediates, formation of *cis*- and *trans*-2-butene from valine requires at least the simultaneous occurrence of an ionic path.[3] This might involve methyl or hydrogen migration in IIa to yield a carbonium ion β to the carboxylate group and subsequent decarboxylation to yield olefins. Alternatively, it has been suggested that protonation of IIb by unchanged amino acid or other reaction products could yield an alkyl diazonium ion.[4] Loss of nitrogen from the diazonium ion and subsequent established reactions of the resultant alkyl carbonium ion could account for the product distribution including the cyclopropanes.[5] If methylcyclopropane arises from carbenoid intermediates, its absence in the ethyl alcohol–water experiment might be explained by rapid trapping reactions. On the other hand this result could imply that only IIa is formed under these conditions and that it undergoes ionic rearrangements exclusively and then decarboxylation.[6]

Experimental

The amino acids used were optically inactive reagent grade materials (Matheson Coleman and Bell). Dimethylformamide was shaken with potassium hydroxide pellets and lump calcium oxide, and distilled from molecular sieves. *p*-Dioxane was shaken with potassium hydroxide pellets, refluxed for 50 hr. over sodium metal, and distilled. Isoamyl nitrite (Matheson Coleman and Bell) was used as commercially obtained.

Diazotization Reaction Conditions.—The method will be described for a typical reaction with valine. A heterogeneous mixture consisting of 0.1 g. (8.5×10^{-4} mole) of *dl*-valine, 1 ml. (7.5×10^{-3} mole) of isoamyl nitrite, and 25 ml. of anhydrous dioxane was heated with stirring under an atmosphere of prepurified nitrogen at 63° until gas evolution ceased (6–10 hr.). The reaction time is apparently a function of the rate of solution of amino acid in the solvent, since rates are strongly dependent on particle size. Approximately 25 ml. of gas was evolved and this was collected over mercury in a gas buret. The gas was analyzed by vapor phase chromatography yielding the composition: nitrogen[7] (82%), carbon dioxide (12%), nitrous oxide (5%), and hydrocarbon fraction (<1%). The presence of nitric oxide is inferred by the formation of traces of solid on the surface of the mercury in the gas buret, and the appearance of the characteristic nitrogen dioxide coloration (and solids) when the product gases were allowed to bubble through a mercury bubbler into the atmosphere in a separate experiment.

V.p.c. Analyses.—The hydrocarbon content of each gas sample was quantitatively analyzed using a 10 ft. × 0.125 in. 20% silicone SF-96 (60/80 firebrick) column (0°, nitrogen flow 20 ml./min.) in conjunction with an Aerograph (Wilkens Instrument Co.) electrometer and flame ionization detector. Retention times for the hydrocarbon gases under these conditions are methane (88 sec.), ethylene (111 sec.), ethane (125 sec.), propylene (227 sec.), propane (240 sec.), cyclopropane (375 sec.), isobutane (455 sec.), isobutene and 1-butene (600 sec.), *trans*-2-butene (745 sec.), methylcyclopropane (825 sec.), and *cis*-2-butene (865 sec.). The inorganic gases were identified using a 15 ft. × 0.25 in. silicone column in conjunction with an Aerograph A-90-C chromatograph equipped with a thermal conductivity detector. Proper and reproducible temperature was obtained in this latter instrument by placing Dry Ice in the oven.

Preliminary Analysis of Nonvolatile Products.—A reaction mixture from decomposition of valine in dioxane was distilled not quite to dryness and an infrared spectrum was taken of the liquid residue (reference pure dioxane). Bands were observed at 3420 (s), 1800 (w), 1780–1720 (s), 1640 (s), 1590 (sh), and 1555 cm.$^{-1}$ (s). The strong hydroxyl absorption is probably due to water and isoamyl alcohol, both anticipated reaction products. The infrared spectrum can also accomodate the presence of various esters and acids which might be expected and isovaleraldehyde (from isoamyl nitrite decomposition). An infrared spectrum of the distillate showed strong bands at 3420, 1640, and 1590 cm.$^{-1}$ (sh). The first is probably due to water, and the latter two are tentatively assigned to unchanged isoamyl nitrite.

Acknowledgment.—The invaluable assistance of Dr. Jerry A. Bell with the v.p.c. analyses is gratefully acknowledged. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.[8]

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(3) Rearrangement reactions of isobutylidene apparently do not yield *cis*- or *trans*-2-butene [L. Friedman and H. Shecter, *J. Am. Chem. Soc.*, **81**, 5512 (1959).

(4) L. Friedman, private communication.

(5) M. S. Silver, *J. Am. Chem. Soc.*, **82**, 2971 (1960); P. S. Skell, *et al.*, *ibid.*, **82**, 2971 (1960); **84**, 3962, 3963 (1962).

(6) We have no strong preference for the zwitterion IIa over an α-lactone intermediate. However, the diazonium ion origin of the intermediate implies that it would be more ionic than α-lactone intermediates which arise in nucleophilic substitution reactions of α-halocarboxylic acid salts.

(7) Corrected for the initial nitrogen present in the system.

(8) After these studies were completed, it was learned that Dr. Lester Friedman had obtained similar results with other amino acids. Helpful discussions with him are gratefully acknowledged.

A Convenient Spectrophotometric Method for Following the Reactions of Arenesulfonates[1]

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A convenient spectrophotometric method has been developed for following the reactions of methyl *p*-toluenesulfonate (tosylate). This should be of general interest in view of the widespread use of arenesulfonates for studies of organic reactions. The absorptions of methyl tosylate and tosylate anion are sufficiently different so that the reactions can be followed spectrophotometrically; at 261 mμ (in water) methyl tosylate has ϵ 671 and tosylate anion has ϵ 344. For reactions in transparent solvents, rate measurements are made by simply measuring the decrease in optical density (absorbance) with time. First-order rate constants determined by this method for the reactions of methyl tosylate in the presence of a large excess of various nucleophiles (conditions which preclude the use of titrimetric or conductometric methods) in methanol[2] were reproducible to 0.5 to 3%. The first-order rate constant for the hydrolysis of methyl tosylate in water at 25.00° of 7.98 ± 0.05 (average deviation from mean of three trials) $\times 10^{-6}$ sec.$^{-1}$, as determined by this

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[1] Supported in part by the Atomic Energy Commission under Contract No. AT(30-1)-905 and by N.S.F. and N.I.H. predoctoral fellowships.

[2] C. G. Swain and W. D. Burrows, unpublished results.