TABLE V
FISSION PRODUCTS FROM THE CATIONS OF PENTAMETHYLHEPTANE

Cations	No. of products
t-Butyl + isobutylene	10
t-Amyl + pentenes	6
t-Hexyl + hexenes	6
t-Heptyl + heptenes	6
Trimethylpentyl + trimethylpentenes	7
Dimethylhexyl + dimethylhexenes	3

these isomers can split in two ways so that the total of possible fission reactions is 19. Of the 38 fission products only 3 have the carbon skeleton of a dimethylhexane. Although this mechanism may account for some dimethylhexane formation, it is clear that any enhanced selectivity must result from a mechanism such as the addition of the methallylic cation to isobutylene.

The data at 0% $MCyC_5$ concentration are at much too high a conversion level to consider seriously with the other data. It is quite surprising that the addition of only 5 vol. % of $MCyC_5$ reduces the total reaction of the 2,2,4-trimethylpentane from about 20 to about 1%. The depletion of isobutane in the absence of $MCyC_5$ is undoubtedly due to secondary alkylation of olefinic fragments produced by cracking. The over-all result is a complex mixture which does not reflect the initial reactions.

According to the arguments developed in this discussion, the primary reactions of the 2,2,4-trimethylpentyl cation include isomerization to other trimethylpentyl cations and β-fission to form two C_4 fragments. Dimethylhexanes are not formed primarily by rearrangement but rather arise from a combination of isobutylene with the methallylic cation along with the possibility of some C_{12} cracking. High selectivity to trimethylpentanes is achieved during butene alkylation because isobutane itself approaches the effectiveness of methylcyclopentane as a hydride donor. (Extrapolation of data presented in the previous paper[8] indicates that isobutane would be almost as reactive as methylcyclopentane.)

Experimental

The general techniques employed during this study were essentially identical with those described previously.[8] A mixture of 2,2,4-trimethylpentane and methylcyclopentane (1 ml.) was contacted with 1 ml. of tritiated sulfuric acid (specific activity of approximately 1 mc./g.) for 10 min. or longer in a dental Wig-L-Bug shaker. Analysis was then performed on the hydrocarbon layer using the radioassaying gas chromatograph.

Product compositions in mole per cent were calculated from the total counts under each radio peak and a knowledge of the specific activity of each component. As outlined in the results section, the specific activities followed the general rule of $2n + 1$ where n is the number of carbon atoms. In each reaction isobutane was formed to a sufficient extent to analyze chemically as well as by radioassay. Hence the chemical chromatogram generally exhibited two peaks: isobutane and isooctane. Isobutane by chemical analysis shown in the next to last row of Tables III and IV represents the proportion of isobutane in this mixture.

The extent of reaction (the fraction of initial 2,2,4-trimethylpentane that undergoes ionization) was calculated from the product composition, using appropriate corrections for molar response.[15] In order to perform this calculation some assumption must be made regarding the stoichiometry of the reactions involved. This arises because insufficient hydrogen deficient species are observed to balance the hydrogen rich species, such as isobutane, that are formed during the reaction. At the rather low conversion levels involved it is not unreasonable to assume that hydrogen deficient species will wind up as acid-soluble cyclic dienes.[16] If we choose a C_{12} as a representative example, the following stoichiometric reactions can be written. The amount

$$5C_8H_{18} \longrightarrow 7C_4H_{10} + C_{12}H_{20} \quad (8)$$

$$22C_8H_{18} \longrightarrow 28C_5H_{12} + 3C_{12}H_{20} \quad (9)$$

$$12C_8H_{18} \longrightarrow 14C_6H_{14} + C_{12}H_{20} \quad (10)$$

$$26C_8H_{18} \longrightarrow 28C_7H_{16} + C_{12}H_{20} \quad (11)$$

of octane reacted for each lighter paraffin formed was calculated according to these equations. Except for the case where no methylcyclopentane was present the calculated extent of reaction is fairly insensitive to the stoichiometry chosen and the calculated number should be a good approximation of the true conversion. For the 0% methylcyclopentane case the calculation is only qualitative because the presence of unmeasured quantities of C_{10}–C_{12} paraffins in the hydrocarbon phase is indicated by the fairly large quantity of C_9 present.

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(16) N. C. Deno, D. B. Boyd, J. D. Hodge, C. U. Pittman, Jr., and J. O. Turner, *J. Am. Chem. Soc.*, **86**, 1745 (1964).

The Thermal Decomposition of Benzylidene-2-azidoanilines

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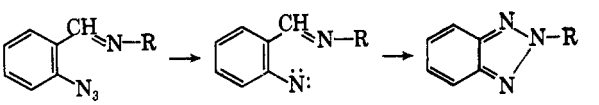
The synthesis and thermal decomposition of a series of benzylidene-2-azidoanilines are described. These decompositions resulted in a loss of nitrogen and intramolecular cyclization at the carbon atom of the azomethine linkage to produce 2-substituted benzimidazoles in good yields.

In a recent communication[1] from this laboratory, we described the synthesis and thermal decomposition of a series of 2-azidobenzylideneamines. These decompositions resulted in five-membered intramolecular cyclizations which produced indazoles in high yields. As an extension of the above investigation, we wish to



describe in this report the results of the decomposition of benzylidene-2-azidoanilines **1** in which the position of the carbon and nitrogen atoms in the azomethine linkages of the 2-azidobenzylideneamines is reversed.

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TABLE I

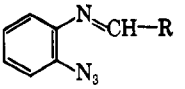
BENZYLIDENE-2-AZIDOANILINES

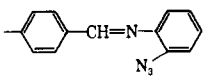
No.	Azide	Yield, %	M.p., °C.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
I	N-(2-Azidophenyl)succinimide	93	142	$C_{10}H_8N_4O_2$	55.55	55.60	3.73	3.68	25.94	25.88
II	2-Azidoaniline[a]	97	60–61	$C_6H_6N_4$	53.72	53.71[c]	4.51	4.72	41.77	41.76
III	Benzylidene-2-azidoaniline[b]	...	...	...	...	...	...	...	...	...
IV	4-Methylbenzylidene-2-azidoaniline[b]	...	...	...	...	...	...	...	...	...
V	4-Chlorobenzylidene-2-azidoaniline	63	52	$C_{13}H_9N_4Cl$	60.83	60.74	3.53	3.51	21.83	21.87
VI	4-Nitrobenzylidene-2-azidoaniline	88	132	$C_{13}H_9N_5O_2$	58.43	58.70	3.40	3.64	26.21	26.50
VII	1,4-Xylylidenebis(2-azidoaniline)	85	163–164	$C_{20}H_{14}N_8$	65.56	65.60	3.86	4.03	30.59	30.70

[a] Undergoes substantial decomposition when exposed to the atmosphere for 0.5 hr. [b] Viscous oils which could not be crystallized and which decomposed upon attempted short-path distillation. [c] Sample analyzed within 10 min. after preparation.

TABLE II

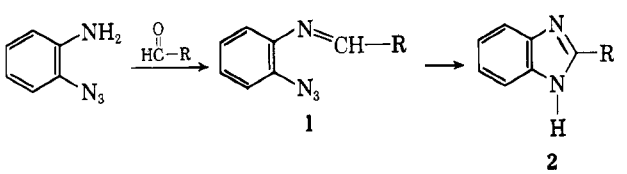
DECOMPOSITION OF BENZYLIDENE-2-AZIDOANILINES



No.	R	Dec. temp., °C.	Product	Yield, %	M.p., °C.	M.m.p.,[a] °C.
III	C_6H_5–	150[b]	2-Phenylbenzimidazole	45	293–294[c]	293–294
IV	4-$CH_3C_6H_4$–	140	2-(4-Methylphenyl)benzimidazole	50	282[d]	281–282
V	4-ClC_6H_4–	140	2-(4-Chlorophenyl)benzimidazole	96	296[e]	295–296
VI	4-$NO_2C_6H_4$–	140	2-(4-Nitrophenyl)benzimidazole[f]	96	315[g]	
VII		140–145	1,4-Phenylene-2,2′-dibenzimidazole[h]	85	475–490 dec.	475–490 dec.

[a] All the authentic samples for the mixture melting points were prepared by fusion of *o*-phenylenediamine with the appropriate acid in the general manner as described by Walther and Pulawski.[3] [b] 1,2-Dichlorobenzene. [c] Lit.[4] m.p. 291°. [d] Lit.[5] m.p. 268°. [e] Lit.[6] m.p. 303°. [f] Picrate m.p. 250–255°; the value of 250° dec. was reported by O. Fischer and F. Limmer [*J. prakt. Chem.*, **74**, 72 (1906)]. [g] Lit.[7] m.p. 322°. [h] *Anal.* Calcd. for $C_{20}H_{14}N_4$: C, 77.39; H, 4.51; N, 18.05. Found: C, 77.30; H, 4.56; N, 17.70.

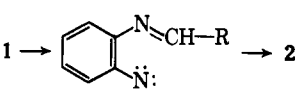
The synthesis of the benzylidene-2-azidoanilines was conveniently effected by the condensation of the appropriate benzaldehyde with 2-azidoaniline. The new azides prepared for this investigation are summarized in Table I. A smooth liberation of nitrogen occurred upon heating these azides in 1,2-dichlorobenzene at approximately 140°. As in the case of the 2-azidobenzylideneamines reported earlier, the thermal decomposition of these azides resulted in cyclization at the azomethine linkage. The results of the thermal decompositions of



these benzylidene-2-azidoanilines are summarized in Table II. The corresponding 2-substituted benzimidazoles **2** obtained were identified by (1) taking mixture melting points with authentic samples prepared[2] by the fusion of *o*-phenylenediamine with the appropriate acids, and (2) comparison of the melting points with values[3-6] reported in the literature.

The synthesis of 2-azidoaniline was accomplished by first converting 2-nitroaniline to the known succinimide.[7] The nitro group was then catalytically reduced in N,N-dimethylformamide. The resulting aniline was diazotized and converted to the azide by the conventional method.[8] The free amine was obtained by hydrolysis of the imide with strong base, and the desired 2-azidoaniline was extracted from the solution. This sequence, which is similar to that described by Smith, Hall, and Kan,[9] provided the necessary 2-azidoaniline in an over-all yield of approximately 75%. The protection of the amine by converting it to the imide circumvented the problems encountered in other possible syntheses. Alternate routes for the preparation of benzylidene-2-azidoaniline involving methods such as the selective reduction of 2-nitrophenyl azide or the diazotization of N-benzylidene-1,2-phenylenediamine were unsuccessful.

The thermal decomposition of the benzylidene-2-azidoanilines resulted in good yields of the corresponding 2-substituted benzimidazoles, particularly where the azides could be isolated and purified before decomposition. These yields were comparable to the yield of indazoles[1] (ranging from 75 to 97% with the majority being over 90%) obtained from the thermal decompositions of 2-azidobenzylideneamines. The results of these decompositions can be readily explained by a mechanism involving a univalent, uncharged, electron-deficient nitrogen atom. This intermediate is frequently called an azene, but has also been called a nitrene, imene, imine, and imidogen. It is believed that this intermediate, formed by the loss of nitrogen from the azide, attacked the carbon atom of the azomethine linkage to form the 2-substituted benzimidazoles.



(2) R. Walther and T. von Pulawski, *J. prakt. Chem.*, **59**, 249 (1899).
(3) K. Auers and F. V. Meyenburg, *Ber.*, **24**, 2386 (1891).
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(6) O. Hinsburg and F. Funcke, *Ber.*, **27**, 2191 (1894).
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(8) P. A. S. Smith and B. B. Brown, *J. Am. Chem. Soc.*, **73**, 2440 (1951).
(9) P. A. Smith, J. H. Hall, and R. O. Kan, *ibid.*, **84**, 485 (1962).

A review of the reactions of azene intermediates has been reported recently by Abramovitch and Davis.[10]

In the previous work the decomposition of 2-azidobenzylideneamines was shown to result in the attack of the azene at the nitrogen atom of the azomethine linkage, whereas, in the present system, the cyclization occurred at the carbon atom. Although the data is certainly incomplete, there is no evidence to indicate that the azene has a substantially greater affinity for either the carbon or the nitrogen atoms of the azomethine linkage in these systems.

Experimental[11,12]

N-(2-Aminophenyl)succinimide.—A solution of 44.0 g. (0.2 mole) of N-(2-nitrophenyl)succinimide[7] in 400 ml. of N,N-dimethylformamide was hydrogenated with 4.0 g. of 10% palladium on charcoal on a Parr shaker for 2 hr. The mixture was filtered free of catalyst and the solvent was removed at reduced pressure. The solid residue was triturated with ethanol yielding 35.0 g. (90%) of N-(2-aminophenyl)succinimide, m.p. 236–238° (lit.[7] m.p. 230–232°).

N-(2-Azidophenyl)succinimide (I).—A solution of 19.0 g. (0.1 mole) of N-(2-aminophenyl)succinimide in 100 ml. of concentrated hydrochloric acid and 500 ml. of water was cooled to −5°. The amine was diazotized by the slow addition of 7.5 g. of sodium nitrite in 50 ml. of water. A solution of 8.0 g. of sodium azide in 50 ml. of water was added to the solution. The precipitate was collected and dried yielding 20.0 g. (93%) of N-(2-azidophenyl)succinimide. An analytical sample was prepared by recrystallization from ethanol yielding white plates, m.p. 142°. An absorption band at 2140 cm.$^{-1}$ characteristic of the azido[13] group was observed in the infrared.

2-Azidoaniline (II).—A hydrolysis procedure similar to that described for N-(2-azidophenyl)phthalimide was used. A mixture of 5.0 g. of N-(2-azidophenyl)succinimide and 500 ml. of 10% sodium hydroxide solution was stirred at 65° for 2 hr. The mixture was cooled and extracted twice with 200 ml. of methylene chloride. The methylene chloride extract was dried with sodium sulfate and treated with decolorizing charcoal. The methylene chloride was removed at reduced pressure leaving 3.0 g. (97%) of crude 2-azidoaniline. The crude yellow-brown 2-azidoaniline was purified by dissolving repeatedly in a small amount of methanol and reprecipitating by the addition of water. Bright yellow needles melting at 61–63° (lit.[9] m.p. 63–63.5°) were obtained. These crystals darkened on prolonged exposure to the atmosphere and turned dark brown after 12 hr. Slightly lower yields were obtained when 22 g. (0.1 mole) of N-(2-azidophenyl)succinimide was hydrolyzed in the same quantity of base.

An azido[13] absorption band at 2130 cm.$^{-1}$ was observed in the infrared.

All the benzylidene-2-azidoanilines employed in this study were prepared by condensation of 2-azidoaniline with the appropriate benzaldehyde. The azides prepared in this manner are summarized in Table I. A typical example is given below.

4-Nitrobenzylidene-2-azidoaniline (VI).—To a solution of 2.0 g. of crude 2-azidoaniline in 50 ml. of ethanol, 2.0 g. of 4-nitrobenzaldehyde and a few drops of acetic acid were added. The mixture was heated for a few minutes. Upon cooling 3.5 g. (88%) of golden-colored 4-nitrobenzylidene-2-azidoaniline crystallized. An analytical sample was prepared by recrystallization from ethanol, m.p. 132°.

Thermal decompositions of all the azides were carried out in 1,2-dichlorobenzene under essentially the same conditions. The results are summarized in Table II. Pyrolysis of 4-chlorobenzylidene-2-azidoaniline is described below as a representative example.

2-(4-Chlorophenyl)benzimidazole.—A solution of 2.0 g. of 4-chlorobenzylidene-2-azidoaniline in 100 ml. of 1,2-dichlorobenzene was heated to 140°. The temperature was maintained at 140–145° for 3 hr. The solvent was then removed at reduced pressure. The solid, greenish residue was triturated with a benzene–hexane mixture yielding 1.7 g. (96%) of 2-(4-chlorophenyl)-benzimidazole, m.p. 288–294°. An analytical sample was prepared by recrystallization from ethanol, m.p. 296°.

Acknowledgment.—The authors are deeply indebted to Dr. L. Schieler for his helpful interest in this work and to Mr. S. Hotta for spectral and analytical measurements and valuable preparative assistance.

(10) R. A. Abramovitch and B. A. Davis, *Chem. Rev.*, **64**, 149 (1964).

(11) All melting points are uncorrected.

(12) Analysis were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich., and by Mr. S. Hotta of this laboratory.

(13) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, Chapter 15.

Free-Radical Chemistry of Peptide Bonds. I. Dealkylation of Substituted Amides[1]

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Potassium persulfate in aqueous dipotassium hydrogen phosphate dealkylated N-substituted and N,N-disubstituted amides to amides and N-alkylamides, respectively, in moderate yields. The dealkylated group appeared in the reaction mixture as the corresponding aldehyde or ketone. In addition to dealkylation, formamides were oxidized to carbon dioxide and ammonia. We believe these dealkylations proceed *via* radical attack on the carbon α to the amide nitrogen.

The chemically induced free-radical attack on model systems related to proteins in aqueous solutions has received little attention. Reaction of N,N-dimethylacetamide with peracetic acid in water solution[3] gave N-acetoxymethyl-N-methylacetamide in 13% yield and four hydroxamic acid derivatives. The reaction of simple amino acids with aqueous potassium persulfate[4] gave aldehydes containing one less carbon atom than the starting amino acid and quantitative yields of ammonia and carbon dioxide. The action of alkaline persulfate on tryptophan[5] yielded a complex mixture of products including anthranilic acid, 3-hydroxyanthranilic acid, and *o*-aminophenol.

Potassium persulfate was chosen for study of free-radical attack on model compounds containing the peptide bond, because its mode of decomposition and free-radical attack of other organic compounds[6] is well

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(2) A laboratory of the Western Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture, Albany, Calif.

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(4) K. Lang, *Z. Physiol. Chem.*, **241**, 68 (1936).

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