Ionic Reactions Occurring in Sulfuric Acid. V. Reactions of the 2,2,4-Trimethylpentyl Carbonium Ion

J. E. HOFMANN

Process Research Division, Esso Research and Engineering Company, Linden, New Jersey

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Tritium exchange, between concentrated sulfuric acid and 2,2,4-trimethylpentane, has been employed to study reactions of the corresponding alkyl carbonium ion. At 25°, the primary reactions of the 2,2,4-trimethylpentyl cation are β-scission and isomerization to the other trimethylpentyl isomers. Isomerization leads to a close approach to equilibrium among the four trimethylpentanes, but dimethylhexanes, also formed in fairly large quantities, arise from cracking and alkylation sequences rather than isomerization.

Selectivity to 2,2,4-trimethylpentane (isooctane) has, for some time, been a measure of quality in the acid catalyzed alkylation of isobutane with butenes. For this reason, many investigators have studied the reactions of isooctane with concentrated acid in an effort to determine what reactions control selectivity.[1-6] Although this work has shed much light on the reaction, certain questions, such as the mechanism of dimethylhexane formation during alkylation of butene-2 and isobutylene remain unanswered. (The formation of dimethylhexanes from butene-1 can be readily explained.[7])

As outlined in the previous paper,[8] the application of tritium exchange coupled with a radioassaying gas chromatograph permits a more detailed study of the reactions of alkyl carbonium ions. Thus, it is now possible to study reactions down to very low conversion levels, beyond the limits of ordinary gas chromatography, and also to evaluate the amount of internal return as compared to other reactions. That is, it is possible to measure the relative amount of a carbonium ion that is resaturated, by hydride transfer, to the corresponding paraffin as compared to other reactions.

The present work involved contacting 2,2,4-trimethylpentane with concentrated, tritiated sulfuric acid at room temperature. This work has been separated from the previous studies[8] because of the general complexity of the 2,2,4-trimethylpentane system. The initial carbonium ion can readily undergo isomerization, scission, or additional alkylation reactions. The purpose of this work was to ascertain the extent of each of these reactions and in particular to determine the primary source of dimethylhexanes. Various amounts of methylcyclopentane were included in the reaction system in order to study its effect on the various primary reactions and also to keep over-all conversion levels fairly low.

TABLE I

EFFECT OF METHYLCYCLOPENTANE CONCENTRATION

	Radioanalysis, %					
	Methylcyclopentane, vol. %					
	0	5	10	25	50	75
Isobutane	26.2	72.8	70.0	55.3	35.7	42.8
Isopentane	13.7	4.1	2.0	0.9	2.3	. . .
Isohexanes	10.7	2.2	1.3	. . .	. . .	. . .
Isoheptanes	9.1	. . .	. . .	. . .	. . .	. . .
2,2,4-Trimethylpentane	7.1	7.4	12.4	23.8	31.3	33.8
2,4- + 2,5-Dimethylhexane	8.0	4.9	5.1	3.2	3.7	2.2
2,2,3-Trimethylpentane		0.2	0.2	. . .	. . .	. . .
2,3,4-Trimethylpentane	3.0	3.0	5.1	10.3	14.1	13.4
2,3,3-Trimethylpentane 2,3-Dimethylhexane	4.3	2.9	3.7	4.7	10.9	7.2
3,4-Dimethylhexane	0.7	0.2	. . .	. . .	0.6	0.5
2,2,4- + 2,2,5-Trimethylhexane	17.0	1.4	. . .	. . .	. . .	. . .

TABLE II

EFFECT OF TIME AT 25 VOL. % OF METHYLCYCLOPENTANE

	Radioanalysis, %					
	Time, min.					
	10	15	30	40	60	80
Isobutane	55.3	58.7	48.0	50.9	62.7	56.5
Isopentane	0.9	0.6	0.3	0.9	0.2	0.5
Isohexanes	. . .	0.5	0.2	0.8	0.1	0.3
Isoheptanes	. . .	. . .	. . .	. . .	. . .	. . .
2,2,4-Trimethylpentane	23.8	22.5	27.7	25.2	20.2	19.7
2,4- + 2,5-Dimethylhexane	3.2	3.4	4.6	4.7	3.9	3.8
2,2,3-Trimethylpentane	. . .	0.2	0.3	. . .	. . .	. . .
2,3,4-Trimethylpentane	10.3	9.6	12.6	11.6	8.6	8.9
2,3,3-Trimethylpentane 2,3-Dimethylhexane	4.7	4.1	5.7	5.0	4.0	3.9
3,4-Dimethylhexane	. . .	. . .	. . .	. . .	. . .	0.3
2,2,4- + 2,2,5-Trimethylhexane		0.1	. . .	. . .	. . .	0.3

Results

Distribution of reaction products, based on radioassay, at methylcyclopentane concentrations from 0 to 75 vol. %, are shown in Table I. Each of these experiments was carried out for 10 min. The effect of time, at 25 vol. % of methylcyclopentane, is shown in Table II. Because hydrocarbons of different molecular weights have varying numbers of exchangeable hydrogens, the distribution by radioassay cannot be related directly to chemical composition. Fortunately in several experiments, where conversion was reasonably high, sufficient material was present in the gas chromatographic sample to measure the molar specific activity of a number of the components. These values could then be used to convert the radioanalysis to actual chemical composition.

For comparison purposes, the specific activity of isobutane, which was found to be constant in all experiments, has been defined as 9.0. Using this basis, spe-

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(1) S. F. Birch and A. E. Dunstan, *Trans. Faraday Soc.*, **35**, 1013 (1939).

(2) S. H. McAllister, J. Anderson, S. A. Ballard, and W. E. Ross, *J. Org. Chem.*, **6**, 647 (1941).

(3) F. C. Whitmore and H. H. Johnson, Jr., *J. Am. Chem. Soc.*, **63**, 1481 (1941).

(4) F. Morton and A. R. Richards, *J. Inst. Petrol.*, **34**, 290, 133 (1948).

(5) K. N. Campbell and W. E. Erner, Office of Naval Research, Contract No. N7-ONR-439, Aug. 9, 1950.

(6) C. A. Zimmerman, J. T. Kelly, and J. C. Dean, *Ind. Eng. Chem.*, **1**, 124 (1962).

(7) L. Schmerling, *J. Am. Chem. Soc.*, **68**, 275 (1946).

(8) J. E. Hofmann, *J. Org. Chem.*, **29**, 3039 (1964).

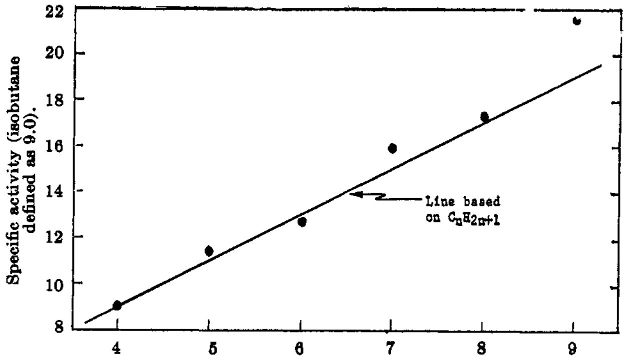

Fig. 1.—Specific activity of reaction products.

TABLE III

EFFECT OF METHYLCYCLOPENTANE CONCENTRATION ON PRODUCT COMPOSITION[a]

	Methylcyclopentane, vol. %					
Product	0	W	10	25	50	75
Isobutane	37.0	82.6	80.8	70.7	51.1	58.5
Isopentane	15.9	3.8	1.8	0.9	2.7	...
Isohexanes	10.5	1.7	1.0	...	...	...
Isoheptanes	7.8	...	...	...	...	...
2,2,4-Trimethylpentane	5.4	4.4	7.6	16.1	23.8	24.5
2,4- + 2,5-Dimethylhexane	6.0	2.9	3.1	2.2	2.9	1.6
2,2,3-Trimethylpentane		0.1	0.1	...	...	...
2,3,4-Trimethylpentane	2.3	1.8	3.1	6.9	10.7	9.7
2,3,3-Trimethylpentane 2,3-Dimethylhexane	3.3	1.7	2.3	3.2	8.3	5.2
3,4-Dimethylhexane	0.6	0.1	...	...	0.4	0.4
2,2,4- + 2,2,5-Trimethylhexane	11.4	0.8	...	...	...	...
Isobutane by chemical analyses	11.7	0.93	0.47	0.28	0.12	0.11
Extent of reaction[b]	19.3	0.84	0.44	0.31	0.20	0.16

[a] Values are given as mole per cent. [b] Values are given as per cent.

cific activities of other reaction products are shown in Fig. 1. It is apparent that the specific activity of each component is equivalent to its total number of hydrogens minus one. This is similar to results obtained by Beeck and co-workers[9] and arises because exchange and intramolecular hydride and methide transfers are fast compared to intermolecular hydride transfer. Knowledge of relative activities then permits the calculation of the composition on a molar basis and these data are shown in Tables III and IV.

As far as can be determined, the specific activity of each C_8 isomer formed during the reaction is constant. In order words, the per cent of radioassay amongst the C_8 isomers is equivalent to mole per cent. The specific activity of that portion of 2,2,4-trimethylpentane which underwent reaction and returned to starting material is, of course, impossible to measure. However, it will be seen that equilibrium appears to exist among the trimethylpentanes and for this reason, the specific activity of 2,2,4-trimethylpentane is assumed to be the same as the other C_8 isomers.

The fraction of 2,2,4-trimethylpentane which actually undergoes reaction, the extent of reaction, is shown in the last row of Tables III and IV. This number is calculated from the product composition and the isobutane formed, which was sufficient in all cases to analyze chemically. (See the Experimental section for details of this calculation.)

TABLE IV

EFFECT OF TIME AT 25 VOL. % OF METHYLCYCLOPENTANE ON PRODUCT COMPOSITION[a]

	Time, min.					
Product	10	15	30	40	60	80
Isobutane	70.7	71.8	63.7	66.4	76.0	73.8
Isopentanes	0.9	0.6	0.3	0.9	0.2	0.5
Isohexanes	...	0.4	0.1	0.8	0.1	0.3
Isoheptanes	...	...	...	...	...	...
2,2,4-Trimethylpentane	16.1	14.8	19.5	17.3	13.0	13.6
2,4- + 2,5-Dimethylhexane	2.2	2.2	3.2	3.3	2.5	2.6
2,2,3-Trimethylpentane	...	0.1	0.3	...	...	...
2,3,4-Trimethylpentane	6.9	6.3	8.9	8.0	5.6	6.1
2,3,3-Trimethylpentane 2,3-Dimethylhexane	3.2	2.7	4.0	3.4	2.5	2.7
	...	...	...	...	...	0.3
2,2,4- + 2,2,5-Trimethylhexane	...	0.6	...	...	...	0.1
Isobutane by chemical analyses	0.28	0.36	0.57	0.62	2.0	1.9
Extent of reaction[b]	0.31	0.40	0.73	0.76	2.05	2.02

[a] Values are given as mole per cent. [b] Values are given as per cent.

Discussion

The specific activity data presented in Fig. 1 provides substantial evidence that all hydrogens, except one, on each isoparaffinic product have been completely equilibrated with the acid. Since only those hydrogens contiguous to the cationic center can undergo exchange, this means that methide and hydride shifts must be rapid enough so that at one time or another each hydrogen is able to exchange with the acid. This finding has been alluded to during several previous investigations.[8-10] The final nonequilibrated hydrogen is the result of intermolecular hydride transfer from another molecule of hydrocarbon.

This conclusion has considerable bearing upon the mechanism of dimethylhexane formation during butene alkylation. A consequence of rapid intramolecular hydride and methide shifts is that thermodynamic equilibrium should be approached wherever isomerization is possible. Such was the case with isohexanes and isoheptanes as long as no change in chain branching was involved.[8] This also holds for the trimethylpentanes as evidenced by the ratio of 2,2,4-trimethylpentane to 2,3,4-trimethylpentane, presented in Fig. 2 and 3 which proves to be independent of conversion level, time, and methylcyclopentane concentration. In contrast, methylcyclopentane concentration has a profound effect on dimethylhexane formation. At low concentration of methylcyclopentane, the dimethylhexanes become a major fraction of the octane isomers formed. The ratio of dimethylhexanes to trimethylpentanes is also not a direct function of time or conversion level. A ratio of 2,2,4-TMC_5/2,4- + 2,5-DMC_6 of 5 is observed after 80 min. with 25 vol. % of $MCyC_5$ at a conversion level of about 2.7% compared to a ratio of 1.5 after 10 min.

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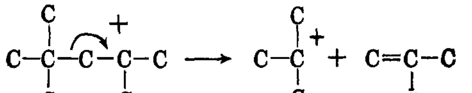
(9) D. P. Stevenson, C. D. Wagner, O. Beeck, and J. W. Otvos, *J. Am. Chem. Soc.*, **74**, 3269 (1952).

(10) J. E. Hofmann and A. Schriesheim, *ibid.*, **84**, 957 (1962).

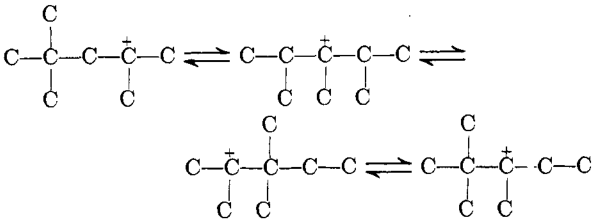
with 5 vol. % of $MCyC_5$ at only 1.1% conversion. This is not what one would expect from a simple isomerization mechanism and indicates that an alternative path must exist for dimethylhexane formation, particularly at low methylcyclopentane concentrations.

To present possible alternatives we must first consider what information is already available. It is fairly well accepted that isomerizations involving a change in chain branching are slow in sulfuric acid.[11] Recent evidence has been presented[8,12] that indicates that such reactions may never occur but actually result from an alkylation and cracking sequence. In the present work, neglecting for a moment the data at 0% $MCyC_5$, it is apparent that the primary reaction of the 2,2,4-trimethylpentyl cation is fission to fragments of *t*-butyl cation and isobutylene (reaction 1), and isomerization



$$\mathrm{C{-}\underset{C}{\overset{C}{C}}{-}C{-}\underset{C}{\overset{+}{C}}{-}C \longrightarrow C{-}\underset{C}{\overset{C}{C}}{}^{+} + C{=}\underset{C}{C}{-}C} \qquad (1)$$

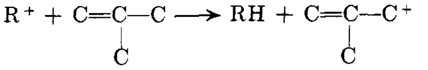
to the other possible trimethylpentyl carbonium ions (reaction 2). (In this reaction no attempt has been



$$\mathrm{C{-}\underset{C}{\overset{C}{C}}{-}C{-}\underset{C}{\overset{+}{C}}{-}C \rightleftharpoons C{-}\underset{C}{C}{-}\underset{C}{\overset{+}{C}}{-}\underset{C}{C}{-}C \rightleftharpoons C{-}\underset{C}{\overset{+}{C}}{-}\underset{C}{\overset{C}{C}}{-}C{-}C \rightleftharpoons C{-}\underset{C}{\overset{C}{C}}{-}\underset{C}{\overset{+}{C}}{-}C{-}C} \qquad (2)$$

made to formulize the individual hydride and methide shifts required for the projected transformation.) At high methylcyclopentane concentration, hydride transfer between the naphthene and the octyl and *t*-butyl cations predominates. This would account for a high yield of isobutane and trimethylpentanes.

At low concentrations of the naphthene, other reactions are possible. The isobutylene formed in reaction 1 may become a competitive source of hydride (reaction



$$\mathrm{R^+ + C{=}\underset{C}{C}{-}C \longrightarrow RH + C{=}\underset{C}{C}{-}C^+} \qquad (3)$$

3). This reaction has been proposed previously[13] and leads to dimethylhexane formation by alkylation (reaction 4) and subsequent hydrogen transfer reactions. (It

$$\mathrm{C{=}\underset{C}{C}{-}C^+ + C{=}\underset{C}{C}{-}C \longrightarrow C{=}\underset{C}{C}{-}C{-}C{-}\underset{C}{\overset{+}{C}}{-}C} \qquad (4)$$

was shown in previous work[13] that the reaction of 2,5-dimethyl-1,5-hexadiene with isobutane in sulfuric acid does in fact lead to dimethylhexanes.) Thus one would expect increasing amounts of dimethylhexanes as the methylcyclopentane concentration is decreased.

As an alternative, an alkylation cracking sequence can also be considered. Addition of the 2,2,4-trimethylpentyl cation, or the cations of 2,2,3- and 2,3,4-trimethylpentane, to isobutylene leads to a pentamethyl heptane (reaction 5). This in turn can rearrange, without any change in chain branching (*via* a series of hydride and methide shifts), to another pentamethylheptane (reaction 6) which is capable of splitting, by β-fission, to fragments of *t*-butyl cation and dimethylhexene (reaction 7). The olefin would then be saturated by hydrogen transfer.[14]

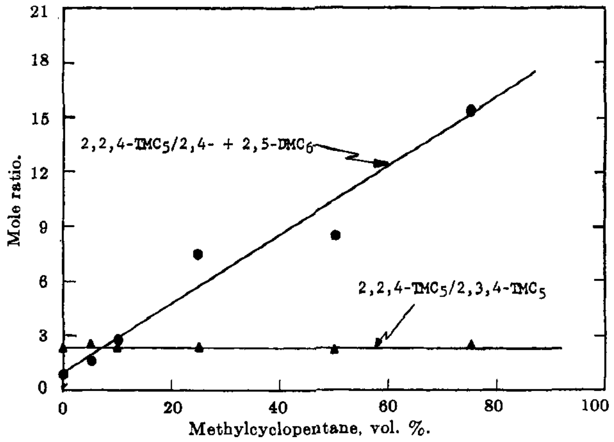


Fig. 2.—Effect of $MCyC_5$ on distribution of octanes.

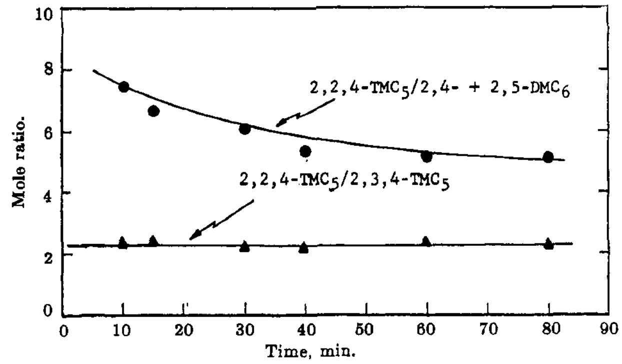
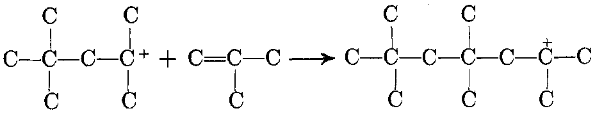
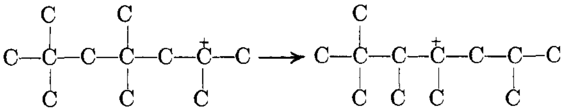


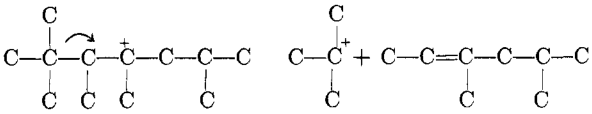
Fig. 3.—Effect of time on distribution of octanes.



$$\mathrm{C{-}\underset{C}{\overset{C}{C}}{-}C{-}\underset{C}{\overset{C}{C}}{}^{+} + C{=}\underset{C}{C}{-}C \longrightarrow C{-}\underset{C}{\overset{C}{C}}{-}C{-}\underset{C}{\overset{C}{C}}{-}C{-}\underset{C}{\overset{+}{C}}{-}C} \qquad (5)$$



$$\mathrm{C{-}\underset{C}{\overset{C}{C}}{-}C{-}\underset{C}{\overset{C}{C}}{-}C{-}\underset{C}{\overset{+}{C}}{-}C \longrightarrow C{-}\underset{C}{\overset{C}{C}}{-}\underset{C}{C}{-}\underset{C}{\overset{+}{C}}{-}C{-}\underset{C}{C}{-}C} \qquad (6)$$



$$\mathrm{C{-}\underset{C}{\overset{C}{C}}{-}\underset{C}{C}{-}\underset{C}{\overset{+}{C}}{-}C{-}\underset{C}{C}{-}C \quad C{-}\underset{C}{\overset{C}{C}}{}^{+} + C{-}C{=}\underset{C}{C}{-}C{-}\underset{C}{C}{-}C} \qquad (7)$$

Because of the number of intermediates involved, this alkylation–cracking scheme would not be selective and one would anticipate the formation of other species such as pentanes, hexanes, and heptanes. Inspection of Table I indicates that the concentration of these species do increase with decreasing methylcyclopentane concentration. Hence, this scheme is not unreasonable as a mechanism for a portion of the dimethylhexane formation. However, a statistical analysis of the situation indicates that any enhanced selectivity to dimethylhexanes would be highly unlikely. Of the 27 possible pentamethylheptane isomers, 17 are capable of splitting by β-fission (the restriction is imposed that reaction must start and end with a tertiary cation). Two of

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(11) H. Pines and J. M. Mavity, "Chemistry of Petroleum Hydrocarbons," Vol. 3, Reinhold Publishing Corp., New York, N. Y., 1955, p. 34.

(12) G. J. Karabatsos and F. M. Vane, *J. Am. Chem. Soc.*, **85**, 729 (1963).

(13) J. E. Hofmann and A. Schriesheim, *ibid.*, **84**, 953 (1962).

(14) J. E. Hofmann, *J. Org. Chem.*, **29**, 1497 (1964).

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

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

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

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

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

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.

Acknowledgment.—The author wishes to thank the Esso Research and Engineering Company for permission to publish this work, and, specifically, Dr. A. Schriesheim for his encouragement and suggestions.

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[15] A. E. Messner, D. M. Rosie, and P. A. Argabright, *Anal. Chem.*, **31**, 230 (1959).

[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

LEROY KRBECHEK AND HIDEYO TAKIMOTO

Chemical Propulsion Department, Laboratories Division, Aerospace Corporation, El Segundo, California

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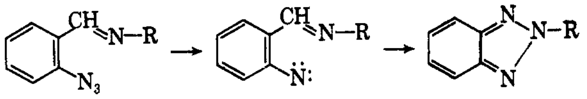
The synthesis and thermal decomposition of a series of benzylidene-2-azidoanilines are described. These decompositions resulted in a loss of nitrogen and intramolecular cyclization at the carbon atom of the azomethine linkage to produce 2-substituted benzimidazoles in good yields.

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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[1] L. Krbechek and H. Takimoto, *J. Org. Chem.*, **29**, 1150 (1964).