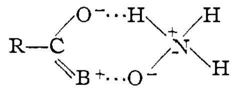
with the carbonyl group and is not an intrinsic property of the oxygen atom since alkylation of hydroxylamine occurs on the nitrogen atom. Furthermore, a mechanism of this kind provides an explanation for the increase in the ratio of O- to N-acylation observed with acylating agents containing bases with increasing electron-donating ability[2] since an increase in the positive character of the base through either inductive or resonance effects would be expected to aid the preliminary alignment of the hydroxylamine molecule favoring oxygen attack



The rapid rate of this reaction, which occurs in aqueous solution, is somewhat analogous to the rapid rates of enzymatic reactions and provides some experimental analogy for the proposed acylation of a serine hydroxyl group in the active site of a number of enzymes (*cf.* ref. 13 and references therein). Although the serine hydroxyl group is ordinarily only weakly nucleophilic, its reactivity may be increased markedly if it is located on the enzyme surface in proper spatial relationship to a nitrogen-containing group which can perform the same function as does the amino group of hydroxylamine.

The reaction of hydroxylamine with O-acylhydroxylamine, in contrast to that with *p*-nitrophenyl acetate, shows a rate maximum at *p*H 6.2, a rate proportional to more than the first power of the hydroxylamine concentration, and a marked rate acceleration with phosphate buffer. These effects, which are similar to those observed in oxime and semicarbazone formation,[14] suggest that this reaction is subject to general acid catalysis by the hydroxylammonium ion and by phosphate, although the lack of precise agreement with the rates calculated for such a mechanism alone as well as the remarkable effectiveness of phosphate in accelerating the reaction over a wide range of *p*H suggest that other factors which are as yet unexplained may be of importance in this reaction. The observation that acid catalysis does not appear to be of importance in the reaction with *p*-nitrophenyl acetate lends additional support to the hypothesis that the hydroxylamine molecule is itself acting as an acid as well as a base in this reaction. The possibility that the reaction of hydroxylamine with ketones and aldehydes is initiated by a rapid step not requiring a separate acid catalyst is currently under investigation.

Experimental

Preparations and determinations were carried out as described in the preceding paper.[2] Methoxyamine hydrochloride (Eastman Kodak Co.) was neutralized with NaOH immediately before use. Acetohydroxamic acid, m.p. 90–91°, from acetic anhydride and neutralized aqueous hydroxylamine hydrochloride, was recrystallized from ethanol and from ethyl acetate. Incubations were carried out in a water-bath at 25.0 ± 0.1° except where otherwise specified. Ethylenediaminetetraacetic acid was added to reaction mixtures containing O-acylhydroxylamine to avoid occasional erratic results apparently due to a trace metal-catalyzed decomposition of O-acylhydroxylamine; this chelating agent did not itself otherwise affect the reaction. First-order rate constants, k_1, were calculated, using the formula $k_1 = (0.693/t_{1/2})$, from the half-times of reaction which were determined graphically from plots of the extent of the reaction, $x_\infty - x_t$, against time on semilogarithmic graph paper. Second-order rate constants were calculated from the slope of the plot of k_1 against concentration of the second reactant. The rate constants are reproducible to within approximately ±5%.

Acknowledgments.—The author wishes to express his appreciation to Professor R. B. Woodward for his hospitality in providing laboratory space and facilities for much of this work and to the U. S. Public Health Service and the National Science Foundation for financial support.

Waltham Mass.

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[13] H. Gutfreund and J. M. Sturtevant, *Proc. Natl. Acad. Sci.*, **42**, 719 (1956).

[14] E. Barrett and A. Lapworth, *J. Chem. Soc.*, **93**, 85 (1908); J. B. Conant and P. D. Bartlett, This Journal, **54**, 2881 (1932).

[Contribution from Avery Laboratory, University of Nebraska]

Reactions of Amines. III. Pyrolysis of N-Alkylacetamides[1,2]

By Henry E. Baumgarten, Frank A. Bower,[3] Robert A. Setterquist[4] and Robert E. Allen

Received March 20, 1958

The pyrolyses of a number of N-alkyl- and N-alkyl-N-methylacetamides have given the corresponding olefins. The reactions required somewhat higher temperatures than the pyrolyses of the corresponding alkyl acetates and first indications were that the former were less selective in the direction of elimination.

The pyrolysis of simple amides to form nitriles is a well known reaction, but the pyrolysis of N-alkylamides appears to have received little study. As far as we have been able to determine Ritter and Minieri[5] were the first to observe that the liquid phase pyrolysis of N-*t*-alkylacetamides gave the corresponding olefins and acetonitrile. They mentioned also the facile acid-catalyzed decomposition of these amides into apparently the same olefins. Wiley, Ketterer and Reed[6] have reported a similar ready elimination in the acid-catalyzed decomposition of N-(*t*-octyl)-*p*-ethylbenzenesulfonamide, which gave isoöctene (2,3,4-trimethyl-2-pentene) and *p*-ethylbenzenesulfonamide. Cook, Dickson, Ellis and Loudon[7] have described, among other

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[1] Paper II, This Journal, **79**, 3145 (1957).

[2] This work was supported in part by grant G-3689 of the National Science Foundation.

[3] Standard Oil Co. (of Indiana) Fellow, 1951–1953.

[4] Minnesota Mining and Manufacturing Co. Fellow, 1955–1956.

[5] J. J. Ritter and P. P. Minieri, This Journal, **70**, 4045 (1948).

[6] R. H. Wiley, C. C. Ketterer and S. F. Reed, *ibid.*, **76**, 4996 (1954).

[7] J. W. Cook, C. T. Dickson, D. Ellis and J. D. Loudon, *J. Chem. Soc.*, 1078 (1949).

examples, the thermal decomposition of N-cyclohexylacetamide in xylene solution in the presence of phosphorus pentoxide, which gave cyclohexene and acetonitrile. A recent report by Bailey and Bird[8] on the formation of olefins from the vapor phase pyrolysis of a number of substituted amides prompts us to describe experiments carried out in this Laboratory on the pyrolysis of several N-alkyl- and N-alkyl-N-methylacetamides.

The acetyl derivatives of two types of amines were studied, simple primary amines and secondary amines in which one of the alkyl groups was methyl. The amines used have either been described before[1] or were prepared by techniques now more or less conventional which are presented in the Experimental section. The acetyl derivatives of the secondary amines were prepared by treatment of the amine with acetic anhydride. Although this same technique was used with fair success with the primary amines, often it gave mixtures of the desired amide with other substances of undetermined structure thought to be the diacylimides. A more satisfactory procedure for the preparation of amides from the primary amines consisted of treating carbon tetrachloride solutions of equimolar amounts of the amine and triethylamine with one equivalent of acetyl chloride. This procedure gave high yields of the amide, substantially free from by-products.

N-(1-Methylcyclohexyl)-acetamide was prepared directly in 72% yield by the Ritter[5,9] reaction using 1-methylcyclohexanol and acetonitrile in sulfuric acid. Inasmuch as a quantity of the acetate of 1-methylcyclohexanol was on hand, we set out to determine whether or not the ester could be substituted for the free alcohol in the Ritter reaction. The amide was obtained in 49% yield, but the reaction was not as clean and the product required more intensive purification.

TABLE I

PYROLYSIS OF N-ALKYLACETAMIDES

Run[a]	Amide	Temp.,[b] °C.	Rate, g./min.	Olefin fraction[c] Conversion, %	Olefin fraction[c] Yield, %
1	$CH_3(CH_2)_5NHAc$	555	0.76	0	0
2		560	.64	4	23
3		592	.43	8	56
4*		592	.16	31	
5	$C_6H_5CH_2CH_2N(CH_3)Ac$	520	.15		31
6		555	.12		22
7		580	.13		18
8*	$C_6H_{11}CH_2NHAc$[d]	570	.32	22	59
9	$C_6H_{11}CH_2N(CH_3)Ac$[d]	560	.15	21	45
10*		592	.14	24	54
11	$C_6H_{11}NHAc$[d]	500	.16	0	0
12		500	.47	0	0
13		540	.17	41[e]	73
14*		588	.15	37[f]	95
15	$C_6H_{11}N(CH_3)Ac$[d]	425	.26	0	0
16		480	.18	0.6	32
17		545	.24	46[g]	58
18*		560	.20	44[h]	67
19*		567	.40	27[i]	59
20		575	.16	42[j]	55
21*		586	.24	97[k]	97
22		600	.13	40[l]	55

[a] See footnote 10. [b] Range ±6°. [c] Crude product (liquefiable in Dry Ice–ethanol), calculated on assumption that entire product was olefin(s) expected. [d] C_6H_{11} = cyclohexyl. [e] Crude cyclohexene, 98%; crude butadiene, 2%. [f] Crude cyclohexene, 65%; crude butadiene, 35% (actual butadiene content, 69% by weight). [g] Crude cyclohexene, 83%; crude butadiene, 17%. [h] Crude cyclohexene; no butadiene fraction. [i] Crude cyclohexene, 78%; crude butadiene, 22%. [j] Crude cyclohexene, 55%; crude butadiene, 45%. [k] Crude cyclohexene, 46%; crude butadiene, 54%. [l] Crude cyclohexene; butadiene not recovered.

TABLE II

PYROLYSIS OF N-(1-METHYLCYCLOHEXYL)-ACETAMIDE

Run[a]	Temp.,[b] °C.	Rate,[c] g./min.	Conversion, %	Yield, %	Fraction *Exo*[d]	Fraction *Endo*[e]
23*	470	0.18	3.3	76	0.25	0.75
24*	515	.25	17	72	.29	.71
25*	540	.16	65	83	.30	.70
26*	540	.52	23	78	.22	.78
27*	555	.27	60	90	.25	.75
28*	560	.07	72	72	.27	.73

[a] See footnote 10. [b] Range ±6°. [c] Average run was 0.1 mole. [d] Methylenecyclohexane. [e] 1-Methylcyclohexene plus any 3-methylcyclohexene (maximum *ca.* 0.5%).

The amides were pyrolyzed by dropping them through a Pyrex or Vycor glass tube packed with $^1/_{16}$th-in. glass helices and heated to various temperatures by a tube furnace. The results of several typical pyrolyses are given in Tables I and II.[10] From these data it is apparent that the pyrolysis of N-alkylacetamides requires substantially higher temperatures than the pyrolysis of the acetates of the corresponding alcohols (which, in our hands, seldom have required temperatures greater than 500°). Acetamides in which the N-alkyl group was secondary or tertiary pyrolyzed at sufficiently low temperatures and in sufficiently good yields to suggest that the reaction may have limited application in preparative work; however, in its present form it does not appear attractive as a degradative tool. On the other hand, acetamides in which the N-alkyl group was primary required temperatures near 600° for even very low yields of olefin. At these temperatures the reaction became quite complex and secondary degradation reactions became important. For example, the gas chromatogram for the volatile organic fraction obtained in the pyrolysis of N-cyclohexylmethylacetamide had twenty-one clearly defined peaks, that for the pyrolysis of N-*n*-hexylacetamide (at 592°) had eleven. Even so the situation was no more complicated than that in the pyrolysis of alkyl phosphates.[11] Thus, the hexene fraction obtained from the pyrolysis of dimethyl *n*-hexyl phosphate at 400°, reported earlier[11] to be a mixture of at least three olefins (by infrared spectra), has now been shown by gas chromatog-

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[8] W. J. Bailey and C. N. Bird, Abstracts of Papers, American Chemical Society Meeting, New York, N. Y., Sept. 8–13, 1957, p. 64P.

[9] J. J. Ritter and J. Kalish, THIS JOURNAL, **70**, 4048 (1948).

[10] Inasmuch as our first experiments soon established that amide pyrolysis lacked some of the essential features of a useful degradative tool, and as such was inferior to the Cope amine oxide pyrolysis or the Hofmann degradation, our study was carried out more or less incidental to other work and extended over a period of six years. Considerable differences in experimental technique and methods of analysis have been inevitable. Only the most recent pyrolyses have been examined using gas chromatography as the analytical tool. These are indicated in Table I by an asterisk after the run number.

[11] H. E. Baumgarten and R. A. Setterquist, THIS JOURNAL, **79**, 2605 (1957).

raphy to be a mixture consisting largely of the three olefins but containing sixteen other substances in lesser amounts as well. The by-products in amide pyrolysis appeared to be largely thermal in origin, for in general below 600° the pyrolyses were accompanied by little or no carbon formation, which has been causally related to isomerization reactions.[12] It should be noted that, although the incidence of by-products was high in number at temperatures above 550°, the principal product was still the expected olefin. The sole exceptions to this observation thus far have been N-cyclohexylmethylacetamide and N-cyclohexylmethyl-N-methylacetamide, which gave two olefins, methylenecyclohexane and a second olefin, tentatively identified as cyclohexene (*vide infra*), as major products as well as smaller amounts of other substances.

The pyrolysis of N-alkyl-N-methylacetamides took place at about the same or somewhat lower temperatures than that of the corresponding N-alkylacetamides. The reaction was not as clean as that with the simpler amides and avoiding the formation of carbon was more difficult.

In the pyrolysis of simple acyclic and alicyclic alkyl acetates the direction of elimination has been shown to follow the Hofmann rule.[12] Both inductive[12] and steric effects[13–15] have been suggested as controlling factors in this elimination, although the weight of recent evidence appears to support the latter. The pyrolysis of amine oxides derived from acyclic amines leads to a nearly statistical distribution of olefins with a slight preference over the statistical ratio for Saytzev elimination, and this result has been interpreted as indicating that the transition state for amine oxide pyrolysis probably has more double bond character than the transition state for the dehydroacetoxylation reaction.[16] In the pyrolysis of several alicyclic amine oxides the elimination followed largely the Saytzev rule.[17] The sole exception was N,N-dimethyl-(1-methylcyclohexyl)-amine N-oxide for which Hofmann elimination predominated.[1,17] Throughout the various recent studies of elimination reactions cited above those involving the 1-methylcyclohexyl group have been unique, leading to the nearly exclusive formation of methylenecyclohexane (Hofmann product), whether by acetate,[12,14] amine oxide[1,17] or quaternary ammonium hydroxide[17] pyrolyses. This high order of selectivity has been attributed to the unique steric factors operative in this system.[1,14,17] Since Bailey and Bird[8] have shown that the pyrolysis of acyclic amides is less selective than that of the corresponding alkyl acetates, both Hofmann and Saytzev products being formed, it was of interest to examine the pyrolysis of N-(1-methylcyclohexyl)-acetamide to determine whether or not the selectivity apparently characteristic of the 1-methylcyclohexyl group would be observed. The results of this study are given in Table II.

From these data it is apparent that the pyrolysis of this amide gives largely the Saytzev product, 1-methylcyclohexene (*i. e.*, the thermodynamically more stable olefin), rather than the Hofmann product, methylenecyclohexane, in a ratio of about 3 to 1. The statistical ratio, based on available hydrogen atoms, is 4 to 3. This selectivity appeared to be independent to a large extent of the rate of addition of the amide and of the temperature at which the pyrolysis was conducted. These pyrolyses were extremely clean with little or no carbonization occurring. Although, as in the other pyrolyses, the number of by-products was large, the amount of by-product formation was small. Even at the highest temperature the estimated total of these extraneous by-products was less than 5%. That the major source of 1-methylcyclohexene probably was not the isomerization of methylenecyclohexane is indicated by the results of the pyrolyses of N-cyclohexylmethylacetamide and N-methyl-N-cyclohexylmethylacetamide (*vide infra*), for the ratios of methylenecyclohexane to 1-methylcyclohexene were 12.8 to 1 and 11.2 to 1, respectively, in these eliminations.

The implication of these results (together with those of Bailey and Bird[8]) is that in this pyrolysis steric (or inductive) effects no longer control the course of the elimination. The transition state is probably found well along the reaction coördinate, so that the products serve as a reasonable model for the transition state.[18] Resonance stabilization of the incipient olefin thus becomes an important factor in the determination of the course of the elimination. The extent of bond breaking in the transition state is apparently greater for the amide pyrolysis than for the amine oxide pyrolysis or alkyl acetate pyrolysis.

The pyrolyses of N-cyclohexylmethyl- and N-methyl-N-cyclohexylmethylacetamide appear to be unique in that the products contained substantial amounts of degraded and isomerized materials. The product from each amide contained, in addition to the expected methylenecyclohexane, a small amount of 1-methylcyclohexene and a surprisingly large amount of cyclohexene, as indicated by the product analyses in Table III. Inasmuch as only a small amount of each of the amides was available, only a preliminary study of these reactions was possible, but the identification of cyclohexene was fairly conclusive.[19] Several mechanisms can be

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(12) W. J. Bailey and C. King, This Journal, **77**, 75 (1955); W. J. Bailey, J. Hewitt and C. King, *ibid.*, **77**, 357 (1955).

(13) T. D. Nevitt and G. S. Hammond, *ibid.*, **76**, 4124 (1954).

(14) S. Siegel and M. Dunkel, Abstracts of Papers, Meeting of the American Chemical Society, Dallas, Texas, April 8–13, 1956, p. 28N.

(15) C. H. DePuy and R. E. Leary, This Journal, **79**, 3705 (1957).

(16) A. C. Cope, N. A. LeBel, J. Lee and W. R. Moore, *ibid.*, **79**, 4720 (1957).

(17) A. C. Cope, C. L. Bumgardner and E. E. Schweitzer, *ibid.*, **79**, 4729 (1957).

(18) G. S. Hammond, *ibid.*, **77**, 334 (1955).

(19) The retention volumes of the unknown substance on two different liquid phases (Perkin–Elmer packing B and silver nitrate–glycol) were identical with those of cyclohexene. The infrared spectrum of a synthetic mixture of acetonitrile, cyclohexene, methylenecyclohexane and 1-methylcyclohexene of the composition indicated by the chromatogram was very nearly identical with that of the pyrolysate, and every peak in the infrared spectrum of cyclohexene appeared in the spectrum of the pyrolysate. One possible source of cyclohexene would be by contamination of the amines from which the amides were prepared with cyclohexylamine or N-cyclohexyl-N-methylamine. However, since the amines were prepared by lithium aluminum hydride reduction of the appropriate cyclohexanecarboxamide, this possibility seems remote. A second possibility for the indirect introduction of cyclohexene into the pyrolysate would be through secondary pyrolysis of methylenecyclohexane and/or 1-methylcyclohexene. However, when a mixture of these materials in the ratio of 1.00 to 2.43 was pyrolyzed at a rate of 0.40 g./min. at 592°, the ratio dropped only to 1.00 to 2.37

written to explain the formation of cyclohexene in these pyrolyses, but, inasmuch as these mechanisms appear to be susceptible to experimental verification, discussion of them will be deferred.

Our experiments were designed to afford the maximum recovery of unreacted amide and maximum yield of olefin. Unfortunately the technique employed often obscured the nature of the principal by-product, acetamide or acetonitrile, in the pyrolyses of the N-alkylacetamides. Bailey and Bird[8] have reported that they obtained largely acetamide. The pyrolysis of acetamide under a variety of conditions has been reviewed by Hurd,[20] who has indicated that acetonitrile, ketene, ammonia and methane, as well as unreacted acetamide, may be formed. We have found at least traces of all of these substances in our pyrolysates (by infrared and gas chromatographic analysis). In most of our pyrolyses in which the volatile fractions were isolated by simple distillation, the distillate came over in two phases (occasionally three). The olefin phase contained part of the acetonitrile (up to 29% of the amount expected based on the olefin yield), reflecting the solubility of the nitrile in the olefin in the presence of an aqueous phase. The second phase consisted largely of water and acetonitrile (with a small amount of ammonium hydroxide). From the relative amounts of the two phases we have inferred that acetonitrile (rather than acetamide) was the principal by-product, although some acetamide could always be recovered. We have quantitative data only on the pyrolysis of N-cyclohexylacetamide at 588°. For this substance the mole ratio of cyclohexene:acetonitrile in the volatile fraction of the pyrolysate (homogenized by addition of the minimum amount of ethanol) was 0.97 to 1.00. Since at this temperature 57% of the olefinic product was cyclohexene (the remainder being largely 1,3-butadiene (24%)), roughly 58% of the acetamide must have been converted to acetonitrile.

The principal by-product in the pyrolysis of the N-alkyl-N-methylacetamides was N-methylacetamide; however, inasmuch as the gas chromatograms appeared to indicate the concurrent formation of a small amount of acetonitrile, the pyrolysis of N-methylacetamide (at 590°, rate 0.40 g./min.) was examined. The pyrolysate contained, in addition to recovered N-methylacetamide, methanol, acetonitrile, water and traces of other unidentified substances, although the yield of acetonitrile was small, about 1.5%.

The nature of the secondary by-products, which in some cases were very numerous (*vide supra*), constitutes a rather involved problem which we have only begun to examine. Unfortunately, at the temperatures necessary for the pyrolysis of the amides studied, secondary pyrolyses of the olefinic products may also be observed. As the temperature approaches 600° the latter become increasingly important, carbonization becomes difficult to avoid, and the effects of operating variables (rate of addition, rate of flow of diluent gas (nitrogen), etc.) are magnified. Although qualitative studies of the effect of high temperatures on olefins have been reported, detailed quantitative studies of the type now possible with gas chromatography as an analytical tool and necessary for a complete description of the present pyrolysis have yet to be described. In the higher temperature pyrolysates from the N-alkylacetamides, ammonia, ammonium acetate, ketene, methane, degraded olefins or paraffins (both liquid and gaseous) and higher molecular weight condensation products have been tentatively identified. In the pyrolysis of the cyclohexyl derivatives, some of the cyclohexene formed was further pyrolyzed at the higher temperatures to give substantial amounts of butadiene (up to 52% yield of crude butadiene) and ethylene. Disproportionation of cyclohexene, 1-methylcyclohexene and methylenecyclohexane occurred also, for benzene, cyclohexane, toluene and methylcyclohexane were found in the pyrolysates.[21] Ring contraction to cyclopentane derivatives probably occurred also,[22] and this possibility will be studied further.

In several experiments the liquid pyrolysates from the cyclohexyl and 1-methylcyclohexyl derivatives were analyzed by gas chromatography for seven possible components (b.p. 80–110°). The results of these analyses are given in Table III. Inasmuch as most of the lower boiling liquid components have yet to be identified with certainty, analysis for these was not possible; however, based on the reasonable assumption that the molecular weights of these components would not exceed that of cyclohexene, it was possible to estimate an upper limit for the total amount of low-boiling products.[23]

From the N-alkyl-N-methylacetamide pyrolysates, methylamine and methylammonium acetate have been isolated. In the pyrolysates from both types of amides, the presence of a substance of uncommonly unpleasant odor and unknown structure was very apparent. This material may have been derived from the cyanic acid or methyl isocyanate formed in the decomposition of the acetamide or N-methylacetamide,[20] or it may have been one of the nitrogen analogs of ketene ($CH_2{=}C{=}NH$ or $CH_2{=}C{=}NCH_3$), although the latter have yet to be isolated in amide pyrolyses.

Experimental[24]

N-(β-Phenylethyl)-formamide.—To 13 g. (0.25 mole) of 90% formic acid contained in a round-bottomed flask was

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after one pyrolysis and to 1.00 to 2.30 after a second. Most of the pyrolysis products (at least fourteen in number) which were gaseous have not been identified, although both butadiene and isoprene were tentatively identified on the basis of their retention volumes. Five liquid products (other than the starting materials) which boiled in the range 70–95° were detected by following the course of a fractional distillation through an 85-plate, concentric-tube column with gas chromatography. These materials made up roughly 8% of the total liquid product boiling up to 110°. Although one of the five liquid products appeared to be cyclohexene, the amount present was quite small, estimated to be 1.8% of the total product. This quantity of cyclohexene is too small to account for the relatively large quantity formed in the pyrolysis of the amides. Three of the other four components appeared to be cyclohexane, benzene, and methylcyclohexane.

(20) C. D. Hurd, "The Pyrolysis of Carbon Compounds," The Chemical Catalog Co. (Reinhold Publ. Corp.), New York, N. Y., 1929, p. 582.

(21) *Cf.* W. C. Bain and P. D. Ritchie, *J. Chem. Soc.*, 4407 (1955).

(22) *Cf.* H. Adkins and A. K. Roebuck, THIS JOURNAL, **70**, 4041 (1948).

(23) R. H. Eastman, *ibid.*, **79**, 4243 (1957).

(24) Melting points are corrected; boiling points are uncorrected. Analyses by Micro-Tech Laboratories, Skokie, Ill.

TABLE III

PARTIAL ANALYSIS OF PYROLYSATES

No.	Component	R_v[a]	Composition[b] (%) of run no. 8	10	14	18	19	21	28
1	Cyclohexane	0.791 ± 0.004	1.7	7.0	6.8	6.5	4.6	4.0	0.7
2	Cyclohexene	1.000	41.6	48.6	87.1	86.4	85.9	94.1	0.5
3	Benzene	1.135 ± 0.003	1.5	5.8	6.1	7.1	9.2	1.8	0.5
4	Methylcyclohexane	1.32 ± .01	[c]	[c]					[c]
5	Methylenecyclohexane	1.66 ± .01	51.2	33.6					27.2
6	1-Methylcyclohexene	2.05 ± .02	4.0	3.0					69.8
7	Toluene	2.65 ± .05	[d]	2.2					1.4
8	Low-boiling component[e]	≤0.600 .	10.2	11.0	11.9	15.1	9.1	12.0	2.0
9	Acetonitrile	0.452 ± 0.002	12.9[f]	1.5	28.3[g]	1.6	7.8	1.2	[h]

[a] Retention volume relative to cyclohexene for Perkin–Elmer packing B (useful over range 70–90°). [b] Composition calculated by following formulas. Composition of first seven entries = $f_iA_i/\sum_{i=1}^{7} f_iA_i$, of the eighth $= f_8A_8/\sum_{i=1}^{8} f_iA_i$, of the ninth $= f_9A_9/\sum_{i=1}^{9} f_iA_i$, where $f_9 = 1.000$, A_i = area from gas chromatogram curve measured by planimeter. The multiplicative correction factor f_i was determined for each component from analysis of known mixtures and by arbitrarily setting $f_2 = 1.000$. [c] Peak present but not sufficiently resolved for accurate measure. [d] Not measured. [e] Includes all components, $R_v \leqslant 0.600$, except acetonitrile. [f] Includes only acetonitrile in hydrocarbon phase. [g] Total acetonitrile determined on three-phase sample homogenized by addition of ethanol. [h] Method of isolation precluded measurement (see Experimental).

added with cooling 30 g. (0.25 mole) of β-phenylethylamine. A short Vigreux column was attached to the flask and the mixture was distilled at atmospheric pressure until no more liquid distilled under 110°. The residual liquid was distilled at reduced pressure giving 36.5 g. (97%) of N-(β-phenylethyl)-formamide, b.p. 192–196° (20 mm.) (lit.[25] b.p. 192–194° (20 mm.)).

Methyl-β-phenylethylamine.—To stirred suspension of 10.4 g. (0.30 mole) of lithium aluminum hydride in 400 ml. of absolute ether a solution of 29 g. (0.20 mole) of N-β-phenylethylformamide in 100 ml. of absolute ether was added dropwise at such a rate to maintain a gentle reflux. After the addition the amide was allowed to stand overnight and the excess lithium aluminum hydride was decomposed.[26] The ether layer was separated, and the aqueous layer was extracted with ether (50 ml.). The combined ether extracts were dried over potassium carbonate, filtered, and distilled giving 25 g. (93%) of methyl-β-phenylethylamine, b.p. 200–205° (lit.[27] b.p. 205°).

N-Methyl-N-(β-phenylethyl)-acetamide.—A mixture of 12.5 g. (0.09 mole) of methyl-β-phenylethylamine and 20 g. (0.20 mole) of acetic anhydride was heated under reflux for 20 minutes and distilled through a short Vigreux column under reduced pressure giving 13.1 g. (80%) of N-methyl-N-(β-phenylethyl)-acetamide,[28] b.p. 165–171° (12 mm.).

N-Cyclohexylformamide was prepared as described above for N-(β-phenylethyl)-formamide. The product was obtained in 90–97% yield, b.p. 145–146° (16 mm.) (lit.[25] b.p. 155–157° (22 mm.)).

Methylcyclohexylamine[29] was prepared in 75% yield by the reduction of N-cyclohexylformamide with lithium aluminum hydride as described above for methyl-β-phenylethylamine. The product boiled at 147–150° (lit.[30] b.p. 147–148°).

N-Cyclohexyl-N-methylacetamide was prepared by the acetylation of methylcyclohexylamine as described above for N-methyl-N-(β-phenylethyl)-acetamide. The product, b.p. 136° (17 mm.) (lit.[31] b.p. 249° (740 mm.)), was obtained in 81% yield.

N-*n*-Hexylacetamide (a).—To a vigorously stirred 202-g. (2.00-mole) portion of *n*-hexylamine under reflux 306 g. (3.00 moles) of acetic anhydride was added dropwise. After the addition was complete, the mixture was heated under reflux for two hours. The excess acetic anhydride was decomposed by addition of water or methanol (1 mole) and the mixture was distilled. Two fractions were collected, 147 g. (b.p. 140–150° (14 mm.)) and 149 g. (b.p. 152° (14 mm.), 156° (16 mm.), n^{25}D 1.4441). Although the infrared spectrum of the product indicated that the second fraction was the desired amide, the elementary analysis indicated that the material was far from pure.

(b).—To a solution of 144 g. (1.43 moles) of *n*-hexylamine and 144 g. (1.43 moles) of triethylamine in 600 ml. of carbon tetrachloride was added dropwise with stirring and cooling (ice) a solution of 112.4 g. (1.43 moles) of acetyl chloride in 400 ml. of carbon tetrachloride. The addition required 1.5 hr. After standing overnight the mixture was filtered from the triethylamine hydrochloride, the filter cake was washed with carbon tetrachloride and the solution was evaporated on a steam-bath. Distillation of the residue gave 147 g. (72%) of N-*n*-hexylacetamide, b.p. 134–135° (2 mm.), n^{25}D 1.4442.

Anal. Calcd. for $C_8H_{17}NO$: C, 67.09; H, 11.96; N, 9.78. Found: C, 66.73; H, 11.95; N, 9.89.

N-Cyclohexylmethylacetamide.—The procedure described under (b) for N-*n*-hexylacetamide was used to prepare N-cyclohexylmethylacetamide in 64% yield as a clear, viscous liquid, b.p. 133° (1 mm.), which solidified in the receiver, m.p. 44.5–46°.

Anal. Calcd. for $C_9H_{17}NO$: C, 69.63; H, 11.04; N, 9.02. Found: C, 69.33; H, 11.26; N, 8.92.

N-Cyclohexylmethyl-N-methylacetamide was prepared by the acetylation of N-cyclohexylmethyl-N-methylamine with acetic anhydride as described above for N-methyl-N-(β-phenylethyl)-acetamide. The yield of the amide, b.p. 140–144° (17 mm.), was 80%.

Anal. Calcd. for $C_{10}H_{19}NO$: C, 71.01; H, 11.24. Found: C, 70.55; H, 10.46.

N-(1-Methylcyclohexyl)-acetamide (a).—To a stirred solution of 57 g. (0.50 mole) of 1-methylcyclohexanol and 20.5 g. (0.50 mole) of acetonitrile in 250 ml. of glacial acetic acid was added dropwise with cooling ($T < 40°$) 50.5 g. (0.50 mole) of concentrated sulfuric acid. The solution was allowed to stand overnight and poured onto crushed ice. The amide separated as an oil which slowly solidified. After collection by filtration and air-drying, the crude product weighed 34.8 g. (45%). The filtrate was neutralized (with cooling) and refiltered, yielding after air-drying an additional 27.0 g. (35%) of crude material. The crude material, m.p. 83–85°, needed little purification but was recrystallized from Skellysolve B,[32] giving 56 g. (72%) of N-(1-methylcyclohexyl)-acetamide as white needles, m.p. 84–85°.

Anal. Calcd. for $C_9H_{17}NO$: C, 69.63; H, 11.04; N, 9.02. Found: C, 69.69; H, 10.90; N, 8.92.

(b).—The procedure of (a) above was repeated except that 78 g. (0.50 mole) of 1-methylcyclohexyl acetate was substituted for the 1-methylcyclohexanol. The reaction mixture became dark brown (rather than pale yellow) and

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(25) F. F. Blicke and C. Lu, THIS JOURNAL, **74**, 3933 (1952).

(26) V. M. Micovic and M. L. Mihailovic, *J. Org. Chem.*, **18**, 1190 (1953).

(27) K. Kindler, *Arch. Pharm.*, **265**, 389 (1927).

(28) T. B. Johnson and H. H. Guest, THIS JOURNAL, **32**, 761 (1910).

(29) Now available from E. I. du Pont de Nemours and Co., Inc.

(30) H. Heckel and R. Adams, THIS JOURNAL, **47**, 1712 (1925).

(31) A. Skita and H. Rolfes, *Ber.*, **53B**, 1342 (1920).

(32) A hydrocarbon solvent, b.p. 60–69°.

on pouring onto ice the product precipitated as brown, flat needles, 50 g. (65%). Recrystallization from Skellysolve B[32] gave only partial removal of the brown color, so the product was recrystallized from dilute ethanol (charcoal), giving 38 g. (49%) of N-(1-methylcyclohexyl)-acetamide, m.p. 84–85°.

Pyrolysis Procedure.—The apparatus and procedure for the pyrolysis were essentially the same as those described previously.[11] In the later experiments the temperature of the furnace was controlled by means of an Amplitrol (Thermo Electric Mfg. Co.) proportioning controller, which was found capable of maintaining the temperature within ±5° or less at 600°. The calibration of the instrument appeared to change with time so that use of a pyrometer and thermocouple as described previously was essential, the pyrometer being positioned to read the maximum temperature in the column (which was found to be as much as 60° above the temperature near the ends).

The addition of solid amides was facilitated by means of an electrically heated dropping funnel. A unique feature of the funnel used was a Teflon needle valve similar to that described by Nester.[33] An alternative design employed a heated Hershberg funnel.[34]

Two procedures were used in working up the pyrolysates. (a) The crude mixture was distilled through a short Vigreux column and all material boiling up to 10° above the boiling point of the expected olefin(s) was collected. Tap water (temperature *ca.* 12°) was used to cool the condenser and normally no effort was made to collect gaseous or very low boiling components. In the pyrolyses of N-cyclohexylacetamide and N-cyclohexyl-N-methylacetamide, however, the liquifiable product (in Dry Ice–ethanol) was transferred, with due regard for the very low boiling point of some components, to a simple distillation set-up and distilled. The low boiling components were collected in a receiver cooled in Dry Ice–ethanol. These are listed in Table I as the crude butadiene fraction. This fraction for run 14 was analyzed for actual butadiene content by gas chromatography. The fractions boiling from room temperature (*ca.* 30°) to 90° are listed in Table I as the crude cyclohexene fraction. The unreacted amide was recovered by recrystallization or fractional distillation under reduced pressure of the residue.

(b) The crude pyrolysate was taken up in a small amount of ethanol and the resultant solution was steam distilled. The water-insoluble portion of the steam distillate was mechanically separated and analyzed as described below. The steam non-volatile residue was distilled under reduced pressure or recrystallized. From the standpoint of convenience and ease of manipulation (especially with pyrolysates from solid amides) this procedure was preferable; however, water-soluble components of the pyrolysate were lost during the work-up. This procedure was used for all experiments listed in Table II.

The volatile fraction was analyzed by (1) fractional distillation through a Podbielniak column[35] and oxidation[1] of any olefin to the glycol in the early experiments, (2) infrared spectra in later experiments and (3) gas chromatography employing a Perkin–Elmer model 154-B vapor fractometer in the most recent experiments. Those volatile fractions which separated into two or more phases were mechanically separated and each phase was analyzed separately. For the analysis by gas chromatography, stainless steel columns (200–300 × 0.7 cm.) packed with Perkin–Elmer column packing B or 30% (by weight) of a saturated solution of silver nitrate in ethylene glycol on Celite 545 (100–200 mesh) were used with helium as the mobile phase. The weight percentage composition of each olefin mixture was obtained by determining the ratios of the individual peak areas (measured by use of a planimeter) to the sum of all the areas, each individual area being corrected by a multiplicative factor (determined from the analysis of mixtures of standard substances). The results are considered accurate to within ±1% (relative).

The gas chromatographic analyses of certain of the crude cyclohexene fractions (run nos. 14, 18, 19, 21) are given in Table III. In the analyses of runs 8 and 10 the fractions boiling from 30–110° were analyzed. In the analyses of runs 23–28 (Tables II and III) the entire steam volatile product was analyzed; only in run 28 were more than traces of products other than methylenecyclohexane and 1-methylcyclohexene obtained.

In order of increasing retention volumes, compounds resolved by the Perkin–Elmer B packing were: methylenecyclopentane, (1-methylcyclopentene, cyclohexane), cyclohexene, benzene, methylcyclohexane, (methylenecyclohexane, 3-methylcyclohexene, 4-methylcyclohexene), 1-methylcyclohexene, toluene. Compounds appearing within one set of parentheses were not resolved from each other. For the silver nitrate–glycol column: (cyclohexane, methylcyclohexane), (1-methylcyclopentene, benzene, 1-methylcyclohexene), toluene, (4-methylcyclohexene, cyclohexene, 3-methylcyclohexene), methylenecyclohexane.[36]

To identify ethylene as one product of the pyrolysis of N-cyclohexyl-N-methylacetamide a 0.20-mole portion of the amide was pyrolyzed at 575° (0.20 g./min.) with no nitrogen passing through the system and the gas evolved (*ca.* 2 l.) was collected over water. The gas was analyzed by infrared spectroscopy and found to consist largely of ethylene together with a small amount of butadiene and other substances. In general, however, the gaseous products were not collected.

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[33] R. G. Nester, *Anal. Chem.*, **28**, 278 (1956).

[34] E. B. Hershberg, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 129.

[35] J. Cason and H. Rapoport, "Laboratory Text in Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1950, p. 237.

[36] This column will resolve 3-methylcyclohexene and 4-methylcyclohexene (E. Gil-Av, J. Herling and J. Shabtai, *Chemistry & Industry*, 1483 (1957)) but not in the presence of cyclohexene.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF BOSTON UNIVERSITY]

Synthesis of Unsaturated Fatty Acids: *dl*-Ricinoleic Acid[1]

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RECEIVED MARCH 5, 1958

9-Chlorononyne-1, as its lithium derivative, adds to 1,2-epoxyoctane to give 1-chloro-11-hydroxyheptadecyne-8. The corresponding iodide with potassium cyanide gives 1-cyano-11-hydroxyheptadecyne-8, which on saponification leads to *dl*-ricinstearolic acid. Addition of one mole of hydrogen forms *dl*-ricinoleic acid. Further hydrogenation of methyl *dl*-ricinoleate gives methyl *dl*-12-hydroxystearate.

From the standpoint of synthesis, the significant structural feature in ricinoleic acid (VIII) is the β-hydroxy-*cis*-olefinic grouping. In earlier syntheses of ricinoleic acid, two different methods were employed for the formation of this grouping. In one scheme, the essential step was a Reformatsky condensation of propargyl bromide,[2] or of a γ-substituted propargyl bromide,[3] with an appropriate aldehyde. A second method centered around the

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[1] Abstracted from the Dissertation submitted by Carolyn B. Abrahams to the Graduate School of Boston University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1957.

[2] L. Crombie and A. G. Jacklin, *Chemistry & Industry*, 1197 (1954); *J. Chem. Soc.*, 1740 (1955).

[3] L. Crombie and A. G. Jacklin, *ibid.*, 1622 (1957).