21372-11-2; **13**, 21372-12-3; **14**, 21372-13-4; **15**, 21372-14-5; **15** (HCl), 21372-15-6.

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N-Alkyl Cleavage of Amides. I. Amide Racemization in Polyphosphoric Acid[1]

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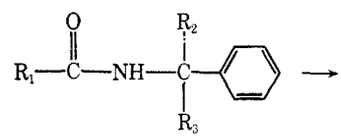
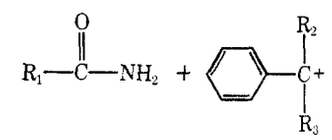
The behavior of a number of secondary amides on treatment with polyphosphoric acid indicates that the stability of the potential cationic fragment (the N-alkyl group) is an important factor for facile N-alkyl fission. When amides with optically active N-alkyl groups were subjected to the cleavage process, significant and structure-dependent amounts of racemization were observed in the recovered amides, indicating that recombination had taken place. Possible mechanisms for the N-alkyl heterolysis of amides have been considered in the light of these results.

Although the acid-catalyzed oxygen–alkyl fission in the reactions of certain esters has been well documented in the literature,[3] the analogous N-alkyl heterolysis of amides has not been investigated extensively. In a study of the effect of ring substituents on the ease of N-alkyl cleavage of N-*t*-butylbenzamides, Lacey[4] proposed a mechanistic scheme similar to the $A_{al}1$ hydrolysis of esters. Knopka and Conley[5] have reported that amides with a primary or secondary alkyl group substituted on the nitrogen are resistant to N-alkyl cleavage in polyphosphoric acid (PPA). Hill, Conley, and Chortyk[6] have reported that a 20% yield of N-benzoyl-α,α-dimethylbenzylamine (**1**) can be realized from the reaction of α-methylstyrene and benzamide in PPA at 120°. It was shown that **1** undergoes facile cleavage to benzamide under comparable conditions, suggesting that the N-alkyl fission is reversible in some systems. Concurrent studies in these laboratories on the fate of optically active groups in the Beckmann and related carbon–nitrogen rearrangements led us to examine the behavior of the optically active amides normally expected from these reactions in PPA, with particular emphasis on the question of reversibility.

When N-(α-methyl)benzylbenzamide (**2a**) is treated with PPA, heterolysis occurs at the carbon–nitrogen bond, giving rise to benzamide and presumably the 1-phenylethyl cation. Neither styrene nor α-methylbenzyl alcohol was observed by vapor phase chromatography (vpc) of the product mixture, but two major components other than benzamide were evident. These materials were not fully characterized, but the ir spectrum of the yellow oil remaining after separation of the benzamide was quite similar to the spectrum of polystyrene, suggesting that these products were dimers and higher polymers of styrene. Similar products have been obtained from the acid-catalyzed telomerization of styrene[7a] and from the PPA-catalyzed dimerization of 2-isopropenylnaphthalene.[7b]



2a, $R_1 = C_6H_5$, $R_2 = H$, $R_3 = CH_3$
b, $R_1 = C_6H_5$, $R_2 = CH_3$, $R_3 = C_4H_9$
c, $R_1 = CH_3$, $R_2 = CH_3$, $R_3 = C_4H_9$
d, $R_1 = H$, $R_2 = CH_3$, $R_3 = C_4H_9$
e, $R_1 = CH_3$, $R_2 = H$, $R_3 = CH_3$



The N-alkyl cleavage of **2a** is apparently promoted by stabilization of the resultant carbonium ion through conjugative charge dispersal into the phenyl ring of the 1-phenylethyl cation. Substitution of a second alkyl group on the benzyl carbon enhanced the ease of cleavage. Thus, N-benzoyl-α-methyl-α-butylbenzylamine (**2b**) undergoes 97% N-alkyl cleavage when treated with PPA for only 1 hr at room temperature. In contrast, only 3.5% cleavage is obtained from the reaction of **2a** under comparable conditions.

Three monomeric olefins as well as some polymers were observed in the product mixture from the N-alkyl cleavage of N-acetyl-α-methyl-α-butylbenzylamine (**2c**), and two of these olefins were produced from similar reactions of **2b** and the formamide **2d**. The olefins were isolated by preparative vpc and were identical with those obtained from the thermal dehydration of α-methyl-α-butylbenzyl alcohol. The structures were established by ir and nmr spectroscopy as *cis*- and *trans*-2-phenyl-2-hexene and 2-phenyl-1-hexene. These assignments are in agreement with those of the homol-

(1) (a) Presented in part at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965; (b) taken from the Ph.D. Thesis of A. G. Mohan, Seton Hall University, 1966.

(2) To whom inquiries should be directed.

(3) (a) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Bell Publishers, London, 1953, p 779; (b) A. G. Davis and J. Kenyon, *Quart. Rev.* (London), **9**, 203 (1955); (c) C. A. Bunton, E. D. Hughes, C. K. Ingold, and D. F. Meigh, *Nature*, **166**, 679 (1950).

(4) R. N. Lacey, *J. Chem. Soc.*, 1633 (1960).

(5) W. N. Knopka and R. T. Conley, Abstracts, 146th National Meeting of the American Chemical Society, Denver, Colo., Jan 1964, p 57C.

(6) R. K. Hill, R. T. Conley, and O. T. Chortyk, *J. Amer. Chem. Soc.*, **87**, 5646 (1965).

(7) (a) M. J. Rosen, *J. Org. Chem.*, **18**, 1701 (1953); (b) L. A. Paquette and T. R. Phillips, *ibid.*, **30**, 3883 (1965).

ogous 2-phenylbutenes already reported.[8] The presence of the monomeric olefins in the product mixture from the N-alkyl fission of **2b** is not unexpected, since it is known that increasing the bulk on the side chain of styrene retards its rate of polymerization.[9]

In spite of the apparent reversibility of the N-alkyl heterolysis of **1**,[6] repeated attempts to treat benzamide with styrene or α-methylbenzyl alcohol under a variety of conditions failed to yield any significant amount of **2a**. To resolve the question of reversibility, the optically active enantiomorph of **2a** was prepared and treated with PPA. If the fragmentation reaction is interrupted before the N-alkyl cleavage is complete, the extent of racemization in the recovered starting material is a measure of the amount of recombination. This assumes that the alkyl cation diffuses far enough from the vicinity of the nitrogen atom to permit inversion to take place. Table I compares the extent of racemization and N-alkyl cleavage at three different temperatures. The difference in extent of cleavage between the *d*-(+)- and the *dl*-amides is surprising, but may be due to solubility differences in the heterogeneous reaction mixture.

TABLE I

N-ALKYL CLEAVAGE OF N-(α-METHYL)BENZYLBENZAMIDE (**2a**) IN PPA

Starting amide	Reaction time, min temp, °C	Racemization in recovered amide, %	N-Alkyl cleavage, %[a]
dl	60 (25)		3.5
d-(+)	60 (25)	4.8 ± 0.4	9.0
d-(+)	300 (25)	12.6 ± 1.4	
dl	30 (40)		5.7
d-(+)	30 (40)	8.0 ± 3.0	28.5
dl	10 (60)		68.2
d-(+)	10 (60)		87.0
d-(+)	6 (60)	9.6 ± 3.0	81.5

[a] Calculated from relative proportion of benzamide and **2a**.

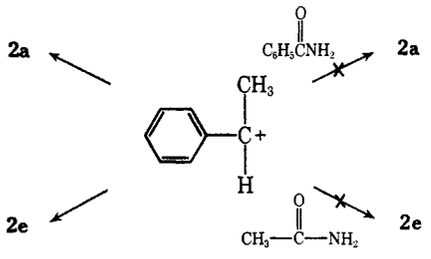
The extent of recombination in the α-methyl-α-butylbenzylamine derivatives is more pronounced. In order that sufficient quantities of unreacted amide could be isolated, the reaction was terminated after only 15 min at room temperature. The N-acetyl compound (**2c**) was racemized to the extent of 18.5 ± 3.5% and the N-benzoyl derivative (**2b**) to about half of this value, 9.2 ± 5.2%.

A remote possibility existed that in the primary and secondary alkyl cases[5] the recombination reaction was very fast relative to the cleavage reaction, so that no products from the amide fragmentation could be isolated. This possibility was eliminated by subjecting optically active N-acetyl-1-cyclohexylethylamine (**3**) to prolonged heating in PPA (20 hr at 80°). Under these conditions, amides with N-*t*-butyl groups fragment completely after only 10 min.[5] There was no evidence of any reaction, and **3** was recovered unchanged with no significant loss in optical activity. It seemed probable that N-neopentylpivalamide (**4**) would undergo fragmentation if the steric crowding and possible rearrangement to the *t*-amyl cation could overcome the otherwise unfavorable heterolysis of the C–N bond at a primary carbon atom. However, no evidence of either N-alkyl or N-acyl cleavage was apparent after prolonged heating of **4** in PPA (23 hr at 80°). This result confirms a similar experiment by Lacey,[4] who demonstrated that N-neopentylbenzamide resisted N-alkyl cleavage in sulfuric acid.

The facile cleavage of the amide derivatives of α-methyl-α-butylbenzylamine (**2b**, **2c**, and **2d**) is surprising in light of the work of Hill and coworkers,[6] who reported that a similar amide, **1**, was only 50% cleaved to benzamide after 10 min at 120°. It is interesting that Lacey[5] found that tertiary alkyl formamides hydrolyze with predominant N-acyl cleavage in sulfuric acid, whereas **2d** reacts by exclusive N-alkyl fission in PPA.

These data suggest that the stability of the potential alkyl cation is an important factor controlling the ease of N-alkyl cleavage. This cannot be the sole factor, since N-acetyl and N-benzoyl-1,1-diphenylmethylamine (**5a** and **5b**) were apparently resistant to N-alkyl cleavage under conditions where the tertiary benzylic systems, **2b**, **2c**, and **2d**, showed appreciable N-alkyl fission. When **5a** was subjected to more drastic conditions, none of the expected products from N-alkyl cleavage were evident and the presence of acetic anhydride in the product mixture suggested N-acyl fission had taken place.

Since the N-alkyl fission of a **2a** apparently involves the formation of the 1-phenylethyl cation, it should be possible to "trap" this cation *via* reaction with acetamide forming N-(α-methylbenzylacetamide) (**2e**). Likewise, the fragmentation of **2e** in the presence of benzamide should produce some **2a** if the free cation is an intermediate in PPA. Neither of the expected products resulting from capture of the 1-phenylethyl cation by a primary amide was observed in the product mixture by vpc within the limits of detection (<0.4%).



Since the recovered **2a** from the PPA-catalyzed cleavage of optically active **2a** showed significant amounts of racemization, there must be some recombination of fragments which can compete with the forward cleavage reaction. Substitution of a tertiary benzylic group on the amide nitrogen facilitates the N-alkyl cleavage process, probably because of the steric crowding in the substrate. Significant racemization in the recovered starting material from the reactions of **2b** and **2c** suggests that the bulk of the departing group does not prevent recombination.

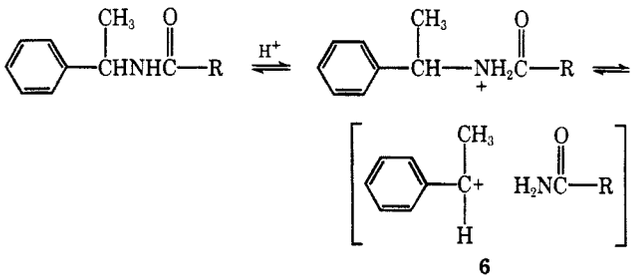
Two mechanistic routes seem reasonable to describe these processes.

One scheme similar to that proposed by Lacey[4] involves initial protonation of the amide at nitrogen

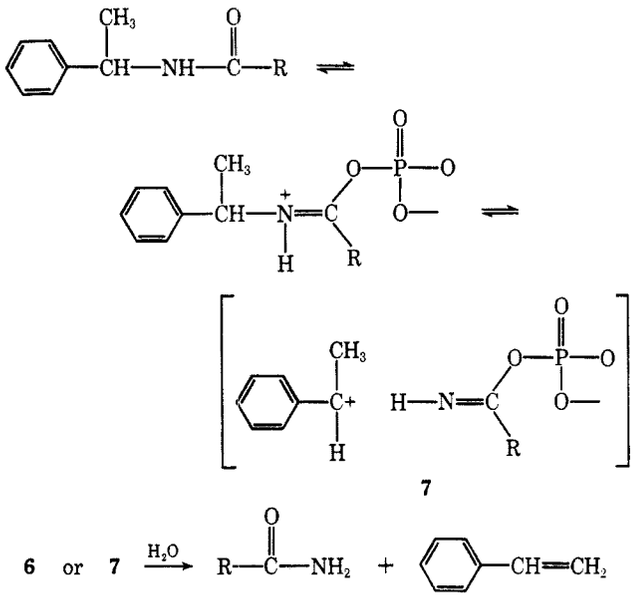
(8) J. A. Kampmeiev and R. M. Fantaziev, *J. Amer. Chem. Soc.*, **88**, 1959 (1966).

(9) G. N. Burnett, "Mechanism of Polymer Reactions," in "High Polymers," Vol. III, Interscience Publishers, New York, N. Y., 1954, p 169.

followed by fragmentation to a carbonium ion and a primary amide.



Alternately, the intermediate steps involve a phosphorylation of the amide followed by collapse of the phosphate ester to yield a carbonium ion and an imide–phosphate, **7**, which ultimately undergoes hydrolysis under the conditions of product isolation. Imido-



phosphate intermediates similar to those in **7** are very likely involved in the well-known hydration of nitriles to primary amides in PPA.[10] However, the intervention of nitriles as intermediates in the PPA-catalyzed cleavage seems unlikely, since the nitrile–olefin reaction should be considerably more efficient than the analogous amide–olefin reaction in view of the report[11] that the Ritter reaction on a similar system (styrene plus acetonitrile in PPA) gives a 35% yield of **2e**.

The intermediate (**6** or **7**) produced from N-alkyl cleavage must involve dissociation to an extent sufficient to permit partial racemization to be detected. Recombination of fragments apparently competes with diffusion of the cationic fragment out of the solvation sphere into the bulk of the solution. Failure of the cation to be "trapped" by other primary amides is consistent with the hypothesis that attack on the solvated cationic intermediate is highly unfavorable. However, it is not certain that the species derived by the action of PPA on a primary amide is the same as the amide fragment produced by the N-alkyl cleavage.

The resistance of amides with primary or secondary alkyl groups substituted on nitrogen to undergo facile N-alkyl cleavage suggests that high stability of the cation produced from fragmentation is a requisite for facile N-alkyl fission. It might be expected that the order of reactivity in the cleavage would parallel that of the alkyl group in the O-alkyl cleavage of esters.[12] However, the 1,1-diphenylmethylamine derivatives, **5a** and **5b**, were resistant to N-alkyl fission under conditions where **2b** is cleaved to the extent of 97%. When **5a** was treated with PPA under more drastic conditions, only N-acyl fission was observed. The only other example of N-acyl cleavage in PPA was reported by Tencza,[13] who observed products of both N-acyl and N-alkyl heterolysis from the action of PPA on N-(1-phenylcyclopropyl)benzamide. Thus, it appears that in the benzhydryl system a different mechanism is in operation; but further studies are required to elaborate on this point.

The relevance of these amide cleavage reactions to the fragmentations encountered with suitably substituted oximes becomes evident in the observation of similar products and through the intervention of similar intermediates in the mechanistic scheme. A number of workers[5,6,13] have recognized that suitably substituted amides and oximes can give rise to the same fragmentation products. For the most part, it appears that oximes fragment directly rather than through amide intermediates, since, with few exceptions,[13] the oximes fragment more rapidly than the corresponding amides. Thus, it seems that oxime fragmentation is a more facile, lower energy process than the N-alkyl cleavage of amides.

Experimental Section

Vapor phase chromatographic studies were performed on an F & M Model 720 programmed temperature gas chromatograph equipped with thermal conductivity detectors using 6 ft × 0.25 in. stainless steel columns (helium flow 60 ml/min). The SGN column refers to one packed with 10% silicone gum nitrile on "Diataport W" (All packings are available from F & M Scientific, Avondale, Pa). The SGN column was usually temperature programmed from 60 to 230° at 20°/min, then maintained isothermally at 230°. The DFX column refers to one packed with 10% "Dowfax 9N9" on 2% sodium hydroxide treated "Chromosorb P," generally operated isothermally.

Nmr spectra were recorded on a Varian A-60 or A-60A spectrometer at room temperature with tetramethylsilane (TMS) employed as an internal reference. Ir spectra were obtained on a Beckman IR-10 grating spectrophotometer Optical rotations were measured on a Rudolph Model 80 polarimeter using a 1-dm tube. Melting points were determined with a Hoover capillary melting point apparatus and are uncorrected.

Unless otherwise indicated, the amides employed in this study were prepared by the usual Schotten–Baumann reaction of the amine with the appropriate acyl chloride or anhydride. Polyphosphoric acid (PPA), 115% *o*-phosphoric acid equivalent, was obtained from the FMC Corp.

Reaction of N-(α-Methyl)benzylbenzamide (2a) with PPA.—The amide **2a**, mp 121–122.5° (lit.[14] mp 120°), was prepared in the usual manner from α-methylbenzylamine. The α-methylbenzylamine was resolved through the *d*-tartrate salt.[15] The *d*-(+)-amide, mp 120–126°, $[\alpha]^{25}D$ 44.6° (*c* 12.3, DMF), was obtained from the *l*-(−)amine (98% optical purity). Compound **2a** (2.3 g, 0.01 mol) was added to 46.9 g of PPA which was stirred at 60°. After 6 min at 60°, the reaction mixture was poured into cold sodium hydroxide solution. The resulting mixture was extracted with chloroform, the combined extracts were dried, and the solvent was evaporated, leaving 1.9 g of a crude solid–liquid mixture. The product mixture was analyzed by vpc

(10) H. R. Snyder and C. T. Elston, *J. Amer. Chem. Soc.*, **76**, 3039 (1954).
(11) C. T. Elston, Ph.D. Thesis, University of Illinois, 1954.
(12) A. G. Davies and J. Kenyon, *Quart. Rev.* (London), **9**, 207 (1955).
(13) T. Tencza, Ph.D. Thesis, Seton Hall University, 1966.
(14) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Compounds," John Wiley & Sons, Inc., New York, N. Y., 1948, p 235.
(15) A. Ault, *J. Chem. Educ.*, **42**, 269 (1965).

(SGN column, 250°), and the calibrated chromatograph showed that the ratio of benzamide to unreacted **2a** was 70.2 to 29.8%. The crude product was then chromatographed on 48 g of neutral Woelm alumina. The hexane and benzene elutions contained a yellow fluorescent oil whose ir spectrum was quite similar to polystyrene. This yellow oil, which showed two major components by vpc, was believed to be a mixture of styrene dimers, since the higher polymers probably would not be volatile enough for the vpc analysis. After successive increases in solvent polarity of the elution solvent, a white solid was isolated from the fraction eluted with ether. This material was shown to be pure **2a** by vpc. The recovered **2a** had $[\alpha]^{26}D$ 45.5 ± 0.4° (*c* 4.25, DMF), which on comparison with the starting amide, $[\alpha]^{27}D$ 47.8 ± 0.3° (*c* 4.10, DMF), gives 4.8 ± 1.5% loss in optical activity or 9.6 ± 3.0% racemization. A control experiment demonstrated that there was no significant change in optical activity when **2a** was subjected to chromatography on alumina. This procedure was repeated at several different times and temperatures and the results are summarized in Table I.

Attempt to Trap the Carbonium Ion Resulting from N-Alkyl Cleavage of 2a with Acetamide.—A mixture of 1.53 g (0.0068 mol) of **2a** and 2.00 g of acetamide was added to 69 g of PPA, stirred for 6.5 hr at 25°, and worked up as described above. Analysis of the product mixture (SGN column, 250°) indicated that no **2e** was present within the limits of detection (estimated as 0.4% relative to the benzamide present). It was demonstrated that **2e** was separable from the other components by adding the authentic material, mp 76–77° (lit.[16] mp 79–81°), to an aliquot of the reaction mixture.

Attempt to Trap the Carbonium Ion Resulting from N-Alkyl Cleavage of N-(α-Methyl)benzylacetamide (2e) with Benzamide.—Benzamide (4.55 g, 0.0376 mol) and **2e** (1.22 g, 0.0075 mol) were added to 115 g of PPA and the resulting heavy slurry was stirred for 5.5 hr at 23–25°. The mixture was then worked up as above. Analysis of the product mixture (SGN column, 250°) indicated that no **2a** was present within the limits of detection (estimated as 0.2% relative to the benzamide). Compound **2a** was shown to be separable from the other components by the addition of the authentic material to an aliquot of the reaction mixture.

Attempts to Add Styrene to Benzamide.—Styrene (1.39 g, 0.0135 mol) was added to a slurry of 8.2 g (0.067 mol) of benzamide in 45 g of PPA which was stirring at room temperature. The reaction mixture turned yellow immediately and stirring was continued for 1 hr. The reaction mixture was then worked up as above. Analysis of the product mixture (SGN column) indicated that no **2a** was present within the limits of detection (estimated as 0.6% relative to the benzamide).

Similar attempts employing sulfuric acid instead of PPA and α-methylbenzyl alcohol in place of the styrene or varying the reaction conditions gave no detectable amounts of **2a**.

Preparation of α-Methyl-α-butylbenzylamine.—α-Methyl-α-butylbenzyl alcohol was prepared by the Grignard reaction of *n*-butylmagnesium bromide with acetophenone. The crude alcohol was then converted to the corresponding formamide by the Ritter reaction with hydrogen cyanide according to a modification of the procedure of Haaf.[17] The crude **2d** was isolated by neutralization of the reaction mixture with sodium hydroxide and extraction with ether. A small sample of the formamide **2d** was distilled, bp 132–133° (0.3 mm), and the purity of the distillate was in excess of 95% by vpc. The ir spectrum, consistent with the expected structure, was virtually identical with that of the crude sample. The crude formamide (118 g, 058 mol) was hydrolyzed in a mixture of 230 ml of ethanol and 72 ml of 50% sodium hydroxide solution by refluxing for 12 hr. After evaporation of the solvent, the crude product was neutralized with hydrochloric acid, extracted with ether to remove nonbasic materials, then made basic and extracted with ether to isolate the amine fraction. After drying, evaporation of the ether yielded 53 g of the crude amine, which was distilled yielding 44 g of α-methyl-α-butylbenzylamine, bp 76–80° (0.6–1.0 mm) [lit.[18] bp 127° (18 mm)], in excess of 98% purity by vpc. The ir spectrum and vpc retention time of this material were identical with those of an authentic sample prepared by the method of Arcus, Kenyon, and Levin.[18] The N-benzoyl derivative, **2b**, mp 147–148°, was identical with that of the authentic material. The N-acetyl derivative, **2c**, mp 110–111°, had characteristic absorptions in the ir spectrum (Nujol) at 3285, 1648, 1552, and 700 cm^{-1}.

Anal. Calcd for $C_{14}H_{21}NO$: C, 76.66; H, 9.65; N, 6.39. Found: C, 76.52; H, 9.72; N, 6.28.

Resolution of α-Methyl-α-butylbenzylamine.—*d*-Tartaric acid (43 g, 0.287 mol) was added to 350 ml of 2-propanol, and to this mixture was added 50 g (0.282 mol) of *dl*-α-methyl-α-butylbenzylamine. The mixture was warmed and 50 ml of ethanol was added to dissolve the remaining solid. Acetone (350 ml) was added, and the solution was brought to a reflux, allowed to cool, and placed in a refrigerator overnight. The pearly white plates which crystallized were filtered, yielding 74 g of the salt, mp 159–167°. The initial stages of the resolution could be readily followed by the melting point of the salt. The above sequence was repeated four times, yielding 10 g of the tartrate salt, mp 180–184°, $[\alpha]^{27}D$ 8.6° (*c* 16, methanol), which yielded 5 g of optically pure amine, $[\alpha]^{27}D$ 12.1 (*c* 2.81, $CHCl_3$). The specific rotation of the amine did not change on further crystallization of the *d*-tartrate salt and was equal in magnitude and of opposite sign to a sample prepared by the Hoffman reaction on optically pure *l*-2-methyl-2-phenylhexanoic acid according to the procedure of Arcus,[18] *et al.*

Products from the N-Alkyl Cleavage of the Amide Derivatives of α-Methyl-α-butylbenzylamine (2b, 2c, and 2d).—Three olefins, *trans*-2-phenyl-2-hexene (**8**), *cis*-2-phenyl-2-hexene (**9**), and 2-phenyl-1-hexene (**10**), were produced by the action of PPA on **2c**. Only **8** and **9** were evident from the reactions of **2b** and **2d** with PPA. These products were isolated by preparative vpc techniques and the ir was determined on each olefin.

Since sufficient amounts of all three olefins could not be isolated from the N-alkyl cleavage reactions, thermal dehydration of α-methyl-α-butylbenzyl alcohol was found to be the most practical method for preparation and characterization of the olefinic products. A sample of crude α-methyl-α-butylbenzyl alcohol was carefully heated under reduced pressure (1 mm) until a smooth reflux could be maintained for 1 hr. The mixture was then fractionally distilled through a 3-ft column packed with glass helices (reflux ratio 20:1). The initial fractions [bp 54–57° (1.0–1.2 mm)] were rich in **8**. The following fractions [bp 57° (1.0 mm)] contained **10** in good purity (88 to 97% by vpc). The distillation residue contained appreciable amounts of **9**. The appropriate fractions were further purified by preparative scale vpc using a Wilkens "Autoprep" with a 20 ft × 3/8 in. column packed with silicone gum rubber on Chromosorb W at 185° (helium flow rate 200 ml/min). The ir spectra and vpc retention times of **8**, **9**, and **10** were identical to the corresponding products obtained from N-alkyl cleavage reactions of **2b**, **2c**, and **2d**.

Analytical samples of the three olefinic products were obtained by preparative vpc. Elemental analysis of each product established that the products were isomeric phenylhexenes. Indices of refraction were as follows: **8**, $n^{25}D$ 1.5133; **9**, $n^{25}D$ 1.5281; **10**, $n^{25}D$ 1.5167.

Anal. Calcd for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: **8**, C, 89.89; H, 10.03; **9**, C, 89.87; H, 9.97; **10**, C, 90.05; H, 10.09.

For 2-phenyl-1-hexene (stereochemistry unspecified), Badger[19] reports bp 62–63° (0.17 mm), $n^{25}D$ 1.5258; Nasarov[20] reports bp 66–68° (1.0 mm), $n^{25}D$ 1.5200; Crawford[21] reports bp 223–226°. For 2-phenyl-2-hexene, Butler[22] reports bp 89–90° (10 mm), $n^{25}D$ 1.5254.

The ir spectra of **8** [1670 (vw), 1375 (s), 888 (m), 813 (w), 757 (s), and 693 (s) cm^{-1}] and **9** [1643 (w), 1377 (s), 880 (m), 833 (w), 747 (s), and 688 (s) cm^{-1}] were consistent with the structure of a phenyl-conjugated trisubstituted olefin.[23] The ir spectrum of **10** [1627 (s), 1375 (s), 890 (s), 772 (s), and 697 (s) cm^{-1}] was consistent with the structure of 2-phenyl-1-hexene. This was confirmed by the nmr, which showed the vinyl protons at τ 4.75 and 4.97 (d, J = 1.4 cps). The relative stereochemistry of the isomeric 2-phenyl-2-hexenes **8** and **9** was assigned on the basis of the chemical shifts of the vinyl protons. Jackman and Wiley[24] have shown that in trisubstituted olefins containing a

(16) E. H. White, *J. Amer. Chem. Soc.*, **77**, 6008 (1955).
(17) W. Haaf, *Ber.*, **96**, 3359 (1963).
(18) C. L. Arcus, J. Kenyon, and S. Levin, *J. Chem. Soc.*, 407 (1951).
(19) G. M. Badger, P. Cheuychit, and W. H. F. Sasse, *ibid.*, 3235 (1962).
(20) I. N. Nazarov and I. L. Kotlyarevskii, *Zh. Obshch. Khim.*, **18**, 903 (1948).
(21) H. M. Crawford, M. E. Sager, and J. E. Warneke, *J. Amer. Chem. Soc.*, **64**, 2862 (1942).
(22) G. B. Butler and T. M. Brooks, *J. Org. Chem.*, **28**, 2699 (1963).
(23) R. T. Conley, "Infrared Spectroscopy," Allyn and Bacon, Inc., Boston, Mass., 1966, pp 99–104.
(24) L. M. Jackman and R. H. Wiley, *J. Chem. Soc.*, 2881 (1960).

phenyl group attached to the double bond, the signal of the proton *cis* to the phenyl would be shifted almost 0.5 ppm downfield from the *trans* proton. On this basis, **8**, having the olefinic proton at τ 4.73, was assigned the *trans* configuration, and **9**, with the olefinic proton at τ 4.33, was assigned the *cis* configuration. These assignments are in agreement with those published on the homologous phenylbutene isomers.[8]

Reaction of Amide Derivatives of α-Methyl-α-butylbenzylamine (2b, 2c, and 2d) with PPA.—Amide **2b** (0.20 g) was added to 12 g of PPA and stirred at room temperature for 1 hr. The slurry was then worked up as above. The product mixture (SGN column) had the following composition (wt % as estimated from relative peak areas): 6% **8**, 2% **9**, 37% benzamide, 52% polymeric olefins, and 3% unreacted **2b**. Optically pure **2b** was treated with PPA for 15 min, following the above procedure. The product was chromatographed on neutral Woelm alumina and the recovered amide, $[\alpha]^{24}D$ −22.9 (*c* 2.3, $CHCl_3$), was racemized to the extent of 9.2 ± 5.2%.

Amide **2c** was treated with PPA for 1 hr by the procedure described above and the product mixture had the following composition: 2% **8**, 7% **9**, 38% polymeric olefins, and 38% unreacted **2d**.

Treatment of N-Neopentylpivalamide (4) with PPA.—Compound **4**, mp 87–89°, was prepared from neopentylamine[25] and pivalyl chloride. This amide had characteristic absorptions in the ir spectrum ($CHCl_3$) at 3480, 2950, 1650, 1510, 1390, and 1360 cm^{-1}.

Anal. Calcd for $C_{10}H_{21}NO$: C, 70.12; H, 12.36; N, 8.18. Found: C, 70.07; H, 12.24; N, 8.08.

Amide **4** (0.180 g, 0.001 mol) was added to 3.7 g of PPA and stirred for 23 hr at 77–80°. The reaction was then worked up as above. Vpc analysis of the extract indicated that only starting material was present. No pivalamide was evident within the limits of detection (0.3%). Evaporation of the solvent yielded 0.10 g of **4** which was identical with an authentic sample (mixture melting point and ir spectrum).

Treatment of N-Benzoyl- and N-Acetyl-1,1-diphenylmethylamine (5b and 5a) with PPA.—Amide **5b** (0.355 g), mp 166–169° (lit.[26] 172°, 166–167°), was added to 7.1 g of PPA and this mixture was stirred for 1 hr at room temperature, then treated as in similar experiments described above. Vpc analysis (SGN column) indicated that only unreacted **5b** was present. None of the expected N-alkyl cleavage products were observed within the limits of detection (0.2% total benzamide plus benzylhydrol). Evaporation of the solvent left 0.30 g of **5b** which was identical with an authentic sample (mixture melting point and ir spectrum).

A similar result was obtained when **5a**, mp 145–148° (lit.[27] mp 152°) was treated with PPA for 1 hr at room temperature. However, treatment of **5a** for 1 hr at 78° caused considerable N-acyl fission, since large amounts of acetic anhydride were evident in the ir spectrum of the crude reaction mixture.

Treatment of N-Acetyl-1-Cyclohexylethylamine (3) with PPA.—Amide **3** was prepared in quantitative yield by the catalytic hydrogenation of **2e** in a Parr apparatus at 48 psig using 15% rhodium on carbon as catalyst. The (+) **3** had mp 96.5–97.5°, and its spectral properties (ir and nmr) were consistent with the expected structure.

Anal. Calcd for $C_{10}H_{19}NO$: C, 70.96; H, 11.31; N, 8.27. Found: C, 70.81; H, 11.19; N, 8.11.

Optically active **3**, mp 101–102.5°, $[\alpha]^{25}D$ 11.7° (*c* 5.27, DMF), was prepared by hydrogenation of optically active **2c** [from (−)-α-methylbenzylamine, 98% optically pure]. The optically active **3** (1.15 g, 0.067 mol) was added to 23 g of PPA which was stirring at 80°. The mixture was stirred for 20 hr at 80°, then worked up as above. Vpc of the chloroform extract (DFX column 200°, SGN column 200°) indicated that only **3** was present. Evaporation of the solvent yielded crude **3**, which after recrystallization from isopropyl ether showed no significant loss in optical activity.

Registry No.—(+) **2a**, 20826-48-6; **2c**, 20826-78-2; (±) **3**, 20826-51-1; **4**, 20826-79-3; **8**, 20826-49-7; **9**, 20826-50-0; **10**, 20826-80-6; α-methyl-α-butylbenzylamine [(±)-tartrate salt], 20858-73-5.

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Formation and Reactions of Dianions Derived from 4-Methylcarbostyril and *trans*-β-Methylcinnamanilide[1]

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Treatment of 4-methylcarbostyril (**1**) with 2 mol equiv of *n*-butyllithium in tetrahydrofuran–hexane effected ionization of the NH proton and one of the methyl protons to form resonance-stabilized dianion **2**. Reaction of dianion **2** with carbonyl compounds, alkyl halides, and carbon dioxide afforded products arising from condensation of the electrophilic reagent at the exocyclic carbanion site. These reactions represent the first examples of successful carbon–carbon condensations at the methyl group of **1**, a position which has previously been considered to be unreactive. *trans*-β-Methylcinnamanilide (**12**) also underwent similar twofold ionization with *n*-butyllithium to afford dianion **13**. Protonation and alkylations of dianion **13** took place predominately at the α-carbanion site, while condensations with benzophenone and 9-fluorenone occurred preferentially at the terminal carbanion position.

Although 4-methylcarbostyril (**1**) has structural features which might be expected to impart some measure of acidity to the hydrogens of its methyl group, there appear to be no examples in the literature of reactions involving even transient carbanion formation at this position. Indeed, failure of **1** to undergo typical carbon–carbon condensation at its methyl group has been cited as evidence that the methyl protons do not possess any appreciable active hydrogen character.[3]

We now wish to report that treatment of **1** with 2 mol equiv of *n*-butyllithium in tetrahydrofuran–hexane for

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