

The Schmidt Reaction of α -Aralkyl-Substituted Carboxylic Acids¹R. M. PALMERE^{2a} AND R. T. CONLEY^{2b}Department of Chemistry, Seton Hall University, South Orange, New Jersey 07079,
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When 2-phenyl-2-methylhexanoic acid (1) was treated with sodium azide in polyphosphoric acid (ppa), the products of the reaction were aniline (2), 2-hexanone (3), 2-phenyl-1-hexene (4), *trans*-2-phenyl-2-hexene (5), *cis*-2-phenyl-2-hexene (6), and low polymeric material. In order to gain some insight into the route by which aniline was formed, a series of α -di- and trisubstituted acids were examined and found to yield varying amounts of aniline. 2-*p*-Tolyl-2-methylhexanoic acid was reacted to yield *p*-toluidine. The results of these experiments indicate the first step of the reaction to be decarboxylation to an aralkyl cation. In order to substantiate this proposal, the expected intermediates from a "Normal" Schmidt reaction of 1 were prepared by independent syntheses and subjected to rearrangement conditions: the acyl azide 7, the isocyanate 8, and the amine 9, were examined. All of the projected intermediates failed to give aniline on treatment with ppa without azide present. The mechanism is described.

The transformation of carboxylic acids to amines *via* the Schmidt reaction³ (*i.e.*, hydrazoic acid in sulfuric acid) has been a useful synthetic tool.⁴

The most intriguing example of the anomalous behavior of a carboxylic acid was reported by Arcus and coworkers.⁵ 2-Phenyl-2-methylhexanoic acid upon treatment with sodium azide in sulfuric acid gave aniline (55%). They proposed that in the presence of sulfuric acid 2-phenyl-2-methylhexanoic acid (1) was protonated to form the dihydroxycarbonium ion which attacked the nitrogen of hydrazoic acid. This intermediate loses a molecule of nitrogen with the subsequent migration of phenyl to the remaining electron deficient nitrogen to form phenyl isocyanate and the isomeric hexenes. The phenyl isocyanate then decomposes to the observed aniline. However, certain anomalies such as fragmentation^{6,7} and isomerization⁸ of certain acids in sulfuric acid have limited the usefulness of this reaction.

With the ever growing popularity of ppa as a medium for rearrangements⁹ and since it has been reported as a good solvent for the Schmidt reaction of spiro ketones,¹⁰ ppa was used in this study.

In order to clarify the reaction pathway for the apparent phenyl migration reported by Arcus and coworkers⁵ and to investigate the fragmentation of acids under Schmidt conditions, (*i.e.*, strong acid media), it was of interest to determine the fate of the possible intermediates (the acyl azide, the isocyanate, the amine, and the olefins) in the Schmidt reaction of acids with or without azide present.

Discussion and Results

When 2-phenyl-2-methylhexanoic acid (1) was heated at 50° with the equivalent of sodium azide for 8 hr in

ppa, the products of the reaction were aniline (2), 2-hexanone (3), three isomeric phenyl-substituted hexenes (4-6), and a low polymeric material.¹¹ None of the isomeric hexenes described by Arcus⁵ were observed. Furthermore, the products obtained from acid 1 under these reaction conditions without sodium azide present were the three isomeric phenyl-substituted olefins (4-6) and polymeric material. Since styrene and substituted styrenes have been shown to polymerize in both ppa¹² and concentrated acid^{13,14} it was necessary to show that the olefins formed were polymerized under the reaction conditions. The three isomeric phenyl-substituted hexenes prepared independently (*i.e.*, the dehydration of 2-phenyl-2-hexanol) were polymerized in ppa. The results (Table I) show that the polymeric materials were derived from the phenyl-hexenes.¹⁵ In addition treatment of the polymeric product with sodium azide in ppa did not produce aniline.

TABLE I
PRODUCTS OBTAINED FROM THE TREATMENT
OF THE THREE OLEFINS WITH PPA

Reactant	<i>trans</i> -2-Phenyl-2-hexene			Polymer, %
	2-Phenyl-1-hexene (4), %	(5), %	<i>cis</i> -2-Phenyl-2-hexene (6), %	
2-Phenyl-1-hexene (4)	None	1.7	None	98.3
<i>trans</i> -2-Phenyl-2-hexene (5)	None	5.4	None	94.6
<i>cis</i> -2-Phenyl-2-hexene (6)	1.3	3.2	34.3 ^a	61.2

^a Interestingly *cis*-2-phenyl-2-hexene (6) is slowest to react and is in good agreement with Table III. A study of the rates of polymerization would be necessary to explain why all three olefins are not observed with compound 5.

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(2) (a) Abstracted from the Ph.D. Thesis of R. M. Palmere, Seton Hall University, 1966. (b) To whom inquiries should be addressed at Wright State University.

(3) P. A. S. Smith, "Molecular Rearrangements," Vol. I, 1st ed, P. de Mayo, Ed., Interscience, John Wiley & Sons, Inc., New York, N. Y., 1963, pp 483-567 and references therein.

(4) R. B. Wagner and H. D. Zook, "Synthetic Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1953, pp 677-678.

(5) C. L. Arous, J. Kenyon, and S. Levin, *J. Chem. Soc.*, 407 (1951).

(6) C. Schuerch, Jr., and E. H. Huntress, *J. Amer. Chem. Soc.*, **71**, 2233 (1949).

(7) C. Schuerch, Jr., and E. H. Huntress, *ibid.*, **71**, 2238 (1949).

(8) A. Lundren, *ibid.*, **82**, 3228 (1960).

(9) (a) H. R. Snyder, C. T. Elston, and D. B. Kellom, *ibid.*, **75**, 2014 (1953); (b) H. R. Snyder and C. T. Elston, *ibid.*, **76**, 3039 (1954).

(10) R. T. Conley and B. E. Nowak, *J. Org. Chem.*, **26**, 692 (1961).

(11) While it is convenient to consider the low polymeric material as one component, it was shown by vpe to contain at least three components (having long retention times) which were trapped and found to have virtually identical ir spectra (and quite similar to that of polystyrene) differing only in the relative intensity of various absorptions.

(12) L. A. Paquette and T. A. Phillips, *ibid.*, **30**, 3883 (1965).

(13) W. E. McEwen, M. Gilliland, and B. I. Sparr, *J. Amer. Chem. Soc.*, **72**, 3212 (1950).

(14) M. T. Rosen, *J. Org. Chem.*, **18**, 1701 (1953).

(15) Established by ir spectral comparison of the polymers obtained from the olefin polymerization with those from the Schmidt reaction.

It would appear that on heating the acid **1** with sodium azide in ppa, that there are at least two competing reactions taking place: the first, the addition of azide to the acid (footnote *a*, Table IV); secondly, the decarboxylation of the acid to give olefins which undergo polymerization.

The effect of the preheating time on the products of the Schmidt reaction in ppa (*i.e.*, time of heating before the sodium azide was added) was varied. These results are shown in Table II.

TABLE II
EFFECT OF TIME AT 50° ON 2-PHENYL-2-METHYLHEXANOIC ACID WITH AND/OR WITHOUT SODIUM AZIDE

Pre-heating time, hr	Time with sodium azide, hr	Isomeric olefins, %	Polymer %	Aniline, %
8		10.8	79.7	
8	4	12.6	77.4	0.3 ^a
4	8	17.1	67.7	0.6 ^a
	8	6.2	34.6	57.7 ^{a,c}
	12	7.6	33.3	54.0 ^{b,c}

^a Isolated as aniline hydrochloride. ^b Isolated as benzanilide. ^c Interestingly, as the concentration of azide was increased under the reaction conditions noted, the yield of aniline was proportionately greater.

As can be clearly seen by examining the data in Table II, the maximum yield of aniline and polymer are dependent upon the contact time of acid with azide.

Although Arcus and coworkers⁵ proposed a phenyl migration to produce an isocyanate intermediate, we thought that perhaps an alternate pathway was also feasible; namely, the reaction may have occurred by an N⁺ insertion analogous to that proposed by Lansbury and Colson¹⁶ for hindered ketones or by a cationic intermediate as proposed by Schuerch and Huntress⁶ for α -trisubstituted alkyl acids.

When 2-*p*-tolyl-2-methylhexanoic acid was treated with sodium azide under the reaction conditions, *p*-toluidine (73%) was obtained. This experiment eliminated the possibility of an N⁺ insertion mechanism. It is reasonable to assume that the first step of the reaction involves the formation of carbonium ion capable of transformation to olefin and to polymer. The attack of azide on this intermediate would be expected to form aniline and ketone since it has been shown^{12,17-19} that hydrazoic acid adds to olefins in the presence of sulfuric acid to give aralkyl azides which rearrange to ketones and amines.

Since the observed products were aniline and a ketone as well as olefins, it was necessary to show that the three olefins obtained from decarboxylation of **1** would add azide under Schmidt conditions to give aniline (**2**) and 2-hexanone (**3**). The product distributions from these studies are shown in Table III. From these data it seems realistic to propose that aniline arises from the reaction of azide with the cation, and that this reaction competes with the olefin formation and polymerization processes. Moreover, if the carbonium ion produced

TABLE III
REACTION OF THE THREE ISOMERIC OLEFINS WITH SODIUM AZIDE IN PPA AT 50°

Olefin	Aniline, %	Polymer, %	Unreacted olefin, %
2-Phenyl-1-hexene (4)	53.4	45.0	1.2 ^a
<i>trans</i> -2-Phenyl-2-hexene (5)	43.7	46.0	4.6
<i>cis</i> -2-Phenyl-2-hexene (6)	12.9	51.7	35.4 ^a

^a Includes isomeric olefins.

via decarboxylation was phosphorylated, it should be possible to prepare this intermediate from the corresponding 2-phenyl-2-hexanol. This alcohol should give the intermediate which could either eliminate to form the olefins or be attacked by azide to give the aralkyl azide^{12,17-19} required for the rearrangement to aniline and ketone. When 2-phenyl-2-hexanol was treated with sodium azide in ppa, only 29% aniline was obtained indicating a competitive polymerization occurring in this case compared with the results during Schmidt reaction of the acid (**1**). Since diphenyl methyl alcohol, when treated in sulfuric acid with sodium azide, gave aniline,²⁰ and the azide of triphenylcarbinol can be isolated from sulfuric acid,²¹ it would appear that the stability of the azide formed from the cation is the controlling factor in this type of rearrangement. With these data in mind, it was decided to study a series of aralkylcarboxylic acids. The groups in the α position were varied in order to determine the yield of aniline as a function of structure. These results are summarized in Table IV and indicate the limitations of this process. In only two cases was the amine from "normal rearrangement" obtained. Phenylacetic acid gave only benzylamine (no aniline could be detected), and 2-phenylhexanoic acid gave 49.2% the expected 1-phenylpentylamine from the "Normal" Schmidt reaction as well as 46.4% aniline. Surprisingly, 1-phenylcyclohexanecarboxylic acid gave 54% aniline and 46% recovered acid. None of the expected amine, 1-phenylcyclohexylamine, was detected.

Assuming that the mechanism of the Schmidt reaction of acids²² to form amines parallels that of the Curtius rearrangement, then any of the normal intermediates (*i.e.*, acyl azide, isocyanate, or amine) could be an intermediate in the formation of aniline. These intermediates, the acyl azide (**7**), the isocyanate (**8**), and the amine (**9**) (prepared *via* a modification of the Curtius reaction²³), were treated with ppa with and without azide present (Table V). From the amount of aniline produced, it must be concluded that the α -aralkyl acids are decarboxylated prior to cation formation in ppa rather than rearrangement to any of the expected intermediates as depicted in the sequence of steps in Scheme I.

Experimental Section

Melting and boiling points are uncorrected. Ir spectra were obtained with a Beckman IR-10 grating spectrophotometer. The nmr spectra were determined on a Varian A-60A in deuterio-

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SCHEME I
SUMMARY OF REACTION STEPS IN THE FORMATION OF ANILINE FROM 2-PHENYL-2-METHYLHEXANOIC ACID

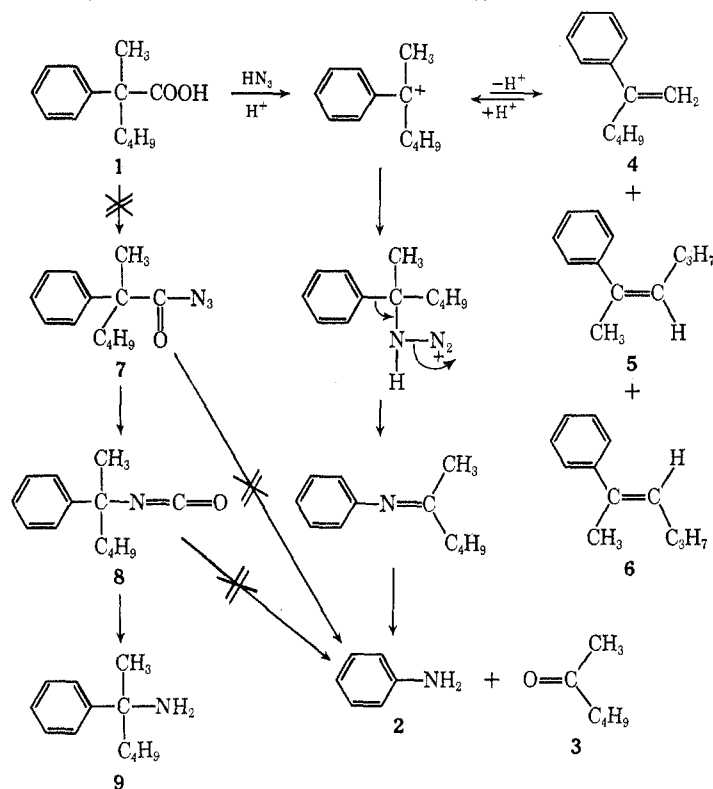


TABLE IV
REACTION OF α-SUBSTITUTED PHENYLACETIC ACIDS WITH SODIUM AZIDE AT 50°

$\begin{array}{c} \text{R}_1 \\ \\ \text{R}-\text{C}_6\text{H}_4-\text{C}-\text{COOH} \\ \\ \text{R}_2 \end{array}$			$\xrightarrow[\text{ppa}]{\text{NaN}_3}$	products				
R	R ₁	R ₂	Registry no.	Recovered acid, %	Olefin, %	Polymer, %	Normal amine, %	Aniline, %
H	H	H	103-82-2	32.3	None	None	67.7	None
H	H	C ₄ H ₉	24716-09-4	None	None	2.3	49.2	46.4
H	H	C ₆ H ₅	117-34-0	95.1	None	None	None	4.0
H	CH ₃	C ₆ H ₅	5558-66-7	87.1	None	None	None	12.9
H	C ₆ H ₅	C ₆ H ₅	595-91-5	98.0	None	None	None	None
H	-CH ₂ -(CH ₂) ₃ -CH ₂ -		1135-67-7	46.0	None	None	None	54.0
H	CH ₃	C ₄ H ₉	2955-41-1	0.01 ^a	6.3	34.6	None	57.7 ^b
CH ₃	CH ₃	C ₄ H ₉	24716-14-1	None	4.9	21.0	None	73.3 ^c

^a Ir shows a small amount of azide present. ^b Isolated as the hydrochloride. ^c *p*-Toluidine.

TABLE V
TREATMENT OF POSSIBLE SCHMIDT INTERMEDIATES OF 2-PHENYL-2-METHYLHEXANOIC ACID IN PPA WITH AND WITHOUT SODIUM AZIDE

Compd	Sodium azide, equiv	Time, hr	Temp, °C	Aniline, %
Acyl azide	...	8	50	None ^{b,c}
	1	8	50	25.7
Isocyanate	...	8	50	None ^{b,c}
	1	8	50	44.4
Amine	1	8	50	None ^d

^a One equivalent of azide is consumed to form the intermediate; therefore, these reactions were carried out without added azide. ^b None (less than 0.1%). ^c Products were olefins and polymer. ^d Only starting amine was isolated.

nitrile on Chromosorb P, programmed from 60–220° at 20°/min with a helium flow rate of 60 cm³/min; preparative vpc employing Wilkens "auto-prep" using 20 ft by 3/8 in. silicone rubber on Chromosorb W with a helium flow rate of 200 cm³/min, 185° isothermal.

Acids and Esters.—The general procedure of Kenyon, Meyers, and Hauser²⁴ was employed for the synthesis of the following esters and acids; unless otherwise noted, the vpc of each compound indicated only one component. The ir spectrum was in agreement with the structure.

Ethyl 2-phenylhexanoate (81%):²⁵ bp 103–105° (2 mm) [lit.²⁴ 74–76° (0.1 mm)]. *Anal.* Calcd for C₁₄H₂₀O₂: C, 76.32; H, 9.15. Found: C, 76.35; H, 9.21.

Ethyl 2-(*p*-tolyl)propionate (81%): bp 116–118° (10 mm) [lit.²⁴ 121° (11 mm)]. *Anal.* Calcd for C₁₂H₁₆O₂: C, 74.97; H, 8.39. Found: C, 79.77; H, 8.29.

Ethyl 2-phenyl-2-methylhexanoate (75%): bp 132–135° (4

chloroform or carbon tetrachloride and are referred internally to tetramethylsilane. Vpc was performed on a F & M Model 720 gas chromatograph as follows: 6 ft by 0.25 in. 10% silicone gum

(24) W. G. Kenyon, R. E. Meyers, and C. R. Hauser, *J. Org. Chem.*, **28**, 3108 (1963).

(25) Per cent yield of product obtained.

mm) [lit.²⁶ 122–125° (4.5 mm)]. *Anal.* Calcd for C₁₅H₂₂O₂: C, 76.87; H, 9.46. Found: C, 76.72; H, 9.42.

Ethyl 2-(*p*-tolyl)-2-methylhexanoate (59%): bp 132–134° (2.5 mm). *Anal.* Calcd for C₁₈H₂₄O₂: C, 77.33; H, 9.74. Found: C, 77.19; H, 9.82.

2-Phenylhexanoic acid (80%): bp 181–183° (20 mm) [lit.²⁴ 173–178° (19 mm)]. *Anal.* Calcd for C₁₂H₁₆O₂: C, 74.44; H, 8.39. Found: C, 74.51; H, 8.32.

2-Phenyl-2-methylhexanoic acid (89%): bp 154–156° (4 mm) [lit.²⁷ 155° (4 mm)]. *Anal.* Calcd for C₁₃H₁₈O₂: C, 75.69; H, 8.79. Found: C, 75.58; H, 8.81.

2-(*p*-Tolyl)-2-methylhexanoic acid (45%): bp 148–150° (1.0 mm). *Anal.* Calcd for C₁₄H₂₀O₂: C, 76.32; H, 9.15. Found: C, 76.43; H, 9.04.

2,2-Diphenylpropionic acid (86%): mp 173–174° (lit.²⁸ 173–174°).

1-Phenylcyclohexanecarboxylic acid was prepared by the procedure of Case²⁹ to give 8.5% desired product: mp 121–122° (lit.²⁹ 123°).

2-Phenyl-2-hexanol was prepared from *n*-butyl magnesium bromide and acetophenone as described by Conant and Carlson²⁷ (60%): bp 129–131° (4 mm) [lit.^{27,30} 129–130° (4 mm)].

Olefin Synthesis.—The three isomeric phenyl-substituted hexenes, 2-phenyl-1-hexene (4), *trans*-2-phenyl-2-hexene (5), and *cis*-2-phenyl-2-hexene (6), were prepared by the dehydration of 2-phenyl-2-hexanol as described by Mohan and Conley.³⁰ Each olefin was obtained by preparative vpc. The elemental analysis and refractive indices of each olefin were in good agreement with authentic samples obtained from A. G. Mohan,³⁰ also, the vpc retention time, ir, and nmr spectra were identical.

Amines and Related Compounds.—Table VI summarizes the products isolated by a modified Curtius³³ rearrangement of the corresponding acids. The following general procedure was used for the synthesis of amines.

TABLE VI

Compd	Bp (obsd), °C (mm)	Bp (lit.), °C (mm)
1-Amino-1-phenylpentane	110–111 (12)	110 (12) ^a
2-Phenyl-2-hexylisocyanate	62–64 (0.5)	
2-Amino-2-phenylhexane	110–112 (2)	127 (18) ^b
1,1-Diphenylethylamine	141–143 (4)	140–142 (4) ^c
1-Phenylcyclohexylamine	84–86 (1.0)	84–89 (1.0) ^d

^a Krugmann and Co., British Patent 813,524 (May 21, 1951).

^b See ref 5. ^c A. W. Weston and K. E. Hamilton, Jr., Abbott Laboratories, U. S. Patent 2,801,072 (Nov 18, 1958); *Chem. Abstr.*, 53, 7216g (1959). ^d Parke, Davis & Co., British Patent 853,775 (Nov 9, 1960).

2-Phenyl-2-methylhexanoic acid (5.9 g, 0.29 mol) was suspended in 5 ml of water and acetone was added to form a solution. The solution was cooled to 0° and 3.4 g (0.033 mol) of triethylamine in 65 ml of acetone was added, followed by 4.17 g (0.037 mol) of ethyl chloroformate in 15 ml of acetone. The solution was stirred an additional 30 min at 0° after the addition was completed. Sodium azide (2.87 g, 0.043 mol) in 10 ml of water was added dropwise, maintaining the temperature at 0°. After the addition was completed the mixture was stirred for 1 hr, was poured into ice water, and was extracted with ether. The ether portion was dried (MgSO₄) and most of the ether was removed at reduced pressure. Since acyl azides are known to decompose violently with heat and shock, some of the ether solvent was allowed to remain. The infrared spectra of 2-phenyl-2-methylhexanoic acid azide showed a characteristic azide band at 2150 (N₃ str) and 1725 cm⁻¹ (C=O str).

The solution of acyl azide was diluted with 25 ml of dry toluene and the residual ether was removed *in vacuo*. The solution of acyl azide in toluene was added dropwise to a hot flask equipped with an efficient condenser. After the evolution of nitrogen had ceased (1 hr) the crude product was examined by vpc (93% isocyanate). The 2-phenyl-2-methylhexyl isocyanate distilled at

62–64° (0.05 mm); *n*_D²⁰ 1.5021; ir 2250 cm⁻¹ (N=C=O stretching frequency); vpc (silicone gum nitrile) showed only one component.

The 2-phenyl-2-methylhexyl isocyanate (4.53 g) was refluxed with 30 ml of 20% aqueous hydrochloric acid for 16 hr. The clear solution was cooled, extracted with ether, and the aqueous portion was evaporated at reduced pressure. The residual semi-solid crystallized from ethyl acetate–ether, mp 133–141°.

Recrystallization from ethylacetate–ether gave 2.21 g, mp 141–143° (lit.⁸ 144–147°), of the 2-phenyl-2-hexylamine hydrochloride. *Anal.* Calcd for C₁₂H₂₀NCl: C, 67.45; H, 9.37; N, 6.57; Cl, 16.61. Found: C, 67.51; H, 9.41; N, 6.61; Cl, 16.73.

The amine hydrochloride was converted to the free amine with sodium hydroxide, 2-phenyl-2-hexylamine, bp 110–112° (2 mm) [lit.⁸ 127° (18 mm), lit.³⁰ 76–80° (0.6–1.0 mm)].

The *N*-benzoyl derivative was prepared, 2-benzamido-2-phenylhexane, mp 146–147° (lit.^{8,30} 146–147°).

The *N*-acetyl derivative had mp 110–111° (lit.³⁰ 110–111°).

Schmidt Reactions.—All reactions were carried out in 17–20:1 weight ratio of ppa to reactant. A typical reaction procedure is described. A summary of the data is found in Tables I to V.

2-Phenyl-2-methylhexanoic Acid.—To a solution of 2.07 g (0.01 mol) of 2-phenyl-2-methylhexanoic acid in 40 g of ppa gently stirred at 50° was added 0.650 g (0.01 mol) of sodium azide maintaining the temperature at 50°. The mixture was gently stirred for 8 hr (gas evolution). The flask was removed from the bath, filled with crushed ice, and stirred until the aqueous ppa could be poured into a separatory funnel. The mixture was extracted three times with 50-ml portions of methylene chloride to remove any unreacted acid and neutral products. The methylene chloride extracts were combined and washed successively with 10% sodium hydroxide solution and water. The extracts were dried (MgSO₄), filtered, and evaporated under reduced pressure to give 1.78 g of crude oil. The crude oil was analyzed by vpc (silicone gum nitrile). Six components were trapped and characterized as follows.

First Component.—Retention time 1.3 min (47.7%),³¹ identified as 2-hexanone by comparison of its ir spectrum and retention time with that of an authentic sample; the 2,4-dinitrophenylhydrazone, mp 106° (aqueous-alcohol) (lit.³² 106°), no depression upon admixture with an authentic sample; the semicarbazone, mp 122–124° (lit.³² 122°).

Second Component.—Retention time 3.2 min (5.1%), characterized as *trans*-2-phenyl-2-hexene by spectral comparison (ir and nmr) with an authentic sample.

Third Component.—Retention time 3.6 min (0.3%), characterized as 2-phenyl-1-hexene from its retention time and peak enhancement with an authentic sample.

Fourth Component.—Retention time 4.0 min (0.9%), characterized as *cis*-2-phenyl-2-hexene from its retention time and peak enhancement with an authentic sample.

Fifth Component.—Retention time 7.0 min (0.5%), unidentified.

Sixth Component.—Retention times 8.3 and 9.1 min (34.5% total), were identified as polymeric materials by their retention times and ir spectral identity with polymeric products from the polymerization of the olefins in ppa.

The sodium hydroxide extract was acidified with hydrochloric acid and extracted with methylene chloride. The methylene chloride was washed with water, dried (MgSO₄), and evaporated *in vacuo* to give 30 mg (0.01%) of 2-phenyl-2-methylhexanoic acid identified by its ir spectrum. The aqueous ppa portion was made alkaline with solid sodium hydroxide while adding ice chips to maintain the temperature below 25°. The basic solution was extracted with methylene chloride. The extracts were washed with water, dried (MgSO₄), and evaporated *in vacuo* to give 0.594 g of crude oil. Vpc analysis of the crude oil (silicone gum nitrile) showed a single component, retention time 3.2 min (57.7%), identified as aniline by comparison of its ir spectrum, retention time, and enhancement of the peak with an authentic sample.

(26) W. G. Kenyon, E. M. Kaiser, and C. R. Hauser, *J. Org. Chem.*, **30**, 2937 (1965).

(27) J. B. Conant and B. H. Carlson, *J. Amer. Chem. Soc.*, **54**, 4048 (1932).

(28) M. T. Bateman, *ibid.*, **49**, 2917 (1927).

(29) F. H. Case, *ibid.*, **56**, 715 (1934).

(30) A. G. Mohan and R. T. Conley, *J. Org. Chem.*, **34**, 3259 (1969).

(31) The yield of component in all cases is based upon amount of crude isolated and the relative abundance of the component obtained from the vpc peak area.

(32) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th ed, John Wiley & Sons, Inc., New York, N. Y., p 316.

Derivatization of the crude oil by dissolution in anhydrous ether and treatment with hydrogen chloride yielded 0.694 g (57.5%) of aniline hydrochloride, mp 196–198° (lit.³³ 198°). Mixture melting point determination gave no depression.

In a second identical experiment the aniline (54%) was isolated and characterized as its benzanilide derivative. The oil described above was treated with benzoyl chloride in pyridine to give 1.07 g, mp 161–163° (lit.³³ 163°).

(33) I. Heilbron, "Dictionary of Organic Compounds," Vol. I, Oxford University Press, 1953.

Registry No.—Ethyl 2-(*p*-tolyl)-2-methylhexanoate, 24716-15-2; 2-phenyl-2-hexyl isocyanate, 24716-16-3.

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Proton Nuclear Magnetic Resonance Spectra of Arylmethyl Systems¹

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The proton nmr spectra of a number of arylmethyl derivatives ArCH_2X , where ArH is an alternant aromatic hydrocarbon, have been measured. The differences in chemical shift of the methylene protons appear to be due primarily to ring current effects rather than hyperconjugation.

Since the early days of nmr spectroscopy, much attention has been paid to the factors affecting the chemical shifts of protons attached to atoms in aromatic rings.^{3,4} As a result of extensive experimental and theoretical studies, a reasonably consistent picture of such chemical shifts has emerged. This satisfactory situation does not, however, extend to side-chain protons in, *e.g.*, methyl derivatives of such systems, and there has been controversy in such cases concerning the possible role of hyperconjugation.

Fraser and his collaborators⁵ measured the nmr spectra of a number of *para*-disubstituted benzene derivatives $\text{XC}_6\text{H}_4\text{CH}_2\text{Y}$ and correlated the chemical shifts of the methylene protons using the Hammett relation; they concluded from these correlations that the differences were due to the effect of the substituent X on hyperconjugative interactions between methylene and the ring. On the other hand, Ouellette and van Leuwen⁶ interpreted the chemical shifts of methyl in monomethyl derivatives of benzene, naphthalene, anthracene, phenanthrene, and benzo[*a*]anthracene in terms of diamagnetic shielding of the methyl protons by aromatic ring currents; they did not consider the possible role of hyperconjugation, and the monomethyl derivatives of benzo[*c*]phenanthrene showed deviations which they attributed to interference with ring currents due to nonplanarity of the molecule.

The work of Fraser, *et al.*,⁵ is not conclusive because substituents containing heteroatoms can exert long-range magnetic shielding effects;⁷ the correlation with the Hammett relation could therefore have been fortuitous, particularly in view of the small number of compounds studied in some of their series and the scat-

ter of the Hammett plots. It is also possible that the effects of substituents on ring current could roughly follow the Hammett relation; this possibility cannot be excluded on the basis of their results since these referred only to one ring system.

If, on the other hand, hyperconjugation in compounds of the type ArCH_3 is important, one would expect it to vary with the nature of the aryl group. The variations observed by Ouellette and van Leuwen⁶ could then have been due to this rather than to magnetic shielding, the correspondence with the latter being due to coincidence. As a rough measure of the conjugation between Ar and CH_3 in ArCH_3 , one may take the corresponding interaction between Ar and CH_2 in the odd AH (alternant hydrocarbon) ArCH_2 ; this in turn is given approximately by the NBMO (nonbonding MO) coefficient (a_{or}) at the position in Ar adjacent to methylene.⁸

Figure 1 shows a plot of the chemical shifts reported by Ouellette and van Leuwen⁶ against a_{or} ; there is clearly a reasonable linear relation between the two quantities and the scatter could well be due to the crudity of this procedure for estimating the hyperconjugative interactions in ArCH_3 . Only four points deviate significantly from the line and these are all for compounds where the methyl is severely hindered, *viz.*, 4-methylphenanthrene (A), 1-methylbenzo[*a*]anthracene (B), 12-methylbenzo[*a*]anthracene (C), and 1-methylbenzo[*c*]phenanthrene (D). There is evidence that steric compression may lead to significant chemical shifts.⁹

It is particularly striking that the points for the remaining five methylbenzo[*c*]phenanthrenes behave normally in the plot of Figure 1; Ouellette and van Leuwen⁶ were forced to neglect them since the observed chemical shifts deviated from their relation calculated on the basis of magnetic shielding by ring currents. They attributed the discrepancy to the known nonplanarity of benzo[*c*]phenanthrene; this, however, seems unconvincing since the angular distortions of the individual rings are too small to influence the π MO's significantly, since the total strain

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(2) NASA Trainee, 1965–1968.

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(7) See M. J. S. Dewar and Y. Takeuchi, *J. Amer. Chem. Soc.*, **89**, 390 (1967), and references cited there.

(8) See M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1969.

(9) See *e.g.*, F. A. Davis and M. J. S. Dewar, *J. Amer. Chem. Soc.*, **90**, 3511 (1968), and references cited there.