half-life of only 45 minutes, its rotation decreasing from α_D $-43°$ (l 0.5, homogeneous) to $-3°$ after three hours. In run no. 7 from 20 g. of hydratropic acid as the starting quantity, there was obtained 1.06 g. of a white solid when the ether layer was washed with ammonia. Recrystallized from ethanol–water, the solid had m.p. 160–160.5° (repd. for α-phenylisobutyramide 160–161°).[32]

Anal. Calcd. for $C_{10}H_{13}ON$: C, 73.62; H, 8.03; N, 8.58. Found: C, 73.64; H, 7.82; N, 8.30.

In run no. 11, a high-boiling product (1.5 g. from 10 g. of hydratropic acid as the starting quantity), b.p. 135–200° (10 mm.), on standing turned purple and partially solidified. Recrystallized from petroleum ether, the solid, which was soluble in sodium carbonate, had m.p. 78.5–79.0° (repd.[32,16a] for α-phenylisobutyric acid 77–78° and 80–81°[33]).

Anal. Calcd. for $C_{10}H_{12}O_2$: C, 73.14; H, 7.37. Found: C, 73.26; H, 7.12.

(B).—From preliminary runs it appeared that the addition of hydratropic acid to the theoretical quantity (two moles) of methyllithium gave yields of ketone varying from 10 to 55%. The product was usually contaminated, to judge by the high refractive index, and always racemized to a variable (30–70%) extent. Increased (up to four) mole ratios of methyllithium gave improved results.

To 0.20 mole of methyllithium in 225 ml. of ether was added 7.5 g. (0.050 mole) of 89.8% optically pure hydratropic acid (α^{28}_D +43.50° (l 0.5, homogeneous) and $[\alpha]^{27}_D$ +82.5° (c 2.23, benzene)) over a period of 20 minutes at room temperature (run no. 12, Table II). Stirring was continued for 20 more minutes, and the solution was then poured into ice-water. The ether layer was washed four times with water (until washings were neutral), dried over sodium sulfate, and distilled, to give 6.8 g. of a liquid, b.p. 77° (1 mm.), n^{25}_D 1.5087, α^{27}_D +102.7° (l 0.5, homogeneous). Slow fractionation gave fraction I, b.p. 79–80° (5 mm.), 1.49 g., n^{25}_D 1.5072, α_D +133.16° (l 0.5, homogeneous); fraction II, b.p. 80–81° (5 mm.), 1.96 g., n^{25}_D 1.5077, α_D +124.4° (l 0.5, homogeneous); fraction III, b.p. 81–84° (5 mm.), 1.87 g., n^{25}_D 1.5087, α_D +107.4° (l 0.5, homogeneous); and a residue, 1.20 g., n^{25}_D 1.5128. The contaminant was assumed to be 2-methyl-3-phenyl-2-butanol because the original liquid gave a Lucas test for a tertiary carbinol yet did not form a phthalate derivative under ordinary conditions.[34] The reported rotation of the carbinol is very low.[35] Fraction I had an infrared spectrum identical with that of *dl*-3-phenyl-2-butanone; it was about 10% racemized.

Other significant preparations are listed in Table II. In runs no. 13, 15 and 16, the product was treated with semicarbazide acetate and the precipitated semicarbazone subjected to steam distillation in the presence of phthalic anhydride[8] in order to recover chemically pure 3-phenyl-2-butanone.

(+)-3-Phenyl-2-butanone Semicarbazone.—A solution of 376 mg. of semicarbazide hydrochloride and 500 mg. of sodium acetate in 3.5 ml. of water was added to 485 mg. of 87.1% active (+)-3-phenyl-2-butanone (run no. 2, Table I) dissolved in 3.0 ml. of 95% ethanol. Slow crystallization gave 560 mg. (84%) of solid. Four crystallizations from 95% ethanol gave 140 mg. of white prisms, m.p. 180–181°, $[\alpha]^{24}_D$ +117.8° (c 1.67, chloroform).

Oxidation of Optically Active 3-Phenyl-2-butanone.—The procedure followed was that described for the inactive ketone, with the exception that the period of reagent contact was shortened to 43 hours; the results are summarized in Table III. In run no. 10, 4.41 g. of ketone (optical purity 32.3%), a sample of which gave a semicarbazone, m.p. 163–167°, $[\alpha]^{25}_D$ +39.0° (c 1.73, chloroform), upon oxidation yielded a product, 4.42 g., b.p. 52–68° (0.3 mm.), n^{25}_D 1.4956, α^{25}_D $-14.24°$ (l 0.5, homogeneous). The latter was dissolved in a small volume of ethanol, treated with a solution of 1 g. of semicarbazide hydrochloride and 2 g. of sodium acetate in 20 ml. of water, and the mixture was concentrated and distilled. The product, 3.03 g. of liquid, had b.p. 101° (16 mm.), n^{25}_D 1.4934, α^{25}_D $-19.00°$ (l, 0.5, homogeneous), which changed to α^{25}_D $-19.75°$ subsequent to treatment with Girard reagent-T. The residue from the distillation consisted of a white solid, which upon recrystallization from ethanol yielded 200 mg. of semicarbazone, m.p. 161–165°, $[\alpha]^{27}_D$ +40.2° (c 1.95, chloroform). This experiment is indicative of the substantial absence of racemization of the ketone during the oxidation.

In two instances (runs 5 and 10) the acetate ester was hydrolyzed to phenylmethylcarbinol; the procedure was that described for the inactive acetate.

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[32] O. Wallach, *Chem. Centr.*, **70**, II, 1047 (1899).

[33] A. Bistrzycki and L. Mauron, *Ber.*, **40**, 4370 (1907).

[34] S. Winstein and B. K. Morse, THIS JOURNAL, **74**, 1133 (1952). These authors gave n^{25}_D 1.5158 and b.p. 85–87.3° (4.8 mm.).

[35] A. Camphell and J. Kenyon, *J. Chem. Soc.*, 436 (1947).

[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

Migration Aptitudes in the Stieglitz Rearrangement[1]

BY MELVIN S. NEWMAN AND PETER M. HAY

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Approximate migration aptitudes for the *p*-methoxyphenyl (9.1), *p*-chlorophenyl (0.55) and *p*-nitrophenyl (0.38 to 0.18) groups have been determined by a study of the Stieglitz rearrangements of appropriately substituted triarylmethylhydroxylamines.

Previous quantitative studies of migration aptitudes of aryl groups have been confined mainly to reactions in which the group migrates from one carbon to an adjacent carbon.[2] We thought it of interest to study migration aptitudes in which the migration proceeds from carbon to nitrogen.

Preliminary experiments were directed toward a reaction of triarylcarbonium ions in sulfuric acid with sodium azide. However, when it was found that only triphenylmethyl azide resulted from the reaction of triphenylcarbinol with sodium azide and sulfuric acid,[3] this approach was abandoned. Attention was next directed toward the rearrangement of triarylmethylhydroxylamines, the Stieglitz rearrangement.[4] A study of previous work revealed that the substitution of a chlorine or bromine atom in the para position had little effect on the migration aptitude of a phenyl group.

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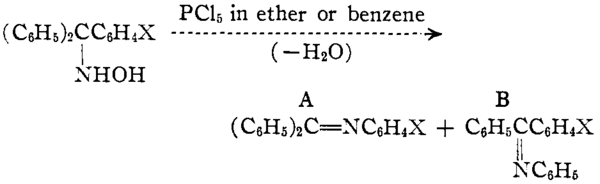
[1] Taken from the Ph.D. thesis of P. M. Hay, Ohio State University, 1952.

[2] H. Adkins in H. Gilman's "Organic Chemistry," Vol. I, 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1937, p. 1068.

[3] C. L. Arcus and R. J. Mosley, *Chemistry and Industry*, 701 (1951), reported the same result.

[4] C. W. Porter, "Molecular Rearrangements," Chemical Catalog Co. (Reinhold Publ. Corp.), New York, 1928, pp. 30–34, and references therein.

In this paper we report on the rearrangement of three triarylmethylhydroxylamines



$$\underset{\displaystyle NHOH}{(C_6H_5)_2\underset{|}{C}C_6H_4X} \xrightarrow[(-H_2O)]{PCl_5\text{ in ether or benzene}} \overset{A}{(C_6H_5)_2C{=}NC_6H_4X} + \overset{B}{C_6H_5\underset{\displaystyle NC_6H_5}{\underset{\|}{C}}C_6H_4X}$$

where for I, $X = OCH_3$; for II, $X = Cl$ and for III, $X = NO_2$.

The substituted hydroxylamines were prepared by an improved method which consisted in the addition of the appropriate trityl chloride in benzene or ether to a solution prepared by adding an excess of hydroxylamine hydrochloride to a solution of sodium ethoxide in absolute ethanol.

The rearrangements were carried out by refluxing the hydroxylamines in ether containing phosphorus pentachloride. The resulting anils were hydrolyzed by acid into mixtures of ketones and amines. Anils of type A, resulting from migration of the substituted phenyl radical, yielded benzophenone and substituted aniline, whereas anils of type B, resulting from phenyl migration, yielded a substituted benzophenone and aniline. Thus, the migration aptitude of various groups could be determined by analysis of either the mixture of amines formed or of the ketones.

The analytical method chosen varied with the compounds. For the *p*-chloro compound, II, the amine fraction was analyzed by quantitative bromination. For the *p*-methoxy compound, I, the bromination method was inadequate and a quantitative infrared spectral method was developed. This method was made sufficiently accurate only after several methods of separating and purifying the ketone fraction had been evaluated. For the *p*-nitro compound, III, both the amine and ketone fractions were analyzed, the agreement being only fair but sufficiently accurate to place the *p*-nitrophenyl group in proper order as regards migration aptitude.

The migration aptitudes (M.A.) of the substituted phenyl groups as compared to a migration aptitude of 1 for phenyl were calculated by the formula

$$\text{M.A.} = \frac{2(\%\text{ substituted aniline})}{\%\text{ aniline}} = \frac{2(\%\text{ benzophenone})}{\%\text{ substituted benzophenone}}$$

The values obtained were as follows: *p*-$CH_3OC_6H_4$, 9.1; *p*-ClC_6H_4, 0.55; and *p*-$NO_2C_6H_4$, 0.18 (from ketone analysis) to 0.38 (from amine analysis). Qualitatively, this order for the *p*-methoxyphenyl and *p*-chlorophenyl is the same as that which obtains in the rearrangement of symmetrical pinacols.[2] It is also the same as that observed in the reaction of substituted 1,1-diarylethylenes with hydrazoic and sulfuric acids, which also involves a rearrangement from carbon to nitrogen.[5] Quantitatively, the *p*-methoxyphenyl group showed a much greater tendency to migrate in the pinacol rearrangement. The *p*-nitrophenyl group has not been included previously in studies on the pinacol rearrangement. It should be emphasized that the values for migration aptitude in our study are only of qualitative significance since the analytical methods were not of great accuracy.

It is a pleasure to acknowledge assistance from a du Pont Grant-in-aid.

Experimental

Preparation of Trityl Chlorides.—*p*-Chlorophenyldiphenylcarbinyl chloride[6] and the methoxy analog[7] were prepared in 61 and 86% yields from the carbinols, respectively, by heating with acetyl chloride in petroleum ether, b.p. 90–100° (Skellysolve C). After removal of most of the solvent the chlorides crystallized and were purified by recrystallization from Skellysolve C. *p*-Nitrophenyldiphenylcarbinyl chloride,[8] m.p. 92–94°, was prepared in 46% yield by condensing *p*-nitrophenylphenyldichloromethane with benzene using aluminum chloride.[7] The crude product was heated with an excess of acetyl chloride which was removed. The residue was recrystallized several times from petroleum ether.

Preparation of Triarylmethylhydroxylamines.—A solution prepared by dissolving 3.2 g. (0.139 mole) of sodium in 60 cc. of absolute alcohol was added to a warm solution of 10.2 g. (0.147 mole) of hydroxylamine hydrochloride in 200 cc. of absolute alcohol. After cooling to 0° a solution of 15.6 g. (0.05 mole) of *p*-chlorophenyldiphenylcarbinyl chloride in 250 cc. of ether was added. After one hour water was added and the ethereal solution was washed and dried. Dry hydrogen chloride was passed in until two layers were evident. When this two phase mixture was shaken with water a white solid separated. This was collected, washed with ether, and stirred with ether and 10% sodium hydroxide solution for ten hours after which no more solid remained. The ether solution was dried and concentrated. The crystals which then separated were collected and washed with ether. A total of 12.1 g. (78%) of *p*-chlorophenyldiphenylmethylhydroxylamine (II)[7] was thus obtained in two crops. This compound proved sensitive and melted with decomposition over a range from 88 to 108°. It could be recrystallized from dry ether–petroleum ether mixtures from which it separated as colorless crystals. On exposure to air or on storage decomposition took place. Accordingly, only freshly recrystallized samples were used for rearrangement studies.

In a similar manner, the *p*-methoxy, I, and *p*-nitro, III, analogs, m.p. 100–111° dec., and m.p. 147–161° dec., were prepared in 83 and 51% yields, respectively.

Anal. Calcd. for $C_{20}H_{19}O_2N$: C, 78.7; H, 6.3; N, 4.6. Found: C, 78.6; H, 6.5; N, 4.6. Calcd. for $C_{19}H_{16}O_3N_2$: C, 71.2; H, 5.0; N, 8.7. Found: C, 71.3; H, 5.0; N, 8.9.

***p*-Chlorophenyldiphenylmethylhydroxylamine (II) Rearrangements.**—A solution of 2 g. of II in 30 cc. of dry benzene was treated with 2 g. of phosphorus pentachloride. After holding at room temperature for 90 minutes, the mixture was refluxed for one hour. Two liquid layers were noted midway through the reaction. The mixture was washed with dilute hydrochloric acid and water, and saturated sodium chloride solution. Because no really satisfactory method for analyzing the mixture of ketones in the benzene layer was found, this solution was not used further. The aqueous acid extracts were combined and made alkaline. The anilines were taken into ether and this solution dried. On passing in dry hydrogen chloride the amine hydrochlorides were precipitated in about 80% yield from II. For analysis see below.

***p*-Methoxyphenyldiphenylmethylhydroxylamine (I).**—A solution of 2 g. of I in 100 cc. of dry ether was treated with 2.0 g. of phosphorus pentachloride and the mixture was then refluxed for 3 hours. After hydrolysis the mixture was separated into amine and ketone fractions as above. Since the analysis of the amine mixture was not successfully ac-

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(5) W. E. McEwen, M. Gilliland and B. I. Sparr, THIS JOURNAL, **72**, 3212 (1950). It is of interest to note that studies on picryl ethers of oximes by A. W. Chapman and F. A. Fidler, *J. Chem. Soc.*, 448 (1936), show that the rate of rearrangement of *p*-methoxyphenyl from carbon to nitrogen is considerably greater than that of *p*-nitrophenyl.

(6) J. Stieglitz and P. N. Leech, THIS JOURNAL, **36**, 272 (1914).

(7) M. Gomberg and C. C. Bachler, *ibid.*, **45**, 207 (1923).

(8) A. Baeyer and V. Villiger, *Ber.*, **37**, 606 (1904).

complished only the ketonic analysis will be described below. The yield of ketone was 30 and 35% in two runs. It is probable that the yield would have been higher had the rearrangement reaction been carried out in benzene since low yields were obtained in other rearrangements in ether. However, since the ratio of anilines formed were the same regardless of the yield in other cases the experiments were not repeated in benzene for the methoxy analog. In preparation for analysis, the crude ketone mixture was slowly distilled under about 1 mm. pressure from the melted state to a cold surface. Several other methods of purification were less satisfactory.

***p*-Nitrophenyldiphenylmethylhydroxylamine (III).**—A solution of 0.50 g. of III and 1.0 g. of phosphorus pentachloride in 25 cc. of benzene was refluxed for 90 minutes. Two liquid layers were present. Methanol and water were added and the mixture was refluxed for 30 minutes. The isolation of basic and neutral fractions was performed as above. The basic fraction yielded 0.35 g. (93%) of amine hydrochlorides and the neutral fraction afforded 0.33 g. (99%) of mixed ketones after purification by slow evaporative distillation. A second run on III yielded similar fractions.

Analytical Procedures. Amines.—The mixtures of amine hydrochlorides from the rearrangements of II and III were analyzed by treatment with bromine in acetic acid.[9] The excess bromine was determined iodometrically. The method was checked by analysis of known mixtures of amine hydrochlorides. The average percentage of aniline found for six closely agreeing analyses was 73.5%. The average of three checks on a known mixture containing 75% aniline was 70%. If one adds this correction of 5% to the value 73.5% one obtains 78.5% of aniline which leads to a migration aptitude of 0.55 for the *p*-chlorophenyl group.

The amine analysis in the case of aniline–nitroaniline mixtures averaged 84.0% aniline and the checks on synthetic mixtures indicated that no correction was needed. The migration aptitude for *p*-nitrophenyl calculated from this value is 0.38.

Ketones.—For the analysis of the ketone mixtures isolated and purified as described above an infrared spectrographic method was used. Known mixtures of each pair of ketones (benzophenone–*p*-nitrobenzophenone and benzophenone–*p*-methoxybenzophenone) were prepared. The optical transmission of these mixtures in chloroform and carbon tetrachloride solution, respectively, were determined at significant wave lengths. Curves relating composition to transmission were drawn and used to estimate the composition of unknown mixtures. For the benzophenone–*p*-nitrobenzophenone mixture, the wave lengths of 6.5, 7.4 and 11.7 μ were chosen as at these wave lengths the nitro ketone absorbed strongly while benzophenone absorbed weakly. The average composition of the mixture of ketones formed from rearrangement of III was 90% *p*-nitrobenzophenone and 10% of benzophenone. The value obtained by analysis of a known mixture in this concentration range checked the theoretical to 2%. The results obtained at the three wave lengths were averaged. The value for ketone composition leads to a calculated migration aptitude of 0.18.

For the benzophenone–*p*-methoxybenzophenone mixture, the wave lengths of 6.6, 8.7, 9.7 and 11.8 μ were chosen as these were the wave lengths at which *p*-methoxybenzophenone absorbed strongly while benzophenone absorbed weakly. The average composition of the mixture of ketones formed from I was 82% benzophenone and 18% *p*-methoxybenzophenone. On averaging the results obtained at the four wave lengths the theoretical value was checked to 2%. The value for ketone composition leads to a calculated migration aptitude of 9.1.

Columbus 10, Ohio

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[9] G. O. Curme, Jr., This Journal, **35**, 1162 (1913).

[Contribution from the Department of Chemistry, Purdue University]

The Synthesis of Fluorine-containing Olefins

By E. T. McBee, O. R. Pierce and M. C. Chen

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Several new fluorine-containing alkenes and alkadienes were prepared from esters of hexafluoroglutaric, octafluoroadipic and heptafluorobutyric acids by reaction with a Grignard reagent followed by dehydration of the secondary or tertiary alcohol obtained. Reaction of the olefins with both bromine and chlorine gave normal addition products.

Discussion

As part of a broad program comprising the synthesis of fluorine-containing hydrocarbons, several new fluorinated alkenes and alkadienes were prepared. These materials were intermediates in the preparation of bromofluoro- and chlorofluoroalkenes and alkanes.

Esters of hexafluoroglutaric, octafluoroadipic and heptafluorobutyric acids reacted normally with methylmagnesium halide to give the corresponding tertiary alcohols in good yield. However, ethylmagnesium halide gave not only the expected tertiary alcohols, but also the corresponding secondary alcohols, while *n*-propyl and isopropylmagnesium halide gave principally the secondary alcohols. A more detailed discussion of the reducing action of Grignard reagents may be found elsewhere.[1-3]

Dehydration of the tertiary alcohols was accomplished using a mixture of sulfuric acid and ether. The secondary alcohols, being more difficult to dehydrate, required the use of phosphorus pentoxide and elevated temperatures. This resistance to dehydration is characteristic of alcohols in which the carbinol group is adjacent to a fluorine-containing group.[2]

Additive chlorination and bromination of the olefins was conducted in solutions of chloroform or carbon tetrachloride at temperatures ranging from 25° to that of the refluxing reaction mixture. In all cases, strong illumination of the reaction mixture was required, indicating a relative inertness of these olefins.

Table I lists the compounds prepared, their physical constants, analyses and the reaction yields.

Experimental

Starting Materials.—The two esters, diethyl hexafluoroglutarate and diethyl octafluoroadipate, were prepared by esterification of the corresponding acids obtained by the oxidation of dichlorohexafluorocyclopentene and dichlorooctafluorocyclohexene.[4] Heptafluorobutyric acid was ob-

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[1] E. T. McBee, O. R. Pierce and J. F. Higgins, This Journal, **74**, 1736 (1952).

[2] *Ibid.*, **74**, 1387 (1952).

[3] K. N. Campbell, J. O. Knobloch and B. K. Campbell, *ibid.*, **72**, 4380 (1950).

[4] E. T. McBee, P. A. Wiseman and G. B. Bachman, *Ind. Eng. Chem.*, **39**, 415 (1947).