[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KANSAS]

The Schmidt Reaction Applied to Several Unsymmetrical Diarylethylenes[1]

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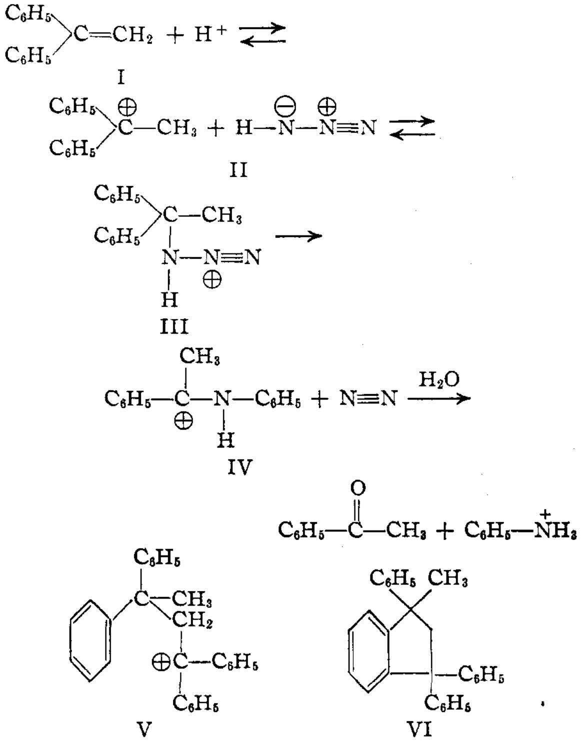
Although the Schmidt reaction as applied to carboxylic acids and ketones has been investigated extensively,[2] little attention has been given to the acid-catalyzed reaction of olefins with hydrazoic acid. An extension of this phase of the Schmidt reaction and a consideration of its probable mechanism constitute the subject of this investigation.

We have found that 1,1-diphenylethylene (I) reacts with hydrazoic acid in chloroform solution, catalyzed by concentrated sulfuric acid, to give acetophenone (together with aniline) in 55% yield and 3-methyl-1,1,3-triphenylindane (VI) in 26% yield. The latter product (VI) is known to be one of the two dimers obtained by treating 1,1-diphenylethylene (I) with concentrated sulfuric acid.[3]

Using a suitable adaptation of mechanisms which have been proposed previously for the Schmidt reaction of carbonyl compounds,[2,4,5,6]



we consider it likely that all the above products arise from a common intermediate, the carbonium ion II, which results from the addition of a proton to 1,1-diphenylethylene (I). The ion II reacts either with a molecule of hydrazoic acid to give the complex III or with a second molecule of 1,1-diphenylethylene (I) to give the new carbonium ion V.[7] With simultaneous loss of nitrogen from III and migration of a phenyl group and its binding pair of electrons,[8] the conjugate acid of acetophenone anil (IV) is formed, which then affords acetophenone and the anilinium ion on hydrolysis.[9] The carbonium ion V undergoes ring closure to give VI.

In the rearrangement of the complex III, the group which migrates to nitrogen will be that one of the three groups in a position to migrate which possesses the greatest intrinsic migratory aptitude.[10] In the corresponding reaction with hydrazoic acid of other unsymmetrical diarylethylenes, in which one or both of the phenyl groups carries a substituent in the para position, the order of migratory aptitudes might reasonably be expected to show a correlation with that of the pinacol–pinacolone rearrangement of symmetrical pinacols, the mechanism of which has many features analogous to the one described here.[11] Such a series of reactions has been carried out, and the anticipated correlation has been qualitatively realized (Table I).

Experimental[12]

1,1-Diphenylethylene (I).—Prepared by the method of Allen and Converse.[13]

Reaction of 1,1-Diphenylethylene (I) with Hydrazoic Acid.—To a suspension of 32.5 g. (0.5 mole) of sodium azide in 100 ml. of chloroform was added dropwise, with external ice cooling and mechanical stirring, 75 ml. of concentrated sulfuric acid. The ice-bath was replaced

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[1] From the theses of Marie Gilliland (1949) and Bertram I. Sparr (1950) in partial fulfillment of the requirements for the degree of Master of Science at The University of Kansas.

[2] H. Wolff, The Schmidt Reaction, "Organic Reactions," Vol. 3, John Wiley and Sons, Inc., New York, N. Y., 1946, pp. 307-336.

[3] E. Bergmann and H. Weiss, *Ann.*, **480**, 49 (1930).

[4] P. A. S. Smith, THIS JOURNAL, **70**, 320 (1948).

[5] J. K. Sanford, F. T. Blair, J. Arroya and K. W. Sherk, *ibid.*, **67**, 1941 (1945).

[6] M. S. Newman and H. L. Gildenhorn, *ibid.*, **70**, 317 (1948).

[7] These reactions fall into the general pattern of the formation and reactions of carbonium ions as described by F. C. Whitmore, *Chem. Eng. News*, **26**, 668 (1948).

[8] For a detailed discussion of the course of such 1,2-shifts see G. W. Wheland, "Advanced Organic Chemistry," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1949, chapt. 12.

[9] C. Schuerch and E. H. Huntress (THIS JOURNAL, **71**, 2233 (1949); **71**, 2238 (1949)) have suggested that the Schmidt reaction of olefins involves a carbonium ion mechanism.

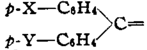
[10] This situation is unlike that reported by P. A. S. Smith and J. P. Horwitz (presented to the Division of Organic Chemistry of the American Chemical Society, San Francisco, Calif., March 27 to April 1, 1949), who studied migratory aptitudes in the Schmidt reaction of various ketones. In the olefin reactions studied here, there is no possibility for a specific steric effect in the rearrangement such as the one previously suggested by Smith[4] for the ketone reactions and supported by the later work.

[11] H. Adkins, Comparison of Chemical Reactivity, in Gilman, "Organic Chemistry," Vol. I, 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1943, pp. 1066-1069.

[12] All m. p.'s are corrected. Analyses by Oakwold Laboratories, Alexandria, Virginia.

[13] "Organic Syntheses," Coll. Vol. I, 2nd ed., 1941, p. 226.

TABLE I

Starting material  $(p\text{-X—C}_6\text{H}_4)(p\text{-Y—C}_6\text{H}_4)\text{C=CH}_2$		% Yield of ketones	
X	Y	p-X-Acetophenone	p-Y-Acetophenone
H	OCH$_3$	49	8
H	CH$_3$	40	8
H	C$_6$H$_5$	39	17
H	H	55	..
H	Cl	18	29
OCH$_3$	CH$_3$	8	39
OCH$_3$	C$_6$H$_5$	11	36
CH$_3$	C$_6$H$_5$	6	21

by a water-bath maintained at about 25°, and 54.0 g. (0.3 mole) of 1,1-diphenylethylene dissolved in 75 ml. of chloroform was added dropwise, with stirring, in the course of several hours. The acid layer became colored dark green. Stirring was continued for another hour after addition of the olefin, and then the reaction mixture was allowed to stand overnight. Crushed ice was added, the reaction mixture stirred thoroughly, and the chloroform layer separated. After distillation of the chloroform, the residual liquid was distilled at reduced pressure, 19.76 g. (55%) of acetophenone being obtained. A portion was converted to the 2,4-dinitrophenylhydrazone, which melted at 248–249° alone and when mixed with an authentic sample of acetophenone D. N. P.

The residue in the distillation flask was warmed with ethanol, and 13.73 g. (26%) of 3-methyl-1,1,3-triphenylindane (VI) was collected. A sample portion, after several crystallizations from ethanol, melted at 144–145° alone and when mixed with an authentic sample of 3-methyl-1,1,3-triphenylindane, prepared by the method of Bergmann and Weiss.[3]

Anal. Calcd. for C$_{28}$H$_{34}$: C, 93.29; H, 6.71. Found: C, 92.92, 93.08; H, 6.61, 6.49.

The original acid layer was made basic with sodium hydroxide solution and steam distilled into 6 *M* hydrochloric acid. Evaporation of the aqueous solution afforded 15.83 g. (41%) of aniline hydrochloride, which melted at 196–197° alone and when mixed with an authentic sample of aniline hydrochloride.

Preparation of the Monosubstituted Diphenylethylenes.—The following olefins were prepared by methods described in the literature: 1-phenyl-1-*p*-tolylethylene,[14] 1-phenyl-1-*p*-anisylethylene,[15] 1-phenyl-1-*p*-biphenylethylene[16] and 1-phenyl-1-*p*-chlorophenylethylene.[17]

1-*p*-Anisyl-1-*p*-biphenylethylene.—The Grignard reagent from 35.5 g. (0.152 mole) of *p*-bromobiphenyl in 400 ml. of ether was prepared in the usual way. To this was added in twenty minutes time 22.5 g. (0.168 mole) of *p*-methoxyacetophenone dissolved in 400 ml. of ether. The mixture was refluxed for another thirty minutes, then allowed to stand overnight. The mixture was hydrolyzed with saturated ammonium chloride solution, the ether solution separated, and the ether distilled. The residue was mixed with 100 ml. of 25% sulfuric acid and refluxed for ninety minutes. The solid olefin was filtered, washed with water and crystallized from absolute ethanol. Colorless leaflets of 1-*p*-anisyl-1-*p*-biphenylethylene were obtained, m. p. 159.8–160.6°, 22.69 g. (52%).

Anal. Calcd. for C$_{21}$H$_{18}$O: C, 88.08; H, 6.34. Found: C, 87.68, 88.07; H, 6.08, 6.18.

1-*p*-Anisyl-1-*p*-tolylethylene.[18]—This olefin was prepared by the method described above, using *p*-bromotoluene and *p*-methoxyacetophenone. Colorless leaflets were obtained from ethanol, m. p. 73.8–74.3°.

Anal. Calcd. for C$_{16}$H$_{16}$O: C, 85.68; H, 7.19. Found: C, 85.95; H, 7.23.

1-*p*-Biphenyl-1-*p*-tolylethylene.—The Grignard reagent was prepared in the usual way from 101.2 g. (0.59 mole) of *p*-bromotoluene in 150 ml. of ether. Most of the ether was distilled off, and a solution of 98.1 g. (0.50 mole) of *p*-phenylacetophenone in 400 ml. of dry benzene was added dropwise over a period of ninety minutes. The mixture was refluxed for one hour, then allowed to stand overnight. The mixture was hydrolyzed with 75 ml. of saturated ammonium chloride solution, the benzene solution separated and the benzene distilled. The residue was mixed with 50 ml. of 20% sulfuric acid and refluxed for ninety minutes. The solid organic material was filtered, washed with water and dried. The filter cake was added to 760 ml. of ethanol containing 94.0 g. of acetic acid and 84.0 g. of Girard "T" reagent. The mixture was refluxed for one hour, then poured into an ice-cold aqueous solution of 72.0 g. of sodium carbonate. The resulting mixture was extracted with ether. On evaporation of the ether and crystallization of the residual solid from ethanol, there was obtained 51.5 g. (38%) of 1-*p*-biphenyl-1-*p*-tolylethylene, colorless leaflets, m. p. 100.5–101.0°.[19]

Anal. Calcd. for C$_{21}$H$_{18}$: C, 93.28; H, 6.71. Found: C, 93.36, 93.68; H, 6.59, 6.52.

Reaction of the Above Olefins with Hydrazoic Acid.—These reactions were carried out in the same manner as described above for the 1,1-diphenylethylene reaction. In each case the ketone fraction was separated into its component parts by distillation *in vacuo*, a Todd column being used to obtain the liquid ketones in pure form. In each case at least one solid derivative (the 2,4-dinitrophenylhydrazone or the oxime) was prepared from a sample portion of each pure fraction, and a mixed m. p. test was carried out with an authentic sample of the derivative. The yields of the respective ketones are summarized in Table I.

In the reaction of 1-phenyl-1-*p*-tolylethylene, both aniline and *p*-toluidine were detected qualitatively. In the reaction of 1-phenyl-1-*p*-anisylethylene, both aniline and *p*-anisidine were detected qualitatively. No attempt was made to detect the amines in the remaining reactions. In almost all of the reactions some solid materials containing both nitrogen and sulfur were formed. These were ignored.

In the reaction of 1-*p*-biphenyl-1-*p*-tolylethylene, it was not feasible to isolate the ketones by direct distillation of the neutral fraction. The mixed ketones were first separated from the other components of the neutral fraction by the use of Girard "T" reagent, then distilled *in vacuo*.

Summary

The Schmidt reaction has been applied to eight unsymmetrical diarylethylenes. An electronic interpretation has been offered for these reactions, one step of which involves a migration of a phenyl group or a para substituted phenyl group and its binding pair of electrons from a carbon to a nitrogen atom. The order of migratory aptitudes has been found to follow the sequence, *p*-anisyl > *p*-tolyl > *p*-biphenyl > phenyl > *p*-chlorophenyl > methyl, this being in qualitative agreement with the migratory aptitudes found in the pinacol–pinacolone rearrangement of symmetrical pinacols.

LAWRENCE, KANSAS RECEIVED JANUARY 3, 1950

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(14) C. D. Hurd and C. N. Webb, THIS JOURNAL, **49**, 546 (1927).

(15) R. Stoermer and M. Simon, *Ber.*, **37**, 4163 (1904).

(16) V. P. Pfeiffer and P. Schneider, *J. prakt. Chem.*, **237**, 129 (1931).

(17) E. Bergmann and A. Bondi, *Ber.*, **64**, 1455 (1931).

(18) Preparation carried out by Miss Martha Holladay.

(19) Bergmann and Bondi, who prepared the olefin in a different manner, report a m. p. of 102–103.[17]