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Comparison of Reactivities of Metallocenylphenylcarbinyl Azides in Acid-catalyzed Decomposition Reactions

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Phenylruthenocenylcarbinyl and osmocenylphenylcarbinyl azides have been prepared and subjected to acid-catalyzed decomposition in various media. Among the products isolated from the decomposition of the ruthenium compound were phenylruthenocenylcarbinol, bis-phenylruthenocenylmethyl ether, benzoylruthenocene, 2,3-ruthenocoindenone, aniline and ruthenocencarboxaldehyde. The last compound has been obtained for the first time. The behavior of osmocenylphenylcarbinyl azide was found to be strikingly different from that of the ruthenium analog in that benzoylosmocene and osmocenylphenylcarbinol were the only products isolated. From the current work and that published previously, the conclusion can be drawn that phenylruthenocenylcarbinyl azide behaves more like its iron than its osmium analog in acid-catalyzed decomposition reactions. An explanation for the results obtained is proposed.

In a previous communication[1] we reported the preparation of ruthenocenecarboxaldehyde by the acid-catalyzed rearrangement of phenylruthenocenylcarbinyl azide. Also, we have described in detail[2] the behavior of ferrocenylphenylcarbinyl azide on treatment with strong acid. The present paper is concerned with a comparison of the reactivities of ruthenocenylphenylcarbinyl azide and the iron and osmium analogs toward acid-catalyzed decomposition.

One of our most striking observations was that the three azides gave substantially different sets and proportions of products on treatment with various types of sulfuric acid solutions. Ferrocenylphenylcarbinyl azide gave a complex mixture of products, including ferrocenecarboxaldehyde, aniline, the two diastereoisomeric forms of 1,2-diferrocenyl-1,2-diphenylethane and their dipositive cations, benzoylferrocene, ferrocenylphenylcarbinol, resinous material and an unidentified iron salt in solution[2]; phenylruthenocenylcarbinyl azide yielded ruthenocenecarboxaldehyde, aniline, phenylruthenocenylcarbinol, benzoylruthenocene, bis-phenylruthenocenylmethyl ether and 2,3-ruthenocoindenone; and osmocenylphenylcarbinyl azide formed benzoylosmocene, a very small amount of osmocenylphenylcarbinol and an unidentified osmium salt in solution.

Experimental[3]

Preparation of Phenylruthenocenylcarbinol.—To a stirred solution of 0.25 g. (0.00075 mole) of benzoylruthenocene[4,5] in 20 ml. of anhydrous ether was added a slurry of 0.13 g. (0.0034 mole) of lithium aluminum hydride in anhydrous ether. The mixture was stirred for 45 min. after the almost immediate disappearance of the yellow color. At this time the reaction mixture was hydrolyzed with a saturated solution of water in ether, the solids removed by filtration and extracted repeatedly with Skelly B solvent. The ether and Skelly B solutions were combined, dried over anhydrous sodium sulfate, and evaporated to give 0.23 g. (92%) of crude material. Repeated recrystallization from Skelly B solvent gave white needles of phenylruthenocenylcarbinol, m.p. 105.6–106.2°.

Anal. Calcd. for $C_{17}H_{16}RuO$: C, 60.40; H, 4.77; Ru, 30.09. Found: C, 60.27; H, 4.95; Ru, 30.28.

Phenylruthenocenylcarbinyl Azide.—To 0.50 g. (0.0014 mole) of phenylruthenocenylcarbinol was added 5.0 ml. (0.006 mole) of a 1.2 *N* solution of hydrogen azide in benzene, followed by 1 drop of formic acid. After 3 days, the mixture was evaporated to dryness in a stream of nitrogen. The residual oil was taken up in benzene and chromatographed on activity III alumina.[6] That formic acid was necessary was shown by the fact that only traces of phenylruthenocenylcarbinyl azide could be obtained in its absence, even when the reaction time was increased to 10 days.

Evaporation of the first yellow fraction gave 0.48 g. (90%) of phenylruthenocenylcarbinyl azide, a yellow oil, $n^{25}\text{D}$ 1.6432, $d^{25.5}$ 1.502. After a period of approximately 3 weeks, crystallization took place. The compound had a m.p. of 48.5–50.0° (recrystallized from Skelly B solvent).

Anal. Calcd. for $C_{17}H_{15}RuN_3$: C, 56.24; H, 4.16; Ru, 28.02; N, 11.58. Found (liq.): C, 56.48; H, 4.44; Ru, 28.13; N, 11.60. Found (solid): C, 56.52; H, 4.35; Ru, 28.05; N, 11.83.

Reaction of Phenylruthenocenylcarbinyl Azide in Sulfuric Acid–Chloroform.—To a stirred mixture of 22.6 ml. of anhydrous chloroform and 13.6 ml. of concentrated sulfuric acid was added 0.8220 g. (0.00226 mole) of phenylruthenocenylcarbinyl azide. The course of the reaction was followed by observation of nitrogen evolution and was found to be complete at the end of 24 hr. The nitrogen evolved amounted to 0.063 g. (0.0023 mole). The mixture was poured onto ice and extracted with chloroform. The chloroform layer was dried over magnesium sulfate, the solvent evaporated, and the residue (0.3340 g.) was chromatographed on activity III alumina. The first fraction (0.028 g.), eluted with Skelly B solvent, was not identified. The second fraction (0.0436 g., 7%), eluted with 2% ether–Skelly B, was identified as ruthenocenecarboxaldehyde, yellow crystals from Skelly B solvent, m.p. 100.2–100.8°.

Anal. Calcd. for $C_{11}H_{10}RuO$: C, 50.95; H, 3.89; Ru, 38.99. Found: C, 51.14; H, 3.90; Ru, 38.64.

The previously unknown ruthenocenecarboxaldehyde was compared with another sample prepared by the action of N-methylformanilide on ruthenocene (see below) and found to be identical in all respects. The third fraction (0.0400 g., 5%), eluted with 2% ether–Skelly B, was identified as 2,3-ruthenocoindenone, by means of infrared and nuclear magnetic resonance spectra and also by a comparison with the corresponding ferrocene compound mentioned later in this paper. Its ultraviolet absorption spectrum shows maxima at 253 and 397 mμ. Recrystallization of 2,3-ruthenocoindenone from Skelly B–benzene gave orange needles, m.p. 134.2–135.0°.

Anal. Calcd. for $C_{17}H_{12}RuO$: C, 61.13; H, 3.62; Ru, 30.45. Found: C, 61.42; H, 3.54; Ru, 30.51.

Continued elution with 100% ether gave 0.0154 g. of unidentified material.

Chloroform extraction of the aqueous layer which had been reduced with zinc dust gave 0.0330 g. of material

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[1] D. E. Bublitz, J. Kleinberg and W. E. McEwen, *Chemistry & Industry*, 936 (1960).

[2] A. Berger, W. E. McEwen and J. Kleinberg, *J. Am. Chem. Soc.*, **83**, 2274 (1961).

[3] All melting points are corrected. Analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

[4] M. D. Rausch, E. O. Fischer and H. Grubert, *Chemistry & Industry*, 756 (1958); *J. Am. Chem. Soc.*, **82**, 76 (1960).

[5] E. O. Fischer and H. Grubert, *Ber.*, **92**, 2302 (1959).

[6] H. Brockmann and H. Schodder, *ibid.*, **74**, 73 (1941).

which gave no identifiable compounds on attempted chromatography.

Two derivatives of ruthenocenecarboxaldehyde were synthesized according to standard procedures. **The semicarbazone** gave light yellow leaflets from ethanol–water; m.p. 208.0–208.4°.

Anal. Calcd. for $C_{12}H_{13}N_3RuO$: C, 45.47; H, 4.13; N, 13.26; Ru, 32.09. Found: C, 45.54; H, 4.35; N, 13.52; Ru, 31.82.

The 2,4-dinitrophenylhydrazone had a decomposition point of 220–222°.

A second reaction was carried out with 2.00 g. of phenylruthenocenylcarbinyl azide, 56 ml. of chloroform and 33 ml. of concentrated sulfuric acid. The reaction mixture was worked up as described above, and 0.05 g. (4%) of ruthenocene was obtained together with 0.09 g. (5%) of 2,3-ruthenocoindenone. Both ruthenocenecarboxaldehyde and benzoylruthenocene were present in trace amounts. That ruthenocene arose in the reaction was shown by its absence when the alcohol, from which the azide had been prepared, was subjected to sublimation (under conditions suitable for sublimation of ruthenocene).

A third reaction with 1.76 g. of phenylruthenocenylcarbinyl azide gave 0.41 g. (32%) of ruthenocenecarboxaldehyde, 0.05 g. (3%) of 2,3-ruthenocoindenone and 0.05 g. (4%) of ruthenocene. A final experiment with 2.10 g. of the azide gave 0.05 g. (3%) of ruthenocenecarboxaldehyde and 0.14 g. (7%) of 2,3-ruthenocoindenone.

Aniline was obtained in an amount essentially equivalent to the ruthenocenecarboxaldehyde when the acidic aqueous layer remaining after reduction with zinc was made basic and extracted with ether.

Reactions of Phenylruthenocenylcarbinyl Azide in Sulfuric Acid–Acetic Acid Solutions.—To 1.84 g. (0.00506 mole) of phenylruthenocenylcarbinyl azide, contained in a closed system such that nitrogen evolution could be measured, was added 50 ml. of an anhydrous 5 *M* solution of sulfuric acid in acetic acid. The mixture was stirred for 48 hr. at room temperature and hydrolyzed by being poured onto 200 g. of ice. The gas evolution corresponded to 0.142 g. (0.00507 mole) of nitrogen.

The acidic aqueous phase was concentrated *in vacuo* to 150 ml. and the mixture was filtered, leaving a residue of 0.07 g. of tar. The filtrate was extracted with benzene in a continuous extractor and the extract consisted of 0.80 g. of a mixture of solids. This material was taken up in a minimal amount of benzene and placed on a column of activity III alumina. Elution with Skelly B solvent gave 0.19 g. of material which, when recrystallized from Skelly B–benzene, afforded 0.06 g. of bis-phenylruthenocenylmethyl ether (see below), white needles, m.p. 153.4–154.4°. An additional 0.1 g. of the ether was obtained by chromatography of the recrystallization mother liquor on activity II alumina.

Anal. Calcd. for $C_{34}H_{30}Ru_2O$: C, 62.06; H, 4.60; Ru, 30.91. Found: C, 62.01; H, 4.57; Ru, 31.10.

Continued elution of the material on the column of activity III alumina, now with 10% ether–Skelly B solvent, yielded four compounds. The first portion of the eluent contained 0.07 g. of benzoylruthenocene, the second a mixture of 0.12 g. of bis-phenylruthenocenylmethyl ether and 0.10 g. of a compound tentatively identified as the imine of benzoylruthenocene (separation of these two compounds being effected on activity II alumina), and the third portion of the eluent 0.22 g. of phenylruthenocenylcarbinol.

The aqueous layer from the benzene extraction was divided into equal parts, the first of which was made directly basic. Extraction with chloroform gave 0.10 g. of material which, on chromatography, gave less than 0.01 g. of benzoylruthenocene, together with other unidentified products.

The second portion of the acidic aqueous phase was reduced with zinc dust and extracted with chloroform to give 0.10 g. of material. Again, chromatography gave a trace of benzoylruthenocene and other unidentified products. The reduced aqueous solution was made basic and extracted with chloroform, but no material was obtained on evaporation of the chloroform.

During the process of making the acidic and reduced acidic solutions basic, the odor of ammonia became apparent.

Another experiment similar to the one described above, but carried out in an anhydrous 10 *M* solution of sulfuric acid in acetic acid, gave the following results. From 1.80 g. (0.00497 mole) of the azide there was obtained 0.00533 mole of nitrogen during a 48-hr. reaction period. Following the concentration step noted above the acid aqueous phase was extracted with benzene, and 0.97 g. of material was obtained on evaporation of the benzene. The material was chromatographed on activity III alumina; elution with 5% ether–Skelly B gave: 0.65 g. of bis-phenylruthenocenylmethyl ether, 0.01 g. of unidentified material, 0.05 g. of 2,3-ruthenocoindenone and 0.17 g. of a mixture of phenylruthenocenylcarbinol and 2,3-ruthenocoindenone. The 0.17 g. of a mixture of phenylruthenocenylcarbinol and 2,3-ruthenocoindenone was rechromatographed on activity III alumina, and 0.02 g. of 2,3-ruthenocoindenone and a trace of benzoylruthenocene were obtained.

Formylation of Ruthenocene.—A mixture of 1.63 g. (0.0106 mole) of phosphorus oxychloride and 1.35 g. (0.010 mole) of N-methylformanilide was stirred under nitrogen for 1.5 hr. The mixture was then diluted with 19 ml. of chlorobenzene and 1.66 g. (0.00718 mole) of ruthenocene was added portionwise. The reaction mixture was heated with stirring for 2.5 hr. at 90° and for an additional 2 hr. at room temperature. The mixture was then stirred with 20 ml. of a saturated solution of sodium acetate for 15 min.

The aqueous layer was separated from the organic layer and washed once with benzene. The organic layers were combined, dried over magnesium sulfate and the solvent removed by evaporation. The residual material was dissolved in a minimal amount of benzene and passed through a column of activity III alumina. The first fraction was composed of 0.69 g. of ruthenocene. The second fraction amounted to 0.53 g. of a mixture of ruthenocenecarboxaldehyde, ruthenocene and N-methylformanilide. The third fraction removed was composed of 0.60 g. of N-methylformanilide.

The second fraction was sublimed and the sublimate then chromatographed on activity III alumina (Woelm) from a Skelly B solution. Evaporation of the first fraction gave 0.33 g. of unchanged ruthenocene. Evaporation of the second fraction gave 0.17 g. (9%) of ruthenocenecarboxaldehyde, yellow needles, m.p. 100.2–100.8°. The infrared spectrum of the aldehyde was superimposable on that of the material obtained from the rearrangement of phenylruthenocenylcarbinyl azide in sulfuric acid–chloroform.

Preparation of Bis-phenylruthenocenylmethyl Ether.—In a manner similar to the procedure of Knoevenagel and Heckel[7] a mixture of 1.0 g. of phenylruthenocenylcarbinol and 1.0 g. of copper powder was heated at 210° for 10 minutes. The mixture was cooled and extracted with benzene. The benzene was removed, the residue taken up in Skelly B solvent and chromatographed on activity III alumina. Elution with Skelly B solvent gave 0.45 g. (44%) of the crude ether, which was further purified by chromatography on activity II alumina. Repeated recrystallization of this material from ethanol–benzene gave yellowish-white needles, m.p. 158.6–159.2°. A mixed melting point with material from the azide solvolysis was 157.6–158.4°. The infrared spectrum of the ether taken in carbon tetrachloride was identical with that of the same compound obtained in the solvolysis of phenylruthenocenylcarbinyl azide.

Preparation of 2,3-Ferrocoindenone.—To a cooled agitated mixture of 3.70 g. (0.027 mole) of anthranilic acid and 2.00 g. (0.029 mole) of sodium nitrite in a minimum amount of water was added dropwise 2.5 ml. of concentrated sulfuric acid. The diazotized anthranilic acid was then added to a solution of 5.00 g. (0.027 mole) of ferrocene in 200 ml. of glacial acetic acid. The reaction mixture was stirred at room temperature for 10 hr., after which it was poured into 500 ml. of ice-water. The solution was stirred and sodium bisulfite added portionwise to reduce ferricinium salts which had been formed. The mixture was then cooled, filtered, and the residual solid dissolved in sodium hydroxide solution and then filtered again to remove the unchanged ferrocene. The filtrate was cooled to ice temperature and the o-ferrocenylbenzoic acid which had been formed in the arylation reaction was precipitated by the addition of hydrochloric acid.

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(7) E. Knoevenagel and W. Heckel, *Ber.*, **36**, 2827 (1903).

The acid, removed by filtration, was dried and then taken up in 100 ml. of anhydrous methylene chloride. To the solution was added 10 ml. of oxalyl chloride, and the mixture was allowed to stand overnight at room temperature in the dark. The solvent was removed *in vacuo*, and the unchanged oxalyl chloride removed by pumping at room temperature.

The acid chloride was redissolved in 100 ml. of methylene chloride and a small amount of freshly sublimed aluminum chloride added. After it had been permitted to stand for 2 hr. at room temperature, the reaction mixture was worked up in the usual manner, the organic material being chromatographed on activity III alumina; yield 0.7 g. (11%) of 2,3-ferrocoindenone. Repeated recrystallization of the crude solid from Skelly B solvent gave dark purple-red needles, m.p. 105.0–106.2°.

Anal. Calcd. for $C_{17}H_{12}FeO$: C, 70.86; H, 4.20; Fe, 19.38. Found: C, 70.71; H, 4.01; Fe, 19.04.

Comparison of N.m.r. and Infrared Spectra of 2,3-Ruthenocoindenone and Its Iron Analog.—The nuclear magnetic resonance spectrum of 2,3-ruthenocoindenone was taken by Varian Associates, Palo Alto, Calif. The sample was examined as a deuteriochloroform solution which contained a trace amount of tetramethylsilane. The positions of the peaks are relative to this standard.

The unsubstituted cyclopentadienyl ring produces a single peak, at 5.48 τ, arising from the five equivalent hydrogens.[8] Two of the hydrogens in the substituted cyclopentadienyl ring have identical chemical shifts and produce a triplet signal centered around 4.83 τ. The one other hydrogen on this ring produces a triplet signal just to the right of this at 5.05 τ. The four benzene hydrogens produce a complex set of signals centered around 2.75 τ. The relative areas of these four sets of signals are in agreement with a distribution of four aromatic hydrogens and eight cyclopentadienyl hydrogens, in three groups of two, one and five. The nuclear magnetic resonance spectrum is thus in complete agreement with the proposed structure of the compound, namely, 2,3-ruthenocoindenone.

The nuclear magnetic resonance spectrum of 2,3-ferrocoindenone was taken by Mr. O. Norton of the University of Illinois. The unsubstituted cyclopentadienyl ring produces a single peak at 5.90 τ, arising from the five equivalent unsubstituted hydrogens of one cyclopentadienyl ring. The three hydrogens of the substituted cyclopentadienyl ring produce an unresolved multiplet at 5.05 and 5.13 τ. The four hydrogens of the benzene ring give a complex multiplet centered around 2.75 τ. The tendency for the peaks of the cyclopentadienyl hydrogens to be shifted downfield in the ruthenium compound compared to the iron compound is also observed in the unsubstituted metallocenes themselves. In the case of ruthenocene, the peak falls at 5.44 τ, whereas with ferrocene the peak is found at 5.85 τ. The observed shift to lower τ-values in ruthenocene is probably an indication of a lower electron density in the cyclopentadienyl rings of this material as compared with ferrocene. This parallels the qualitative observation that ruthenocene undergoes electrophilic substitution less readily than ferrocene.[4]

The infrared spectra of both 2,3-ruthenocoindenone and 2,3-ferrocoindenone were taken in carbon disulfide solution and also in carbon tetrachloride. In each solvent, the spectra of the iron and ruthenium compounds were almost identical.

Preparation of Osmocenylphenylcarbinol.—To a stirred solution of 0.25 g. (0.00059 mole) of benzoylosmocene[4] in 25 ml. of ether was added a slurry of 0.10 g. (0.0027 mole) of lithium aluminum hydride in 3 ml. of ether. (In larger scale reactions this mole ratio was maintained at one to one.) The mixture was stirred for 0.5 hour after the disappearance of the yellow color and then hydrolyzed with "wet" ether. The solids were removed by filtration and the ether solution evaporated. The residue was recrystallized from Skelly B solvent, and 0.23 g. (91%) of crude alcohol was obtained. Repeated recrystallization from Skelly B solvent gave snow-white needles of osmocenylphenylcarbinol, m.p. 115.7-116.0°.

Anal. Calcd. for $C_{17}H_{16}OsO$: C, 47.87; H, 3.78; Os, 44.60. Found: C, 48.11; H, 4.01; Os, 44.60.

Preparation of Osmocenylphenylcarbinyl Azide.—To 0.50 g. (0.0012 mole) of osmocenylphenylcarbinol was added 5.0 ml. (0.006 mole) of a 1.2 *N* solution of hydrogen azide in benzene, followed by 1 drop of formic acid. After 3 days the mixture was evaporated to dryness in a stream of nitrogen, and the residual oil was taken up in a minimal amount of benzene and chromatographed on activity III alumina. Evaporation of the first yellow fraction, eluted with Skelly B solvent, gave 0.47 g. (88%) of osmocenylphenylcarbinyl azide, a yellow oil, $n^{25}\text{D}$ 1.6540, d^{27} 1.892.

Anal. Calcd. for $C_{17}H_{15}OsN_3$: C, 45.22; H, 3.35; N, 9.31; Os, 42.12. Found: C, 45.33; H, 3.57; N, 9.32; Os, 42.48.

Reaction of Osmocenylphenylcarbinyl Azide in Sulfuric Acid–Chloroform.—To a stirred solution of 0.4525 g. (0.001 mole) of osmocenylphenylcarbinyl azide in 5.2 ml. of chloroform at 0° was added 2.6 ml. of 100% sulfuric acid. The reaction mixture was then allowed to warm up to room temperature, and stirring was continued for 15 hr. At the end of this time nitrogen evolution (0.0005 mole) had ceased, and the reaction mixture was hydrolyzed by being poured onto ice.

The aqueous acidic phase was extracted with chloroform, and the extract was dried over magnesium sulfate. The solvent was evaporated and 0.03 g. of material obtained. Chromatography on activity III alumina gave 0.01 g. of benzoylosmocene and no other identifiable products.

The aqueous phase was divided into two equal portions, the first of which was made basic with sodium hydroxide. The solution was filtered and 0.21 g. of tar removed. Extraction of the solution with chloroform gave 0.01 g. of unidentified material. The second portion of the aqueous layer was reduced with zinc dust and extracted with chloroform. The chloroform was evaporated, and 0.03 g. of unidentified material was obtained. The reduced solution was made basic and extracted with chloroform, but no material was found to have been extracted.

In all cases, the aqueous solutions were found to give a positive test for osmium on treatment with a saturated solution of potassium thiocyanate, followed by extraction with ether.

Reaction of Osmocenylphenylcarbinyl Azide in Anhydrous 5.0 *M* Sulfuric Acid–Acetic Acid.—In this experiment the products formed in the kinetic study (see below) of the azide decomposition were isolated. The mixtures from the kinetic runs, carried out at 0°, were maintained at 0° until hydrolyzed by being poured onto ice. The combined weight of the starting azide was 0.4512 g. (0.001 mole) and the combined nitrogen evolved amounted to 0.000875 mole.

The aqueous solution obtained from the hydrolysis step was extracted with chloroform. The chloroform was washed with dilute sodium hydroxide solution to remove acetic acid, dried over magnesium sulfate and evaporated to give 0.34 g. of crude material. Chromatography on activity III alumina with Skelly B solvent as eluent gave 0.01 g. of unknown material. On change of the eluent to 5% ether–Skelly B, 0.28 g. (66%) of benzoylosmocene, as shown by its infrared spectrum, melting point and a mixed melting point test, was obtained. Elution with 100% ether gave 0.03 g. of an unidentified material.

Extraction of the acidic aqueous phase for 4 days with chloroform gave 0.05 g. of crude material. The infrared spectrum showed the presence of benzoylosmocene and possibly the acetate of osmocenylphenylcarbinol. Chromatography on activity III alumina gave 0.01 g. of benzoylosmocene and 0.03 g. of a mixture of the carbinol and unidentified material. The carbinol probably arose by the hydrolysis of the acetate on the column, as no evidence of the acetate or any compound having a corresponding infrared carbonyl absorption peak was observed.

The aqueous phase was divided into two equal parts, one of which was made directly basic, the other being reduced with zinc dust and then made basic. Extraction of the above three aqueous solutions gave no identifiable materials.

Kinetics of Decomposition of the Metallocenylphenylcarbinyl Azides.—The apparatus used in all measurements was identical with that described by Gudmundsen and McEwen.[9] Ferrocenylphenylcarbinyl azide was carefully weighed out so that 5.0×10^{-4} mole was taken for each run. The apparatus was assembled and 5.0 ml. of anhy-

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(8) The τ-values cited here were determined according to the method of G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

(9) C. H. Gudmundsen and W. E. McEwen, *J. Am. Chem. Soc.*, **79**, 329 (1957).

drous 5 *M* sulfuric acid in acetic acid was added to the flask, the azide sample vial being placed in the retaining support. The flask portion of the apparatus was then immersed in a constant temperature bath maintained at 25.0 ± 0.2°. After a 20-min. period had been allowed for establishment of thermal equilibrium, the azide was added to the acid and shaking was begun. Volume readings were taken at 5-min. intervals for 100 min. and at 10-min. intervals for the next 100 min.

The pseudo-first-order rate constant was determined from a plot of log $(V_\infty/(V_\infty - V_t))$ *vs.* time in minutes. The average value of k for three runs was 0.387 ± 0.005 hr.$^{-1}$. The data for all runs were treated by the method of least squares and were calculated for the first 50% of reaction.

The procedure was repeated for one experiment at 35° and for one at 40°, with k-values of 1.10 hr.$^{-1}$ and 1.91 hr.$^{-1}$, respectively, being found. Extrapolation of a plot of log k *vs.* $1/T$,°K. gave a k-value at 0.0° of 0.0168 hr.$^{-1}$ and an apparent activation energy for the reaction of 20.2 kcal./mole.

The procedure with phenylruthenocenylcarbinyl azide was identical with that described for the ferrocenylphenylcarbinyl azide decomposition, except that the constant temperature bath was maintained at 0.0°. Identical treatment of the data from two runs gave an average value for k of 10.05 ± 0.05 hr.$^{-1}$ for the first 50% of reaction.

In the decomposition of osmocenylphenylcarbinyl azide the bath was maintained at 0.0°. It was observed that the reaction did not attain homogeneity for at least 2 hours; hence the value for k is less than the true value for a reaction in a homogeneous solution. A value of 0.397 hr.$^{-1}$ was obtained for the specific rate constant by a graphical procedure (the method of least squares) on one of the runs. Nitrogen yields were 82 and 93% of theoretical in two experiments.

Isolation of a New Dibenzoylruthenocene in the Benzoylation of Ruthenocene.—In the preparation of benzoylruthenocene by the procedure described in the literature,[4] a previously unreported dibenzoylruthenocene was isolated.

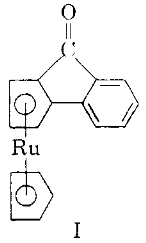
Upon careful chromatography on grade III alumina of the benzoylated products from a large scale run it was observed that 14% ether–Skelly B caused a separation of the material into 3 distinct bands on the column. The first compound was the known monobenzoylated product. The second was shown to be a homoannularly substituted compound by the presence of peaks in the 9–10 μ region of the infrared spectrum and by analysis. The position of substitution has not been established The compound was obtained in the form of yellow needles, m.p. 141.8–142.4°, from benzene–Skelly B solvent.

Anal. Calcd. for $C_{24}H_{18}RuO_2$: C, 65.50; H, 4.12; Ru, 23.11. Found: C, 65.67; H, 4.30; Ru, 22.90.

The last compound to be eluted was shown to be 1,1′-dibenzoylruthenocene[4] on the basis of its infrared spectrum and melting point.

Discussion

The most striking difference in behavior between ferrocenylphenylcarbinyl azide and its ruthenium analog in decomposition reactions carried out in sulfuric acid–chloroform medium is the formation from the former azide of a large proportion of the diastereoisomeric 1,2-diferrocenyl-1,2-diphenylethanes and their ferricinium salts but the absence of corresponding substances from the ruthenium compound. In other respects, namely, the formation of the metallocenylcarboxaldehydes and aniline, but the absence of benzaldehyde and aminometallocenes, the two azides behave similarly. As a matter of fact, the decomposition of phenylruthenocenylcarbinyl azide has given ruthenocenecarboxaldehyde for the first time. An additional difference in the behavior of the two azides in sulfuric acid–chloroform is the fact that the ruthenium compound yields a small amount of a substance of the formula $C_{17}H_{12}RuO$ which has been identified as 2,3-ruthenocoindenone (I) on the basis of its n.m.r. spectrum and comparison with the corresponding ferrocene analog. The ferrocene analog is not formed in the decomposition of ferrocenylphenylcarbinyl azide, but it can be prepared by an unambiguous route (see Experimental).



I

As with the decomposition of ferrocenylphenylcarbinyl azide,[2] a change in the acidity of the medium causes a change in various products obtained from the ruthenium compound. Experiments carried out in solutions of anhydrous sulfuric acid in absolute acetic acid (10 *M* and 5 *M*, respectively, in H_2SO_4) give no ruthenocenecarboxaldehyde and aniline. However, a small quantity of 2,3-ruthenocoindenone (I) is isolated from the reaction carried out in the 10 *M* solution, whereas none is obtained from the 5 *M* solution. In each case, the major constituents of the reaction mixture are the solvolytic products bis-phenylruthenocenylcarbinyl ether and phenylruthenocenylcarbinyl acetate, the latter substance being isolated as the carbinol after chromatography on alumina. Also, in both instances, small amounts of benzoylruthenocene are obtained.

The behavior of osmocenylphenylcarbinyl azide in acid-catalyzed decomposition reactions is substantially different from that of its iron and ruthenium analogs. In chloroform–sulfuric acid, the major course of the reaction consists of a cleavage of the osmocene ring with the formation of a water-soluble osmium salt having a cation containing osmium but not bound to a cyclopentadiene residue. Thus, an aqueous solution of the salt gives a positive color test for osmium on treatment with a saturated solution of potassium thiocyanate and subsequent extraction with ether. However, when the decomposition of the azide is effected in 5 *M* sulfuric acid–acetic acid, benzoylosmocene is obtained in about 70% yield.

In a previous communication,[2] evidence was presented that products of a Schmidt rearrangement of metallocenylphenylcarbinyl azides (aniline and the metallocenecarboxaldehyde) are formed from the diprotonated forms of the azides; *i.e.*, the conjugate acid in which both the azido group and the metal are protonated. Curphey, Santer, Rosenblum and Richards[10] have shown that the ease of protonation of the unsubstituted metallocenes decreases in the order ferrocene > ruthenocene > osmocene. In view of these observations it is understandable that osmocenylphenylcarbinyl azide, of the three azides, would have the smallest tendency to give aniline plus osmocenecarboxaldehyde on acid-catalyzed decomposition.

The fact that a much greater yield of benzoylmetallocene was obtained from osmocenylphenyl-

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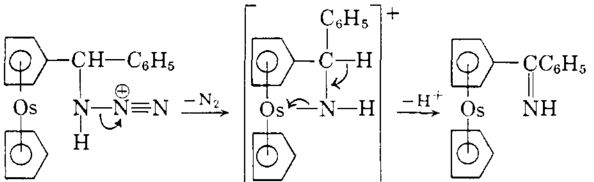
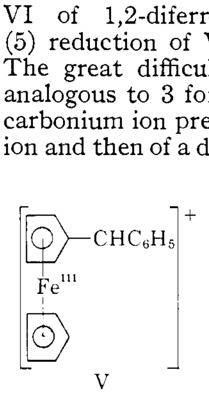
[10] T. J. Curphey, J. O. Santer, M. Rosenblum and J. H. Richards, *J. Am. Chem. Soc.*, **82**, 5249 (1960).

carbinyl azide than from either the iron or ruthenium analog can be explained in the following manner. It has been observed by Richards and Hill,[11] in a study of the rates of solvolysis of metallocenylmethylcarbinyl acetates, that osmium is better able than either iron or ruthenium to offer anchimeric assistance in an intramolecular displacement reaction. Thus, the conjugate acid of osmocenylphenylcarbinyl azide(II), in which only the azido group is protonated, might be expected to lose nitrogen readily to form a transition species III. This, in turn, would give the imine IV on loss of a proton, and the imine, on hydrolysis, would give benzoylosmocene.

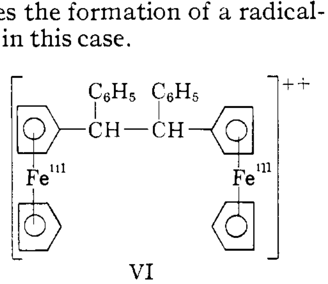


II III IV

Although, as noted above, both ferrocenylphenylcarbinyl azide and its ruthenium analog give the metallocenecarboxaldehyde and aniline in sulfuric acid–chloroform medium, only the former azide yields the diastereoisomeric 1,2-dimetallocenyl-1,2-diphenylethanes and their ferricinium salts. This notable difference is readily explained on the basis of observations reported by Kuwana, Bublitz and Hoh[12] that ruthenocene undergoes oxidation with much greater difficulty than does ferrocene, and, moreover, oxidation of the former involves a one-step two-electron change, whereas the latter undergoes a one-electron oxidation. It has been pointed out[2] that the conversion of ferrocenylphenylcarbinyl azide to 1,2-diferrocenyl-1,2-diphenylethane occurs by the steps: (1) formation of the conjugate acid of the azide in which only the azido group is protonated; (2) the anchimerically assisted dissociation of this conjugate acid to hydrogen azide and the ferrocenylphenylmethylcarbonium ion; (3) an intramolecular oxidation–reduction reaction involving the carbonium ion, in which the ion-radical V is produced; (4) coupling of two such radicals to give the dipositive cation VI of 1,2-diferrocenyl-1,2-diphenylethane; and (5) reduction of VI to give the uncharged dimer. The great difficulty of the occurrence of a step analogous to 3 for the ruthenocenylphenylmethylcarbonium ion precludes the formation of a radical-ion and then of a dimer in this case.



V



VI

Although a variety of mechanism may be postulated[13] to explain the formation of 2,3-ruthenocoindenone from ruthenocenylphenylcarbinyl azide, no evidence is available at present to distinguish among these possibilities. It is of interest, however, that the formation of this compound occurs only in a strongly acidic medium.

A limited number of kinetics experiments was carried out with the three metallocenylphenylcarbinyl azides in 5 *M* solutions of anhydrous sulfuric acid in absolute acetic acid. The rate of nitrogen evolution was much faster for phenylruthenocenylcarbinyl azide than for the iron analog. It was not possible to obtain a satisfactory pseudo-first-order rate constant for the osmium compound because of the limited solubility of the azide in the reaction medium. Not too much significance can be attached to the rate data inasmuch as several competing reactions are undoubtedly taking place.

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(11) J. H. Richards and E. A. Hill, *J. Am. Chem. Soc.*, **83**, 3840 (1961).

(12) T. Kuwana, D. E. Bublitz and G. Hoh, *ibid.*, **82**, 5811 (1960).

(13) D. E. Bublitz, Ph.D. Thesis, University of Kansas, 1961.