(0.0024 mol, 20%) of crude **3**, which after recrystallization was identical with that obtained from the reaction with **4**. Elution with benzene gave 0.13 g of a yellow oil; elution with ether gave 1.37 g of triphenylcarbinol; and elution with chloroform gave 0.08 g of an oil from which N-*t*-butylacetamide sublimed on standing. Triphenylmethane was not noted.

Reaction of Triphenylmethyl Cation Salts with Isobutene.—Isobutene (40 g, 0.71 mol) was bubbled slowly over 6 hr into a solution of 4.1 g (0.012 mol) of triphenylmethyl perchlorate[11] in 45 ml of acetonitrile in a flask equipped with a gas inlet tube, a Dry Ice–acetone condenser, a magnetic stirrer, and a drying tube. The solution was maintained at 30° during the first hour and subsequently at 60°. Dilute aqueous sodium carbonate was added, and the solution was concentrated on a steam bath. The aqueous mixture was extracted with three 20-ml portions of petroleum ether and five 20-ml portions of ether. The extract was washed with two 10-ml portions of water and three 10-ml portions of saturated sodium chloride solution. The solution was dried (Na_2SO_4), and the solvent was evaporated, leaving 3.4 g of semicrystalline material which was chromatographed on a 2.5-cm column packed with 80 g of alumina (Fisher F-20, neutral grade). Elution with pentane gave 1.5 g of **3** contaminated with a small amount of a viscous liquid. Recrystallization from 95% ethanol gave 1.0 g (0.0034 mol, 28%) of **3**. Further elution with ether gave a mixture (1.2 g) of triphenylcarbinol and N-*t*-butylacetamide.

More rapid addition of the isobutene led to formation of much more of the liquid product without altering significantly the yield of **3**. The liquid material was isolated free of **3** by careful chromatography: nmr (neat) τ 8.2 (m, 1, CH_2), 9.0 (m, 3, CH_3), 5.0 (m, weak) ppm.

In another reaction, isobutene was bubbled slowly into an acetonitrile solution containing equimolar portions of triphenylmethyl perchlorate and of collidine. Little of the liquid oligomer was isolated, though **3** still was formed in about the same yield.

Slow addition of isobutene to acetonitrile and dichloromethane solutions of triphenylmethyl fluoroborate also furnished comparable yields of **3**.

Attempted Reactions of Triphenylmethyl Perchlorate with Other Olefins.—*cis*-2-Butene (15 g, 0.27 mol) was added slowly to a solution of 3.9 g (0.011 mol) of triphenylmethyl perchlorate in 50 ml of acetonitrile as described for the reaction with isobutene. The reaction mixture was worked up in the same manner, but little material was obtained by elution with pentane–benzene.

A reaction was attempted with 2,3-dimethyl-2-butene in the same manner except that the olefin was introduced through a dropping funnel and the acetonitrile solution of triphenylmethyl perchlorate contained an equimolar amount of collidine. No material was eluted with pentane–benzene.

4,4,4-Triphenyl-2-methyl-2-butanol (7).—A solution of 1.82 g (0.0058 mol) of methyl 3,3,3-triphenylpropionate[12] in 20 ml of ether and 20 ml of benzene was added to a Grignard solution prepared from 0.4 g (0.0016 mol) of magnesium and 7 g (0.0049 mol) of methyl iodide in 40 ml of ether. The mixture was stirred and warmed for 1 hr and then left overnight at room temperature. The mixture was poured onto 100 g of ice. The layers were separated, and the ether layer was washed several times with a saturated sodium chloride solution and then with water. The solution was dried (Na_2SO_4) and evaporated, leaving 1.16 g (0.037 mol, 64%) of crude product. Recrystallization from methanol gave an analytical sample of **7**: mp 122–123° (lit.[13] mp 116–119°); nmr τ 2.75 (m, 15, aryl H's), 7.12 (s, 2, CH_2), 9.08 (s, 6, CH_3), and 9.28 (broad singlet, 1, OH) ppm.

Preparation of 1,1-Dimethyl-3,3-diphenylindan (3) from 7.—A sample of **7** (50 mg) was added in small portions to 4 ml of trifluoroacetic acid, and 1 ml of dichloromethane was added. The solvent was evaporated after the reaction had stood overnight at room temperature. The nmr spectrum of the crude, solid residue was identical with that of pure **3**. Recrystallization from 95% ethanol gave **3**, mp 109.5–110.5°. The ir and nmr spectra of this solid were identical with those of the solids obtained from reactions of triphenylmethyl cation salts with isobutene and with *t*-butyl ethers.

In an alternate reaction, a solution of 0.36 g of **7** and 17 mg of *p*-toluenesulfonic acid in 5 ml of benzene was refluxed for 2.5 hr. The solution was washed with 1 ml of a sodium chloride–sodium carbonate solution. The solution was dried ($MgSO_4$), and the solvent was evaporated. The solid residue was recrystallized twice from 95% ethanol to give **8** as white plates: mp 141–144°; nmr (CCl_4) τ 2.90 (s, 15, aryl H's), 3.75 (m, 1, =CH—), 8.15 (m, 3, CH_3), and 8.95 (m, 3, CH_3) ppm. Since elemental analyses were not obtained, the physical constants may be slightly off. The ir and nmr spectra of the crude product before recrystallization also exhibited absorptions of **3**. The spectra of the crude solid obtained from a similar reaction in which the solution was refluxed for 16 hr showed it to be a mixture of **3** and **8** containing significantly more **3** than the mixture from the preceding reaction; nearly pure **3** was obtained as a second crop during recrystallization of the crude product from 95% ethanol. Refluxing a similar benzene solution of *p*-toluenesulfonic acid and **8** led to slow formation of **3**.

(12) S. M. McElvain and H. F. McShane, Jr., *J. Amer. Chem. Soc.*, **74**, 2662 (1952).

(13) N. C. Deno and E. Sacher, *ibid.*, **87**, 5120 (1965).

Registry No.—Isobutene, 115-11-7; **1**, 14699-91-3; **3**, 10271-32-6.

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The Formation and Reactions of Ferrocenylphenylglyoxal[1]

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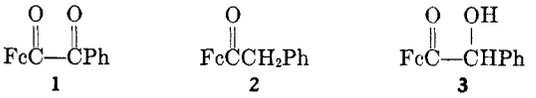
In this Note, we wish to report the preparation and characterization of ferrocenylphenylglyoxal (**1**) and to discuss briefly some of its chemical reactions.



The oxidation of benzyl ferrocenyl ketone (**2**) with activated manganese dioxide[2] in refluxing methylcyclohexane produced variable yields (20–50%)[3] of diketone **1**. A more satisfactory synthesis (95%) of **1** involved the oxidation of mandeloylferrocene (**3**) (from a mixed benzoin condensation of formylferrocene and benzaldehyde)[4] with activated manganese dioxide in refluxing chloroform solution. Although the oxidation of the acyloin **3** proceeded in uniformly higher

(1) Organometallic π Complexes. XV. Part XIV: M. D. Rausch and A. Siegel, *J. Organometal. Chem.*, **11**, 317 (1968).

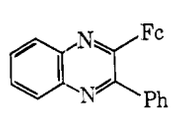
(2) J. Attenburrow, A. F. B. Cameron, J. H. Chapman, R. M. Evans, B. A. Helms, A. B. A. Jansen, and T. Walker, *J. Chem. Soc.*, 1094 (1952).

(3) The yields of diketone **1** were dependent upon the activity of manganese dioxide used. Samples of the latter which remained exposed to air for prolonged periods resulted in diminished yields of **1**.

(4) G. D. Broadhead, J. M. Osgerby, and P. L. Pauson, *J. Chem. Soc.*, 650 (1958).

yields than the oxidation of **2**, precursor **3** is less readily available than **2**, since the latter is formed easily *via* a Friedel–Crafts reaction between ferrocene and phenacetyl chloride.[5] The infrared spectrum of **1** exhibits two carbonyl absorptions at 1660 and 1680 cm^{-1} as well as bands characteristic of ferrocenyl and phenyl substituents. Attempted oxidations of ketone **2** with freshly sublimed selenium dioxide in a variety of solvents[6] led to extensive decomposition.

Treatment of **1** with *o*-phenylenediamine in a melt phase reaction produced an 83% yield of 2-ferrocenyl-3-phenylquinoxaline (**4**). Reactions of this type are



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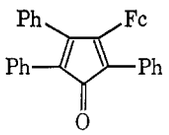

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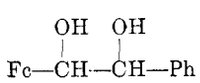
diagnostic for α diketones and acyloins, and often constitute a test for their presence.

A reaction of **1** with dibenzyl ketone in refluxing ethanolic potassium hydroxide afforded 3-ferrocenyl-2,4,5-triphenylcyclopentadienone (**5**) as a light blue amorphous solid in 81% yield. Its infrared spectrum exhibited a carbonyl band at 1710 cm^{-1}, which is characteristic of cyclopentadienone systems.

The reduction of **1** with sodium borohydride in methanol–water produced a 93% yield of 1-ferrocenyl-2-phenylethanediol (**6**). Several attempts to rearrange



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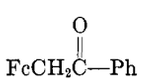

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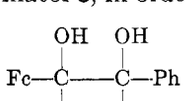
glycol **6** under acidic conditions resulted instead in conversion of **6** into phenacylferrocene (**7**). The latter was identified in each instance by its infrared and nmr spectra, and by mixture melting point determinations with an authentic sample.[7] The formation of **7** from **6**, which likely proceeds *via* dehydration and tautomeric rearrangement, might be expected to be a favored process, since the dehydration of α-ferrocenylcarbinols and the conversion of these carbinols into α-ferrocenylcarbonium ions under acidic conditions are known to be facile processes.[1,8]

It was also of interest to attempt the synthesis of pinacol **8**, in order to investigate the relative migratory



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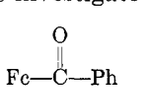

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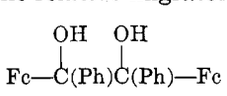

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aptitudes of the ferrocenyl and phenyl substituents under conditions of the pinacol rearrangement. Addition of an excess of phenyllithium to an ethereal solution of **1**, followed by hydrolysis, produced a yellow solution which gradually darkened on standing in air. Benzoylferrocene (**9**) and benzophenone were the only products isolated during an attempted chromatographic separation of the reaction mixture. It is of interest to note that a closely related pinacol, 1,2-diferrocenyl-1,2-diphenylethanediol (**10**), also undergoes facile oxidative cleavage to **9** when solutions of it are exposed to air.[9] Attempts to effect rearrangement of **8** or its dilithio salt under a variety of acidic conditions again led to the formation of **9** and benzophenone.

(5) N. Sugiyama, H. Suzuki, Y. Shioura, and T. Teitei, *Bull. Chem. Soc. Jap.*, **35**, 767 (1962).
(6) N. Rabjohn, *Org. Reactions*, **5**, 331 (1949).
(7) P. L. Pauson and W. E. Watts, *J. Chem. Soc.*, 2990 (1963).
(8) M. Cais, *Organometal. Chem. Rev.*, **1**, 435 (1966).

Experimental Section

All melting points are uncorrected. Infrared spectra were recorded on Beckman IR-10 and Perkin-Elmer 237 spectrophotometers, and nmr spectra were determined on a Varian A-60 spectrometer using tetramethylsilane as an internal standard. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

Oxidation of Benzyl Ferrocenyl Ketone (2).—The ketone[5] (3.1 g, 10 mmol) and activated manganese dioxide[2] (9.0 g) were refluxed in methylcyclohexane (75 ml) for 24 hr. The mixture was cooled to room temperature and filtered. The residue was washed with two 50-ml portions of chloroform and the latter combined with the original filtrate. Concentration of the solvent followed by chromatography on alumina using hexane as eluent produced 1.5 g (47%) of **1**, which formed ruby red plates, mp 85–86°, when recrystallized from hexane: nmr spectrum ($CDCl_3$), τ 1.7–2.5 (m, 5, C_6H_5), 5.06 (t, 2, 2,5 protons), 5.30 (t, 2, 3,4 protons), 5.69 (s, 5, π C_5H_5).

Anal. Calcd for $C_{18}H_{14}FeO_2$: C, 67.96; H, 4.44. Found: C, 68.25; H, 4.57.

Hexane–benzene (1:1) was used to elute 1.1 g of **2**, mp 128–129° (lit.[5] mp 129–130°).

Oxidation of Mandeloylferrocene (3).—Mandeloylferrocene[4] (5.0 g, 16 mmol) and activated manganese dioxide (20 g) were refluxed in chloroform (100 ml) for 6 hr. The mixture was cooled to room temperature and filtered. The residue was extracted with chloroform until the extracts were colorless. The extracts and the filtrate were combined and were evaporated to dryness. Recrystallization of the residue from hexane produced 4.7 g (95%) of the diketone **1** as ruby red plates, mp 85.5–86°. The infrared and nmr spectra of this product were identical with the spectra of **2** obtained from the previous oxidation.

2-Ferrocenyl-3-phenylquinoxaline (4).—Into a 10-ml Pyrex test tube were placed 1.59 g (5.0 mmol) of ferrocenylphenylglyoxal (**1**) and 0.5 g (5 mmol) of *o*-phenylenediamine; the latter had been freshly recrystallized from water. The mixture was heated to a melt phase on a steam bath for 15 min, and then allowed to cool to room temperature. The residue was recrystallized from ethanol to give 1.62 g (83%) of deep purple plates: mp 208–209°; nmr spectrum ($CDCl_3$), τ 2.15 (m, 9, aryl protons), 5.37, (t, 2, 2,5 protons), 5.62 (t, 2, 3,4 protons), 5.90 (s, 5, π-C_5H_5).

Anal. Calcd for $C_{24}H_{18}FeN_2$: C, 73.87; H, 4.65. Found: C, 73.83; H, 4.90.

3-Ferrocenyl-2,4,5-triphenylcyclopentadienone (5).—The diketone **1** (1.59 g, 5 mmol) and dibenzyl ketone (1.0 g, 5 mmol) were heated to reflux in 20 ml of 95% ethanol. A solution of potassium hydroxide (0.2 g) in 2 ml of ethanol was added and refluxing was continued for 30 min. Upon cooling, the blue solid which separated was filtered and washed with 50 ml of cold hexane. Recrystallization of the residue from hexane afforded 2.0 g (81%) of **5** as a light blue amorphous powder: mp 217–217.5° (N_2); nmr spectrum ($CDCl_3$), τ 2.30 (m, 15, C_6H_5), 5.73 (t, 2, 3,4 protons), 6.00 (s, 5, π-C_5H_5), 6.10 (t, 2, 2,5 protons).

Anal. Calcd for $C_{33}H_{24}FeO$: C, 80.49; H, 4.91. Found: C, 80.18; H, 5.26.

1-Ferrocenyl-2-phenylethanediol (6).—To a stirred solution of diketone **1** (1.5 g, 4.7 mmol) in 20 ml of methanol was added 10 ml of a solution of sodium borohydride (1.0 g, 26 mmol) in water. After 6 hr, the deep red solution became yellow. The mixture was diluted with 50 ml of water and filtered. The residue was recrystallized from heptane to produce 1.4 g (93%) of golden yellow needles of **6**, mp 114–115° (N_2).

Anal. Calcd for $C_{18}H_{18}FeO_2$: C, 67.10; H, 5.63. Found: C, 67.30; H, 5.45.

Attempted Rearrangements of 6. A. With Hydrogen Chloride.—Glycol **6** (1.6 g, 5 mmol) was dissolved in 50 ml of dry benzene. With stirring, anhydrous hydrogen chloride was

(9) N. Weliky and E. S. Gould, *J. Amer. Chem. Soc.*, **79**, 2742 (1957

bubbled through the solution for 5 min. The solvent was removed under reduced pressure, and the oily green residue was extracted with two 50-ml portions of ethyl ether. The combined extracts were concentrated and chromatographed on alumina. Hexane eluted 1.0 g (67%) of yellow crystals of phenylacylferrocene (**7**), mp 81–82° (lit.[7] mp 80–82°). A small amount of highly polar material was not removed from the column. However, its R_f value was identical with that of glycol **6**.

B. With Aluminum Oxide.—Glycol **6** (1.6 g, 5 mmol) was intimately mixed with alumina (4.0 g) and placed in a vacuum sublimer equipped with a water-cooled probe. The system was evacuated and partially submerged in an oil bath for 8 hr at 150° (12 mm). Air was then admitted slowly and the yellow sublimate removed from the cold finger of the sublimer. The infrared and nmr spectra of this material were identical with those of phenacylferrocene (**7**) obtained in A. The total amount of **7** collected amounted to 1.0 g (67%), mp 80–81°. A tlc test of the alumina residue indicated a very small amount of **7** together with trace amounts of diketone **1**.

C. With Aqueous Sulfuric Acid.—The glycol **6** (1.61 g, 5 mmol) in 50 ml of acetone and 10 ml of 5% aqueous sulfuric acid solution was refluxed under nitrogen for 8 hr. The solution was cooled to room temperature, diluted with water, and extracted with ethyl ether. The ether portion was washed with water, 5% sodium bicarbonate solution, again with water, and was dried over anhydrous magnesium sulfate. Concentration of the solvent followed by chromatography on alumina using hexane as eluent produced 1.1 g (72%) of phenacylferrocene (**7**), mp 80–82°. No other ferrocene-containing products were detected.

Oxidation of Phenacylferrocene (7).—Phenacylferrocene (1.0 g, 3.3 mmol) and activated magnanese dioxide (5 g) were refluxed in methylcyclohexane (50 ml) for 2 hr. The mixture was cooled to room temperature and filtered. The residue was washed with two 10-ml portions of chloroform. The combined organic portions were concentrated and the residual red oil was crystallized from hexane as ruby red plates (1.0 g, 96%), mp 85–85.5°. A mixture melting point (on admixture with authentic **1**) was undepressed.

Addition of Phenyllithium to 1.—The diketone **1** (2.0 g, 6.3 mmol) was added in one portion to a stirred solution of phenyllithium (80 mmol) in 100 ml of ethyl ether under nitrogen. The mixture was allowed to stir for 3 hr, during which time the color changed from red to green and finally to gray. Water was added dropwise, and the mixture turned yellow. A tlc test (1:1 hexane–benzene) indicated a yellow band, which gradually transformed into a red band of lower R_f, and a colorless band of higher R_f. The ether portion was separated, dried over anhydrous magnesium sulfate, and evaporated to a red oil. Chromatography on alumina yielded the following products in the order cited. (1) Hexane eluted benzophenone, 1.0 g, mp 48–49°. A mixture melting point (on admixture with an authentic sample) was undepressed. (2) 1:1 Hexane–benzene eluted benzoylferrocene, 1.20 g, mp 108–109°. A mixture melting point (on admixture with an authentic sample) was undepressed.

When the gray solution was treated with methyl iodide, dry hydrogen chloride, or aqueous hydrochloric acid, benzophenone and benzoylferrocene were the only products isolated.

Registry No.—**1**, 12310-13-3; **4**, 12310-15-5; **5**, 12310-16-6; **6**, 12310-14-4.

Aziridines. XX. Isomerizations of 1-*p*-Nitrobenzoyl-2-vinylaziridine

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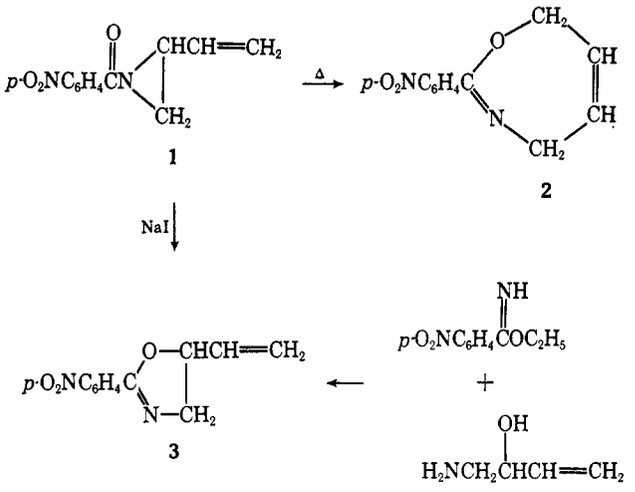
1-Aroylaziridines have been shown to undergo thermal rearrangements to 2-oxazolines, N-allylamides, and α-benzamidobenzalacetophenones. The course of the thermolysis depends in great part upon the substituents attached to the carbon of the aziridine ring. Thus 1-aroylaziridines unsubstituted on the aziridinyl carbons,[1-3] 1-aroyl-2,3-diarylaziridines,[4] and a few 1-aroylaziridines fused to another ring system[5,6] isomerize on heating to 2-oxazolines. 1-Acyl-2-alkylaziridines, on the other hand, almost always pyrolyze into N-allylamides[7] and 1,3-diaroyl-2-arylaziridines in refluxing *p*-xylene from α-benzamidobenzalacetophenones.[4]

We have now observed that 1-*p*-nitrobenzoyl-2-vinylaziridine (**1**) in refluxing toluene follows still another thermal pathway. The product of thermolysis is 2-*p*-nitrophenyl-4,7-dihydro-1,3-oxazepine (**2**). Tetrahydro- and hexahydro-1,3-oxazepines have been described, but **2** appears to be the first example of a dihydro-1,3-oxazepine. Compound **1** also reacted with iodide ion in acetone solution to give 2-*p*-nitrophenyl-5-vinyl-2-oxazoline (**3**). The iodide ion-catalyzed rearrangement of 1-aroylaziridines to 2-aryl-2-oxazolines is a well-known reaction.[4,8] The structure of **3** was confirmed by an alternate synthesis involving the reaction of 1-amino-3-buten-2-ol with ethyl *p*-nitrobenzimidate. Imido esters are known to react with amino alcohols to form 2-oxazolines.[9]

The nmr spectrum of **2** in $CDCl_3$ showed the *p*-nitrophenyl group as a quartet centered at 8.15 (4 H), the olefinic protons as a multiplet at 5.95 (2 H), and two other multiplets at 4.40 (2 H) and 4.80 ppm (2 H). The spectrum is similar to that of 4,6-dioxacycloheptene[10] which shows the olefinic protons as a multiplet at 5.74 ppm and the methylenes in the 3 and 7 positions as a multiplet at 4.32 ppm. On this basis the multiplet at 4.40 ppm in the spectrum of **2** can be assigned to the methylene next to the oxygen atom.



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(7) P. E. Fanta, "Heterocyclic Compounds with Three and Four-Membered Rings," part 1, A. Weissberger, Ed., Interscience Publishers, New York, N. Y., 1964, pp 524–575.
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