TABLE I

REACTION OF α,ω-DIENES WITH DIISOBUTYLALUMINUM HYDRIDE

α,ω-Diene	Mole	$(i\text{-Bu})_2\text{AlH}$(mole)	Hydrolyzed products (composition, %)	
			n-Alkane	Methylcycloalkane
1,4-Pentadiene	0.03	0.063	n-Pentane (100)	.....
1,5-Hexadiene	0.02	0.042	n-Hexane (2.4)	Methylcyclopentane (97.6)
1,6-Heptadiene	0.02	0.042	n-Heptane (99.1)	Methylcyclohexane (0.9)
1,7-Octadiene	0.02	0.042	n-Octane (100)	.....
1,8-Nonadiene	0.03	0.063	n-Nonane (100)	.....
1,9-Decadiene	0.03	0.063	n-Decane (100)	.....
1,10-Undecadiene	0.03	0.063	n-Undecane (100)	.....

phy using a Beckman Megachrom instrument equipped with an Apiezon "L" column, n^{20}_{D} 1.4043.[5]

1,6-Heptadiene.—The procedure used by Marvel and Stille[6] was followed. Reduction of 97.2 g. (0.45 mole) of diethyl pimelate with a solution of 36 g. (0.9 mole) of lithium aluminum hydride in 1400 ml. of ethyl ether yielded 31 g. (53%) of 1,7-heptanediol, b.p. 125–127° (3.5 mm.). The diol (61 g., 0.46 mole) was acetylated with acetyl chloride in ethyl ether, yielding 89 g. (90%) of 1,7-diacetoxyheptane, b.p. 99–100° (0.6 mm.). Using the same apparatus as described for the preparation of 1,4-pentadiene, this acetate was subjected to pyrolysis at 500° with an addition rate of 1 ml./min. to yield 18 g. (45%) of 1,7-heptadiene, b.p. 90–93°. It was purified by distillation over sodium, followed by preparative gas chromatography, n^{20}_{D} 1.4148.[7]

1,7-Octadiene.—The diene (b.p. 115–121°)[8] was digested over sodium, redistilled and purified by preparative gas chromatography, n^{20}_{D} 1.4220.

1,8-Nonadiene.—Diethyl azelate was the starting ester for the preparation of 1,9-nonanediol. Pyrolysis of 162 g. (0.66 mole) of 1,9-diacetoxynonane[8] gave 60% of 1,8-nonadiene, b.p. 120–143°. After digestion over sodium and distillation through a Widmer column, it boiled at 142–143°, n^{20}_{D} 1.4289.[8]

1,9-Decadiene.—Pyrolysis of 87 g. (0.34 mole) of 1,10-diacetoxydecane was carried out at 500° with an addition rate of 2 ml./min., yielding 25 g. (53%) of 1,9-decadiene. The diene was digested over sodium and redistilled through a Widmer column, b.p. 164–165°, n^{20}_{D} 1.4318.[8]

1,10-Undecadiene.—The previously described method[9] was used to give diene of b.p. 86.5–87.5° (31 mm.), n^{20}_{D} 1.4354.

Purity of the prepared dienes, determined by vapor phase chromatography on an 8-ft. squalane column, was found to be 99.9% or higher.

Reaction between α,ω-Dienes and Diisobutylaluminum Hydride.—α,ω-Diene and diisobutylaluminum hydride in a 1:2.1 molar ratio were added to a glass tube flushed with nitrogen. After sealing, the glass tube was kept in an oil bath at 70° for 16 hr. The reaction products from 1,6-heptadiene, 1,7-octadiene, 1,8-nonadiene, 1,9-decadiene, and 1,10-undecadiene were viscous at a room temperature. Those from 1,4-pentadiene and 1,5-hexadiene were not viscous. The products from 1,4-pentadiene and 1,6-heptadiene were diluted with 10 ml. of n-hexane. The products from the other dienes were diluted with 10 ml. of n-heptane. The diluted products were decomposed by successive addition of 2.5 ml. of ethanol, 1 ml. of water, and 25 ml. of 6 N hydrochloric acid. The organic layer was washed twice with water and dried over sodium sulfate. The hydrocarbon produced by the hydrolysis was separated by the gas chromatographic technique. n-Pentane, n-hexane, methylcyclopentane, n-heptane, n-octane, n-nonane, n-decane, and n-undecane were identified by comparing their gas chromatographic retention times and infrared spectra with authentic samples. Methylcyclohexane was identified by comparison of its retention time with an authentic sample. The composition of the products was determined from the peak area of gas chromatogram.

Stability of 1,7-Dialumino-heptane Compound.—A mixture of 1.9 g. (0.02 mole) of 1,6-heptadiene and 6.0 g. (0.042 mole) of diisobutylaluminum hydride was at first heated under the same conditions as described previously (16 hr., 70°), and then for an additional 13 hr. at 125°. The reaction mixture was hydrolyzed as in the aforementioned method. The hydrolyzed product consisted of 91.5% of n-heptane and 8.5% of methylcyclohexane. Thus the additional heating at the higher temperature (125°) increased the yield of methylcyclohexane by 7.6%. Methylcyclohexane was separated by gas chromatographic technique and its infrared spectrum was identical with that of an authentic sample.

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(5) F. Cortese, *J. Am. Chem. Soc.*, **51**, 2266 (1929).

(6) C. S. Marvel and J. K. Stille, *ibid.*, **80**, 1740 (1958).

(7) A. L. Henne and K. W. Greenlee, *ibid.*, **65**, 2020 (1943).

(8) C. S. Marvel and W. E. Garrison, *ibid.*, **81**, 4737 (1959).

(9) J. N. Reformatsky, E. Grischkewitsch-Frochimowsky, and A. Semenzow, *Ber.*, **44**, 1885 (1911).

Ferrocenes. VI. Oxidation in Friedel–Crafts Reactions[1,2]

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During an investigation toward the synthesis of difunctional ferrocenes, a number of attempted Friedel–Crafts reactions under nitrogen resulted in significant oxidation of ferrocene to ferricinium ion.

Although over thirty publications and patents describe Friedel–Crafts reactions on ferrocene with some thirty-five different acyl chlorides, only one was found in which the yield of ferrocene was reported from reduction of the purple aqueous layer obtained upon hydrolysis. In this instance, the reaction of chloroacetyl chloride, aluminum chloride, and ferrocene under conditions chosen for monosubstitution gave 32% ferrocene upon reduction of the aqueous layer.[3] Oxidation can be assumed to be small when hydrolysis produced an aqueous layer that was pale blue[4,5] or when yields of expected products exceeded 90%.[6,7]

Like chloroacetyl chloride, dichloro- and trichloroacetyl chlorides with aluminum chloride were found to oxidize ferrocene significantly; reduction of the purple aqueous layers gave ferrocene in 47 and 48% yields, respectively. Similarly, terephthaloyl, p-nitrobenzoyl, and ethyl oxalyl chlorides gave ferricinium ion in 57, 47, and 64% yields. The high per cent of oxidation with ethyl oxalyl chloride suggests that the failure

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(1) Presented at the 140th National Meeting of the American Chemical Society, Chicago, Ill., September, 1961.

(2) This investigation was conducted under Air Force Contract AF 33(616)-7214, monitored by the Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio.

(3) K. Schlögl, *Monatsh. Chem.*, **88**, 601 (1957). The organic layer yielded 12% chloroacetylferrocene and 16% unreacted ferrocene.

(4) M. Rosenblum and R. B. Woodward, *J. Am. Chem. Soc.*, **80**, 5443 (1958).

(5) M. D. Rausch and L. E. Coleman, *J. Org. Chem.*, **23**, 107 (1958).

(6) M. D. Rausch, M. Vogel, and H. Rosenberg, *ibid.*, **22**, 903 (1957).

(7) E. L. DeYoung, *ibid.*, **26**, 1312 (1961).

of oxalyl chloride to undergo a normal Friedel–Crafts reaction on ferrocene[8] may be due to oxidation.

It is commonly accepted by chemists in the ferrocene field that oxidized products from Friedel–Crafts reactions arise as a result of inadvertent exposure of reaction mixtures to moisture and oxygen.[9] While this may be true in instances of 5% oxidation or less, it is unlikely that this is the case with major oxidations unless a catalytic effect exists that varies greatly with the acyl halide. We found oxidation to be insignificant with *p*-fluorobenzoyl chloride, benzoyl chloride,[6] and *n*-butyryl chloride.[10]

A more attractive interpretation for significant oxidations is that the acylium ion that is formed from the acyl chloride and aluminum chloride may remove an electron from the ferrocene system in competition with acylation, and that the former reaction to give ferricinium ion is a major one if the acylium ion is sufficiently positive. All of the mentioned oxidizing acyl chlorides have electron-withdrawing groups adjacent to the chlorocarbonyl group and should produce an acylium ion more electron deficient than that of a simple acyl halide. With the limited data, however, the delineation between oxidizing and nonoxidizing acyl chlorides is not clear-cut. Thus, while terephthaloyl chloride caused 57% oxidation, *o*-carbomethoxybenzoyl chloride gave 83% monoacylated ferrocene.[11]

$$C_{10}H_{10}Fe \xrightarrow[\text{(b) } H_2O]{\text{(a) RCOCl, } AlCl_3} (C_{10}H_{10}Fe)^+ \quad 37\text{–}64\%$$

R = *p*-$ClCOC_6H_4$–, *p*-$NO_2C_6H_4$–, Cl_3C–, Cl_2CH–, and C_2H_5OOC–

Major oxidation was also encountered when chloroacetal was added to ferrocene and aluminum chloride. Reduction of the aqueous layer gave 37% ferrocene and about 20% ferrocenyl compounds, while the organic layer returned 19% ferrocene and about 15% of a crude ferrocene, m.p. 14–21°. Here, the probable intermediate carbonium ion was bound to two electron-withdrawing groups ($ClCH_2C^+HOCH_2CH_3$) and should be unusually electron deficient. Under different conditions, triphenylmethylcarbonium ion also oxidized ferrocene.[12] While chloroacetal gave both substituted and unsubstituted ferricinium ions, the acyl chlorides gave only the latter, in accord with the failure of acylferrocenes to form isolatable ferricinium derivatives.[13]

The oxidations might appear to be related to the recently reported[14,15] degradation of ferrocene by aluminum chloride, in which oxidation was postulated by Goldberg as an intermediate step.[16] However, electron-rich ferrocene in the latter case was apparently attacked by electron-poor aluminum chloride and in the former case by electron-poor acylium ions. With the differences in attacking species, the results were also different: disruption of iron-cyclopentadienyl bonding *vs.* removal of an electron from the ferrocene system. Goldberg's assumption that oxidation was a step in the degradation required a second assumption that enough air and moisture were inadvertently introduced to bring about the oxidation.[15] If such were the case, a fair amount of ferricinium ion should be present at work-up, but the results, at least at lower temperatures, were not significantly altered by omitting the reduction of the aqueous layer prior to isolation.[17] If oxidation is not an intermediate step—and it seems unnecessary in view of the strong attraction of aluminum chloride for π-electrons—then the degradation reaction is of interest here only as a potential side reaction.

In this regard, it would seem important to prepare the acyl chloride–aluminum chloride complex first rather than to allow ferrocene to come in contact with the aluminum chloride. This procedure was not always followed, however, and in practice the order of addition was not critical. Thus, addition of ferrocene to the Perrier complex from dichloroacetyl chloride gave 47% ferricinium ion, and addition of aluminum chloride to a mixture of ferrocene and trichloroacetyl chloride yielded 37–48% ferricinium ion.

The organic layers from the oxidation reactions were in general examined only to the point at which it was evident that the reactions were unsuitable for preparation of heteroannularly disubstituted ferrocenes in quantity.

Experimental

Reactions of Ferrocene and Aluminum Chloride with Terephthaloyl, *p*-Nitrobenzoyl, and Dichloroacetyl Chlorides.—These reactions are typified by the following example with terephthaloyl chloride. To 30.5 g. (0.15 mole) of terephthaloyl chloride in 100 ml. of dry methylene chloride under nitrogen in an ice bath was added 20.0 g. (0.15 mole) of aluminum chloride in five portions during a 30-min. period. The mixture was stirred in the ice bath while 9.3 g. (0.05 mole) of ferrocene in 50 ml. of dry methylene chloride was added during a 2-hr. period. After the mixture was stirred overnight, it was poured into 100 ml. of methanol, stirred 30 min., and added to 250 ml. of water. The water layer was extracted once with chloroform and treated with zinc dust until the purple had disappeared. Filtration of the aqueous mixture, extraction of the solids with chloroform, and evaporation of the dried extract left 5.34 g. (57%) of ferrocene, identified by infrared comparison.

With *p*-nitrobenzoyl chloride, 47% of the ferrocene was recovered by reduction of the aqueous layer.

With dichloroacetyl chloride at a reactants ratio of 2:5:5 instead of 1:3:3, reduction of the aqueous layer gave material amounting to 47% of the starting ferrocene; the infrared spectrum showed two medium carbonyl bands not present in the spectrum of ferrocene. No methanol was used in the work-up. When boron trifluoride was the catalyst at a reaction time of 3.5 hr. at ice-bath temperature, 16% ferrocene was isolated from the aqueous layer and 62% ferrocene from the organic layer.

Reactions of Ferrocene and Aluminum Chloride with Trichloroacetyl Chloride and with Ethyl Oxalyl Chloride.—To a solution of 3.72 g. (0.02 mole) of ferrocene and 5.6 ml. (0.05 mole) of trichloroacetyl chloride in 40 ml. of dry methylene chloride at

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[8] In one instance it was reported that no reaction took place, and this would appear to be the case if the aqueous layer were routinely reduced prior to isolation [R. Riemschneider and D. Helm, *Chem. Ber.*, **89**, 155 (1956)]. In another instance, 0.5% diferrocenyl ketone was isolated [S. I. Goldberg, *J. Org. Chem.*, **25**, 482 (1960)].

[9] Two referees took this view of a shorter version of the present work.

[10] M. Vogel, M. Rausch, and H. Rosenberg, *J. Org. Chem.*, **22**, 1016 (1957).

[11] A. N. Nesmeyanov, N. A. Vol'kenau, and V. D. Vilchevskaya, *Dokl. Akad. Nauk SSSR*, **118**, 512 (1958).

[12] M. F. Hawthorne, *J. Org. Chem.*, **21**, 363 (1956).

[13] R. B. Woodward, M. Rosenblum, and M. C. Whiting, *J. Am. Chem. Soc.*, **74**, 3458 (1952).

[14] S. G. Cottis and Harold Rosenberg in "Conference on High Temperature Polymer and Fluid Research," Technical Documentary Report No. ASD-TDR-62-372, August, 1962, p. 637.

[15] S. I. Goldberg, *J. Am. Chem. Soc.*, **84**, 3022 (1962).

[16] Goldberg referred to the work of Rosenblum and Santer that concerned the complex $(C_{10}H_{10}Fe \cdot HAlCl_4)_n$. This complex yielded ferrocene upon hydrolysis and not ferricinium ion [*J. Am. Chem. Soc.*, **81**, 5517 (1959)].

[17] H. Rosenberg, private communication.

−30° was added 6.66 g. (0.05 mole) of aluminum chloride in three portions during a 5-min. period. After 2 hr. below −20°, the mixture was poured into ice water and stirred 5 min. The organic layer was extracted three-times with water and the extracts and water layer combined. Treatment of the aqueous solution with zinc dust and subsequent extraction with chloroform gave 1.37 g. (37%) of ferrocene (infrared comparison).

A similar reaction with ethyl oxalyl chloride gave 64% ferrocene (infrared comparison) upon reduction of the aqueous layer.

Reaction of Ferrocene and Aluminum Chloride with Chloroacetal.—Chloroacetal (15.3 g.; 0.1 mole) was added dropwise during an 80-min. period to 9.3 g. (0.05 mole) of ferrocene and 13.3 g. (0.10 mole) of aluminum chloride in 65 ml. of ethylene dichloride under nitrogen at −20°. After 30 min., the mixture was warmed to −5°, added to ice, and the aqueous layer extracted with chloroform. After removal of solvent from the combined organic layers, the residue (5.92 g.) was extracted with 120 ml. of petroleum ether (b.p. 30–60°) in 20-ml. portions and each portion added to 180 g. of alumina and eluted with petroleum ether to give 1.75 g. (19%) of ferrocene. Continued elution with the usual solvents removed distinct fractions (oils), the infrared spectra of which suggested that the ferrocenes present were monosubstituted. Reduction of the aqueous layer with zinc dust, extraction with chloroform, and removal of solvent left moist solid, which when extracted with methanol left 3.04 g. (33%) of crude ferrocene. Removal of methanol and chromatography of the residue (2.73 g.) gave 4% ferrocene and 1.65 g. of solid, m.p. 14–21°, the infrared spectrum of which showed strong bands at 9 and 10 μ (a monosubstituted ferrocene).

1,1′-Bis(*p*-fluorobenzoyl)ferrocene.—A mixture of 37.1 g. (0.263 mole) of *p*-fluorobenzoic acid and 48 ml. (0.658 mole) of thionyl chloride in 25 ml. of benzene was refluxed 7 hr. Volatile material was removed *in vacuo*, 90 ml. of dry methylene chloride was added, and the solution was treated with 31.1 g. (0.233 mole) of powdered anhydrous aluminum chloride. To the mixture in an ice bath was then added dropwise a solution of 17.3 g. (0.093 mole) of ferrocene in 90 ml. of methylene chloride during a 1.5-hr. period, and the mixture was stirred overnight at room temperature. The solution was poured onto ice, stirred 4 hr., and the aqueous phase washed with chloroform. The organic phases were combined, washed twice with water and once with 5% sodium hydroxide solution, dried, and evaporated *in vacuo*. Crystallization of the residue from 150 ml. of toluene yielded 30.4 g. (76%) of 1,1′-bis(*p*-fluorobenzoyl)ferrocene, m.p. 129–130.5°; λ_{max} (log ϵ) 472 (2.83), 350 (3.29), 250 mμ (4.28).

Anal. Calcd. for $C_{24}H_{16}F_2FeO_2$: C, 67.00; H, 3.75; Fe, 12.98. Found: C, 66.95; H, 3.86; Fe, 13.63.

1,1′-Bis(*n*-butyryl)ferrocene.—The reaction of *n*-butyryl chloride, aluminum chloride, and ferrocene was carried out by the method employed by Vogel, *et al.*, for the preparation of 1,1′-dicaprylylferrocene.[10] 1,1′-Dibutyrylferrocene, m.p. 73.0–74.5°, was obtained in 77% yield; lit.[18] m.p. 74–75°.

Acknowledgment.—We are grateful to Mr. Richard Thivierge for technical assistance.

[18] A. N. Nesmeyanov and N. A. Vol'kenau, *Dokl. Akad. Nauk SSSR*, **107**, 262 (1956).

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o-Nitrosobenzamide. A Possible Intermediate in the von Richter Reaction

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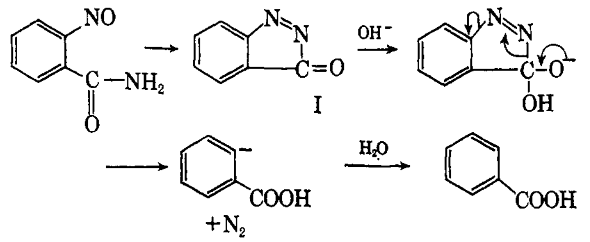
The previously unknown *o*-nitrosobenzamide has been synthesized and its behavior under the conditions of the von Richter reaction studied; the conditions of the von Richter reaction employed were those established by the research of Bunnett and his group.[1] This work was undertaken because of our interest in the peroxy acid oxidations of aromatic amines[2] and of nitrosobenzenes,[3] and because *o*-nitrosobenzamide has been implicated as an intermediate in the von Richter reaction.[4]

o-Nitrosobenzamide was obtained in excellent yield by oxidizing *o*-aminobenzamide with peroxyacetic acid in ethanolic medium at *ca.* 0°. These conditions previously have been shown[2] to favor the formation of nitrosobenzenes as the chief products of the peroxyacetic acid oxidation of aromatic amines. The amido group in the present substrate did not cause any complications. Its indifference to peroxyacetic acid was foreseen on mechanistic grounds[2] and by analogy with the peroxyacetic acid oxidation of nicotinamide to nicotinamide N-oxide in 82% yield.[5] The elemental and spectral analyses of the reaction product confirmed it to be the desired nitrosobenzamide.[2,6]

A recently proposed mechanism for the von Richter reaction[4] requires that *o*-nitrosobenzamide should give benzoic acid and nitrogen gas according to the following reaction sequence.



When *o*-nitrosobenzamide was treated with cyanide ion or hydroxide ion in aqueous ethanolic medium at 150°, the von Richter reaction conditions,[1] benzoic acid was formed with evolution of nitrogen gas as predicted by the Rosenblum mechanism.[4] The yield of isolated benzoic acid was 20% with cyanide ion and 45% with hydroxide ion. The reported yields of benzoic acids from the von Richter reaction range between 10 and 40%.[1] The isolated product melted at 122° and its ultraviolet spectrum in water was superimposable with that of an authentic sample of benzoic acid.

A transient red color appeared immediately upon addition of base to the aqueous ethanolic solutions of *o*-nitrosobenzamide. This color may be attributable to the formation of 3-indazolone, the intermediate I. The preparation of I (in solution) by independent synthesis and its hydrolysis to benzoic acid and nitrogen gas has been reported recently.[7] The solutions of I in acetonitrile were reported to have deep red color.[7]

Experimental

Materials.—*o*-Aminobenzamide (Matheson Coleman and Bell, practical grade) was purified by treatment with decolorizing

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[1] (a) J. F. Bunnett, J. F. Cormack, and F. C. McKay, *J. Org. Chem.*, **15**, 481 (1950); (b) J. F. Bunnett, M. M. Rauhut, D. Knutson, and G. E. Bussell, *J. Am. Chem. Soc.*, **76**, 5755 (1954); (c) J. F. Bunnett and M. M. Rauhut, *J. Org. Chem.*, **21**, 934 (1956).

[2] K. M. Ibne-Rasa and J. O. Edwards, *J. Am. Chem. Soc.*, **84**, 763 (1962).

[3] K. M. Ibne-Rasa, C. G. Lauro, and J. O. Edwards, *ibid.*, **85**, 1165 (1963).

[4] M. Rosenblum, *ibid.*, **82**, 3796 (1960).

[5] E. C. Taylor, Jr., and A. J. Crovetti, *Org. Syn.*, **37**, 63 (1957).

[6] K. Nakamoto and R. E. Rundle, *J. Am. Chem. Soc.*, **78**, 1113 (1956).

[7] E. F. Ullman and E. A. Bartkus, *Chem. Ind.* (London), 93 (1962).