recrystallization from methanol yielded 72 mg. (0.14 mmole, 45%) of **bis-2-iodophenyl sulfone (XVI)**, m.p. 195°. The melting point was not depressed upon admixture with an independently synthesized sample (Table V) and the infrared spectra were superimposable.

Dibenzofuran from 2,2'-Diiododiphenyl Ether.—A mixture of 2 g. of purified copper powder and 0.25 g. (0.59 mmole) of 2,2'-diiododiphenyl ether (XIV, from the decomposition of phenoxiodonium iodide) in a sealed tube was immersed in a silicone oil bath at 255° for 5 hr. The tube was cooled and opened, and the contents were dissolved in ether. Upon concentration to dryness the residue was recrystallized from methanol–water to yield 0.05 g. (0.3 mmole, 50%) of **dibenzofuran**, m.p. 82–84°; there was no depression of the melting point upon admixture with an authentic sample and the infrared spectra were superimposable.

N-Acetyl Carbazole from N-Acetyl-2,2'-Diiododiphenylamine.—A mixture of 100 mg. (0.22 mmole) of N-acetyl-2,2'-diiododiphenylamine (XV) (from the decomposition of N-acetylphenazidonium iodide) and 1 g. of purified copper powder was heated according to the above procedure at 230°. The residue was taken up in ether, filtered, and concentrated; the resulting residue was crystallized from hexane to yield 27 mg. (0.13 mmole, 59%) of N-acetylcarbazole. The melting point (62–64°) was not depressed upon admixture with a sample prepared by acetylation of carbazole and the infrared spectra were superimposable.

Attempted Preparations of 1,3,7,9-Tetranitro-10H-dibenz[*b,e*]iodinonium Salts. A. 2,2',4,4'-Tetranitrodiphenylmethane with Iodyl Sulfate.—When 8.7 g. (25 mmoles) of 2,2',4,4'-tetranitrodiphenylmethane[31] was treated with iodylsulfate according to procedure A and the resulting mixture was poured onto ice, a large amount of iodine was formed along with a solid. The iodine was removed by washing the collected solid with ether. Recrystallization of the solid from glacial acetic acid gave 8.1 g. (23 mmoles, 93%) of starting tetranitro aromatic compound, m.p. 171–173°, undepressed when admixed with an authentic sample. The aqueous filtrate was treated with sodium bisulfite until no more oxidizing power was observed with potassium starch–iodide paper. Clarification with activated carbon, followed by addition of aqueous potassium iodide, gave a yellow precipitate which was filtered to yield 0.4 g. (0.67 mmole, 3%) of **3,7-dinitro-10H-dibenz[*b,e*]iodinonium iodide**, identified by lack of depression of the melting point with an authentic sample of the iodide of cation II and by superposition of their infrared spectra.

B. 3,7-Dinitro-10H-dibenz[*b,e*]iodinonium Bisulfate with Potassium Nitrate in Sulfuric Acid.—An attempt to nitrate the bisulfate of cation II using procedure C-2 with a large excess of potassium nitrate resulted only in recovery of starting material.

Analytical data for the above preparations may be found in Table VIII.

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Acknowledgment.—We are pleased to acknowledge the contribution of Mr. Fred Gruen who did exploratory work in the syntheses employing iodyl sulfate (1953–1957). Thanks are due also to the companies in whose laboratories this work was performed: Burroughs Wellcome and Company, Inc. (L.K.), and The Schering Corporation (G.B.T.).

Organometallic Studies. X.[1a] Reductive Dimerization of α-Metallocenylcarbonium Ions. I[1b]

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Solvolysis of ferrocenylcarbinols followed by reduction with zinc leads to the formation of 1,2-diferrocenylethanes in yields of 60% and better. The reaction sequence is envisaged to consist of reduction by zinc of the initially formed α-ferrocenylcarbonium ion to the ferrocenylcarbinyl radical which upon coupling yields the dimer.

In the course of our studies on the synthesis of metal π-complexes of the pentalene and benzopentalene systems[2–5] the key step in the envisaged reaction sequence involved the formation of an α-metallocenylcarbonium ion. This prompted us to look into some pertinent aspects of the reactions involving such carbonium ions.

Both qualitative and quantitative evidence has been presented to show that carbonium ions adjacent to metallocene systems possess an unusual stability. Thus, ferrocenecarboxaldehyde is soluble in dilute hydrochloric acid.[6] Ferrocenylmethylcarbinol can be dehydrated to vinylferrocene under very mild conditions[7] and the latter adds very readily, across the double bond, weak acids such as hydrogen azide and acetic acid.[8] Ferrocenylphenylcarbinol forms ethers with great ease.[9] The formation of the rearranged product 1,1-diferrocenylethane on alkylation of ferrocene with 1,2-dichloroethane has been ascribed to the rearrangement of the initially formed primary carbonium ion to the more stable α-ferrocenylcarbonium ion.[10]

Quantitative evidence for the stabilization of α-metallocenylcarbonium ions has been obtained from studies on the solvolysis of metallocenylcarbinyl acetates.[11–14] The latter have been shown to solvolyze with rates somewhat greater than that of trityl acetate and this has been taken to indicate stabilization of the α-metallocenylcarbonium ion. A similar conclusion was drawn from the results obtained in a kinetic study of the solvolysis of α-ferrocenylethyl chloride.[15]

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[1] (a) Part IX: M. Cais and N. Narkis, *J. Organometal. Chem.*, in press. (b) This work has been sponsored by Air Force Materials Laboratory, Research and Technology Division, AFSC, through the European Office of Aerospace Research, U. S. Air Force, Contract No. AF 61(052)-752. (c) To be submitted by A. E. as part of the doctorate thesis at the Technion.

[2] M. Cais and A. Modiano, *Chem. Ind.* (London), 202 (1960); *Tetrahedron Letters*, **No. 18**, 31 (1960).

[3] M. Cais, A. Modiano, N. Tirosh, A. Eisenstadt, and A. Rubinstein, XIXth International Congress of Pure and Applied Chemistry, London, July 10–17, 1963, Abstracts of Papers, AB 4-12, p. 166.

[4] M. Cais, A. Raveh, and A. Modiano, *Israel J. Chem.*, **1**, 228 (1963).

[5] M. Cais, A. Modiano, N. Tirosh, A. Eisenstadt, VIIIth International Conference on Coordination Chemistry, Vienna, Sept. 7–11, 1964, Proceedings, Vol. 8, V. Gutmann, Ed., 11B3, p. 229.

[6] M. D. Rausch, *Can. J. Chem.*, **41**, 1289 (1963).

[7] K. Schlogl and H. Mahar, *Naturwiss.*, **48**, 376 (1961).

[8] (a) G. R. Buell, W. E. McEwen, and J. Kleinberg, *Tetrahedron Letters*, **No. 5**, 16 (1959); (b) *J. Am. Chem. Soc.*, **84**, 40 (1962).

[9] N. Weliky and E. S. Gould, *ibid.*, **79**, 2742 (1957).

[10] K. L. Rinehart, Jr., P. A. Kittle, and A. F. Ellis, *ibid.*, **82**, 2082 (1960).

[11] J. H. Richards and E. A. Hill, *ibid.*, **81**, 3484 (1959).

[12] J. H. Richards and E. A. Hill, *ibid.*, **83**, 3840 (1961).

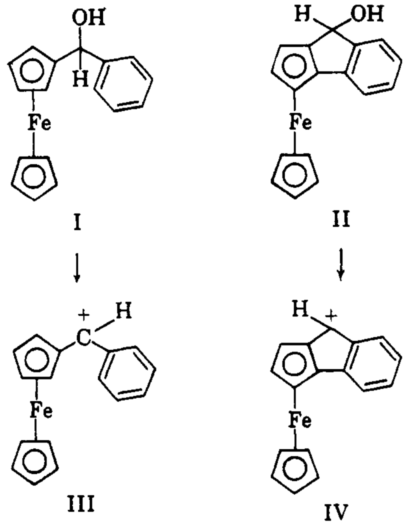
[13] E. A. Hill and J. H. Richards, *ibid.*, **83**, 4216 (1961).

[14] D. S. Trifan and R. Backsai, *Tetrahedron Letters*, **No. 13**, 1 (1960).

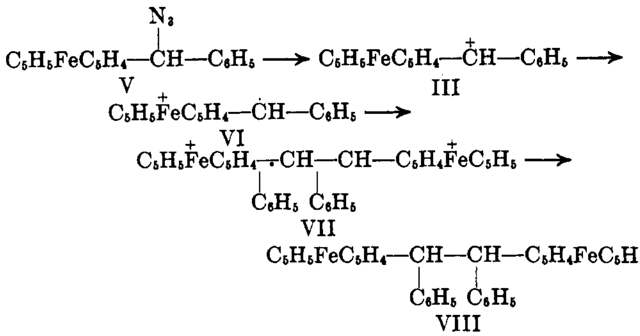
[15] E. A. Hill, *J. Org. Chem.*, **28**, 3586 (1963).

In our work with α-metallocenylcarbonium ions we have been concerned primarily with two aspects of the general problem: (i) the possibility of isolating these stable carbonium ions in the form of salts in order to study their physical and chemical properties, and (ii) the extent to which the fate of these carbonium ions in subsequent reactions is affected by the presence of the metal atom of the metallocene molecule.

The first aspect (i) will be dealt with only in passing in the present communication, with further details to be published at a later date. In order to cover the second aspect (ii) of the problem, we chose as model compound ferrocenylphenylcarbinol (I) because the carbonium ion III obtained from it was expected to behave analogously to that obtained from 2,3-ferrocoindenol (II), our key intermediate in the benzopentalene work.[4,5]



The ferrocenylphenylmethylcarbonium ion (III) has already been mentioned in the literature. Thus, the formation of the diastereoisomers of 1,2-diferrocenyl-1,2-diphenylethane (VIII), in the acid-catalyzed decomposition of ferrocenylphenylcarbinyl azide (V), is visualized[16] to take place through transformation of



$$\underset{\mathrm{V}}{C_5H_5FeC_5H_4\text{—}\overset{\overset{N_3}{|}}{C}H\text{—}C_6H_5} \longrightarrow \underset{\mathrm{III}}{C_5H_5FeC_5H_4\text{—}\overset{+}{C}H\text{—}C_6H_5} \longrightarrow$$

$$\underset{\mathrm{VI}}{C_5H_5\overset{+}{Fe}C_5H_4\text{—}\dot{C}H\text{—}C_6H_5} \longrightarrow$$

$$\underset{\mathrm{VII}}{C_5H_5\overset{+}{Fe}C_5H_4\text{—}\underset{C_6H_5}{\underset{|}{C}H}\text{—}\underset{C_6H_5}{\underset{|}{C}H}\text{—}C_5H_4\overset{+}{Fe}C_5H_5} \longrightarrow$$

$$\underset{\mathrm{VIII}}{C_5H_5FeC_5H_4\text{—}\underset{C_6H_5}{\underset{|}{C}H}\text{—}\underset{C_6H_5}{\underset{|}{C}H}\text{—}C_5H_4FeC_5H_5}$$

the latter into the carbonium ion III which then undergoes *intramolecular* oxidation–reduction to give the radical cation VI. Subsequent coupling of VI forms the dication dimer VII which is reduced to the neutral dimer VIII by *intermolecular* oxidation–reduction reactions with other ferrocene derivatives present in the reaction mixture.

The above reaction sequence is analogous to the one proposed earlier[17] in an attempt to explain the formation of 1,2-diferrocenylethane from the reaction of ferrocenylmethanol with acids, followed by reduction with stannous chloride.

A search of the ferrocene literature has revealed several reports of the formation of a high-melting (varying between ~200–280°) crystalline material for which no structure is suggested. On the basis of the reactions involved in these reports, we feel rather certain that the above-mentioned unknown compound is in effect the diastereoisomeric dimer VIII, which arose through the initial formation of the intermediate ferrocenylphenylmethyl carbonium ion III and by a reaction sequence to be discussed later in this paper.

Thus, in the condensation reaction between benzaldehyde and ferrocene in the presence of hydrogen fluoride there was obtained[18] a blue solution which upon reduction with zinc gave orange crystals, m.p. ~220°; after crystallization from petroleum ether (b.p. 100–120°) the melting point was 260–265°. The elemental analysis reported fits the dimer VIII.

The dimeric structure VIII for this product from the above condensation reaction has already been proposed by Rinehart, *et al.*,[17] on the basis of elemental analysis and infrared spectrum and its formation was explained by a path analogous to that proposed for the formation of 1,2-diferrocenylethane.

The dimer VIII, though not identified as such, has also been isolated from various reduction reactions of benzoylferrocene.[19–20] In addition, Nesmeyanov and co-workers have recently[21–23] reported the formation of the diastereoisomers of the dimer VIII in reactions involving the carbinol I.

We have developed reaction conditions under which the dimer VIII is the major reaction product and is formed in reasonable yields. The procedure is based on what could be called the reductive dimerization of the ferrocenylphenylmethylcarbonium ion (III), and we have reason to suggest that, under suitable conditions, this reductive dimerization could be used as a general reaction of α-metallocenylcarbonium ions.

The procedure is based on treating the metallocenylcarbinol with 1 molar equiv. of hydrobromic acid in glacial acetic acid, and after a reaction time of 2–5 min. excess zinc powder is added as reducing agent.

The reaction time and order of addition of the reagents appear to be quite critical in determining the final composition of the reaction product.

Thus, Pauson and Watts have recently reported[24] that the dropwise addition, over a period of 3 hr., of 0.1 *N* hydrochloric acid to a refluxing ethanol solution containing a ferrocenylcarbinol, zinc dust, and a little titanous chloride, results in the formation of a ferrocenylmethane in high yields. Diferrocenylphenylmethane (87%) and triferrocenylmethane (64%) were

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

(17) K. L. Rinehart, Jr., C. J. Michejda, and P. A. Kittle, *ibid.*, **81**, 3162 (1959).

(18) V. Weinmayer, *ibid.*, **77**, 3009 (1955).

(19) M. D. Rausch, *J. Org. Chem.*, **22**, 903 (1957).

(20) (a) M. Cais and M. Feldkimel, unpublished results; (b) M. Feldkimel, M.S. Thesis, Technion, Haifa, 1960.

(21) A. N. Nesmeyanov, I. I. Kritskaya, and T. V. Antipina, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1777 (1962).

(22) A. N. Nesmeyanov and I. I. Kritskaya, *ibid.*, 352 (1962).

(23) A. N. Nesmeyanov, E. G. Pervalova, and Yu. A. Ustynyuk, *ibid.*, 1967 (1963).

(24) P. L. Pauson and W. E. Watts, *J. Chem. Soc.*, 3880 (1962).

prepared in this manner. By a similar reaction procedure, acetylferrocene was converted to ethylferrocene (87%).

On the other hand, under our reaction conditions, what happens to the unusually stable α-metallocenylcarbonium ion which is first formed in the solvolysis reaction depends on the follow-up reaction procedure.

If excess sodium methoxide is added to the reaction mixture within a short time (less than 5 min.) of the start of the solvolysis reaction, the major reaction product (80%) is the ferrocenylcarbinyl methyl ether, arising from attack of the carbonium ion by the methoxyl anion. It can be inferred from this result that the α-ferrocenylcarbonium ion remains largely unchanged within this short period of time. In other words, in this time *there is no significant inter- or intramolecular oxidation–reduction process*[16,17] *leading to the formation of the radical cation VI, and followed by dimerization to the dication VII.*

Further corroborative evidence to this effect is shown by the fact that, upon isolation of the α-ferrocenylcarbonium ion in the form of its fluoborate or mercuric tribromide salt[25] followed by reaction of the latter salt with methanol, the ferrocenylcarbinyl methyl ether is produced in yields of 70%. We infer from this that the carbonium ion appears to retain its identity as such in the solid salt.

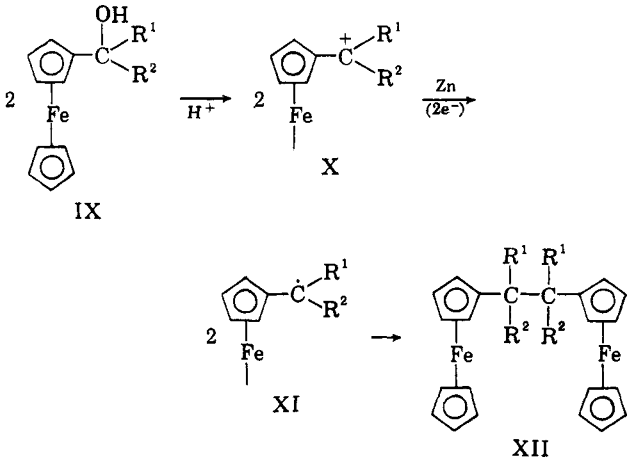
The following additional observations strongly support this view. Consideration of the electronic structure of the carbonium ion III shows that this should be a diamagnetic species. On the other hand the radical cation VI would be expected to be paramagnetic with a magnetic moment equivalent to two unpaired electrons. On measuring the n.m.r. spectrum of ferrocenylphenylcarbinol (I), the following absorptions were obtained (in the ratio 1:9:1:5): τ 7.49 (hydroxyl proton), 5.69_0 (ferrocenyl protons), 4.36 (methine proton), and 2.45 (phenyl protons). Upon the introduction of gaseous hydrobromic acid into the tube containing the carbinol–chloroform solution and remeasuring the n.m.r. spectrum of this solution after 1, 5, 10, and 15 min., the proton resonance absorptions obtained were nearly as sharp as those obtained with the original carbinol solutions free of hydrobromic acid. The changes which did take place appeared to occur in the period between 1 and 5 min.; the net effect was a displacement to somewhat higher fields of the ferrocenyl (τ 5.86), methine (τ 4.8), and phenyl (τ 2.62) protons and a broadening and flattening of the hydroxyl proton resonance spectrum. Should the paramagnetic radical cation VI have been formed in any significant amounts, considerable over-all broadening and/or significant shifts of the proton resonance absorption spectrum should have been observed.

Indeed, this was what happened (considerable over-all broadening) when the same experiment was carried out with ferrocoindenol (II). Moreover in the latter case the magnetic susceptibility measurements[26] of the isolated fluoborate salt gave magnetic moment $\mu_{\text{eff}} \sim 2.3$ B.M. (Bohr magnetons).[3-5]

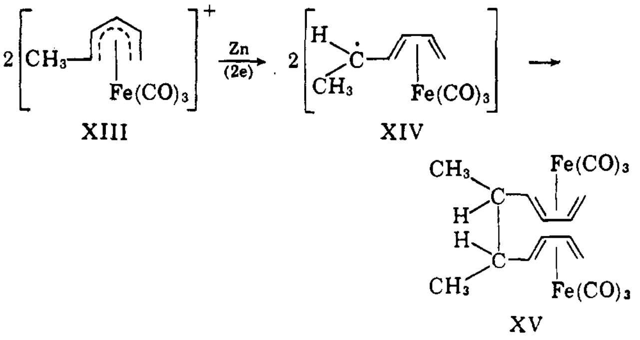
The diamagnetism of the salt of ferrocenylphenylcarbonium ion was not unexpected in view of the report that the isolated perchlorate salt of diferrocenylcarbonium ion was found to be diamagnetic.[27]

We feel that on the basis of all the above evidence it is possible to build a strong case for supporting the suggestion of unusual stability for α-ferrocenylcarbonium ions.[11-15] In addition one can safely conclude that inter- or intramolecular oxidation–reduction processes involving the metal atom of the metallocene moiety contribute only to an insignificant extent, if at all, to the formation of dimeric compounds such as VIII, under our reductive dimerization reaction conditions.

It appears to us that a more plausible reaction sequence would be the one involving first reduction of the carbonium ion X by electron transfer from the zinc metal atom (or other suitable reducing agent) with the formation of the radical XI, followed by a coupling reaction to produce the dimer XII.



The suggested mechanism is in effect analogous to the one proposed by Pettit and co-workers[28] to explain the formation of the dimer XV produced by the reduction, with zinc, of salts of the *syn*-1-methylpentadienyliron tricarbonyl cation (XIII).



The plausibility of the suggested reaction sequence for the reductive dimerization reaction is also evident from the product analysis of the solvolysis reaction carried out for periods of time longer than 5 min.

Table I shows the amounts (in milligrams) of the various products isolated from the solvolysis of 1 g. of ferrocenylphenyl carbinol followed by the addi-

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[25] We have no evidence that the anion is actually the $HgBr_3$ species. The latter could also be the doubly charged negative ion $HgBr_4^{-2}$ in which case the salt would contain two units of the carbonium ion. This in no way affects the arguments brought in the text.

[26] This result will be discussed in detail in a forthcoming publication. We wish to thank Professor S. Kirschner, Wayne State University, Detroit, Mich., and Mr. P. R. Woolliams, University College, London, for the magnetic susceptibility measurements.

[27] C. Jutz, *Tetrahedron Letters*, **No. 21**, 1 (1959).

[28] J. E. Mahler, D. H. Gibson, and R. Pettit, *J. Am. Chem. Soc.*, **85**, 3959 (1963).

TABLE I

PRODUCTS OF REDUCTIVE SOLVOLYSIS OF FERROCENYLPHENYLCARBINOL[a]

Chromatographic fraction[b]	Reaction product (mg.) after different solvolysis times			
	5 min.	1 hr.	6 hr.	20 hr.
a	24	9	20	23
b	575	112	78	77
c	93	117	126	80
d–g	242	751	718	805

[a] One gram. [b] The lettering refers to the chromatographic fractions as described in the Experimental section.

tion of excess zinc powder after allowing the solvolysis reaction mixture to stir at room temperature for 5 min., 1 hr., 6 hr and 20 hr.

As can be seen, the amount of ferrocenylphenylmethane (fraction a) isolated under our reaction conditions is very minute and is the same if the zinc powder is added to the solvolysis reaction after 5 min. or after 20 hr. This is of course in great contrast to the results obtained under the reaction conditions of Pauson and Watts,[24] where the methane derivative was the major reaction product.

There is a significant change in the amount of the next fraction coming off the column (fraction b), with variation of the solvolysis reaction time. This fraction comprises the diastereoisomeric dimers VIII. Over five times as much dimer was obtained if zinc was added to the solvolysis reaction mixture after 5 min. or less than if the zinc addition took place after 1 hr., and the ratio of dimer production was more than 7:1 in favor of the 5-min. reaction compared with the 6-hr. reaction. Extending the reaction time to 20 hr. did not cause any further decrease in the amount of dimer VIII isolated.

This shows that the ferrocenylphenylcarbonium ion enters into additional reactions if allowed to remain in the solvolysis reaction mixture. It is rather certain that these additional reactions involve electrophilic attack by one molecule of the α-ferrocenylcarbonium ion upon one of the aromatic rings of another ferrocenylcarbonium ion. This could take place with the production of either 1,2-homo-, 1,3-homo-, or 1,1′-heteroannular substituted dimers, oligomers, or polymers, depending on the time elapsed before quenching the polymerization reaction by the addition of zinc powder to the solvolysis reaction mixture. The elemental analysis and molecular weight determination for the compound isolated in fraction c (Table I) corresponds to the formula $(C_{17}H_{15}Fe)_2$ the same as for the diastereoisomeric dimer VIII. Compounds isolated from fractions d–g (Table I) fit the same general formula $(C_{17}H_{15}Fe)_n$, with n values up to 4.

As can be seen from Table I, the amount of nuclear substitution products increase with increased length of time of the solvolysis reaction, at the expense of the amount of the diastereoisomeric dimer VIII.

Such nuclear substitution reactions involving α-ferrocenylcarbonium ions have already been reported in the literature. Thus, Pauson and Watts[24] have obtained diferrocenylmethane *via* cation nuclear substitution on the ferrocene nucleus through the use of ferrocene–paraformaldehyde and ferrocene–ferrocenylcarbinol in concentrated sulfuric acid. Recently Neuse and Trifan[29] published the results of an investigation on the self-condensation reaction of several ferrocenylcarbinols IX ($R^1 = R^2 = H$; $R^1 = H$, $R^2 = CH_3$; $R^1 = H$, $R^2 = C_6H_5$; *i.e.*, I) heated, in bulk concentration conditions above their melting points, under nitrogen, in the presence of 0.5–2% Lewis acid catalysts. Under these conditions, the reactions appear to have proceeded cleanly *via* nuclear substitution to give polymeric products with molecular weights ranging from about 1000 to 6000 and containing mixtures of 1,2-homo, 1,3-homo-, and 1,1′-heteroannular substitution products.

Similarly, in a recent investigation of the cleavage of ferrocene by aluminum chloride Cottis and Rosenberg[30] have isolated poly(cyclopentylferrocene) which probably arose *via* nuclear substitution reactions of an intermediate α-ferrocenyl-1-cyclopentylcarbonium ion.

In order to test the generality of the reduction dimerization reaction under our conditions and at the same time to obtain information on the effect of various organic groups on the behavior of α-ferrocenylcarbonium ions, several ferrocenylcarbinols IX ($R^1 = H$, $R^2 = CH_3$; $R^1 = H$, $R^2 = (CH_3)_3C$; $R^1 = H$, $R^2 = CH_3O{\cdot}C_6H_4$; $R^1 = H$, $R^2 = CH_3{\cdot}C_6H_4$) were subjected to the 5-min. solvolysis with zinc reduction reaction.

While it is too early to draw definitive conclusions, some preliminary remarks can be made. The presence of a sterically bulky group was expected to hinder the formation of either the dimer XII or the nuclear-substituted oligomers. Indeed the reductive dimerization reaction with ferrocenyl-*t*-butylcarbinol yielded only one compound, ferrocenyl-*t*-butylmethane.[31]

Increasing the stability of the α-ferrocenylcarbonium ion by substituting, instead of the phenyl group, better resonance-stabilized systems, as for example the anisyl group, was expected to increase the amount of dimer XII with a concomitant decrease in the amount of oligomeric material.

In actual fact a slightly better yield (~67%) of the dimer XII was obtained, but not enough data is available yet to decide whether this result is not just fortuitous. On the other hand, the reductive dimerization reaction with ferrocenyltolylcarbinol gave the dimer XII in 80% yield compared with 57% yield with ferrocenyphenylcarbinol. As expected, ferrocenylmethylcarbinol gave a very low yield of the dimer XII (10%) and a high yield (~70%) of polymeric material, which could be either of the nuclear-substituted type or that resulting from the polymerization of vinylferrocene, the latter being a possible product from proton elimination by the α-ferrocenylmethylcarbonium ion.

It should be noted that, from the reaction of ferrocenylmethylcarbinyl methyl ether with lithium metal in tetrahydrofuran, Nesmeyanov and co-workers[23] isolated the dimer 1,2-diferrocenyl-1,2-dimethylethane in a low yield (~11%), the major reaction product (63%) being ethylferrocene.

It is hoped that work with other metallocenylcarbinols currently in progress will throw further light in understanding the factors influencing the course of the reductive dimerization reaction.

It is interesting to note that reductive dimerization experiments carried out, for comparative purposes,

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(29) E. W. Neuse and D. S. Trifan, *J. Am. Chem. Soc.*, **85**, 1952 (1963).

(30) S. G. Cottis and H. Rosenberg, *J. Polymer Sci., Pt. B*, **2**, 295 (1964).

(31) It is suggested that no rearrangement takes place to form the tertiary carbonium ion owing to the higher stability of the α-ferrocenylcarbonium ion.

TABLE II

PROPERTIES AND YIELDS OF FERROCENYLCARBINOLS

$C_5H_5FeC_5H_4{\cdot}CH(OH)R$

			Carbon, %		Hydrogen, %		Iron, %		Mol. wt.	
R	Yield, %	M.p., °C.	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
C_6H_5	90	78–80	...	...	...	...	...	...	...	...
p-$CH_3{\cdot}C_6H_4$	73	82–83	70.61	70.51	5.92	5.91	18.24	18.32	306	315
p-$CH_3O{\cdot}C_6H_4$	94	72–74	67.10	66.98	5.63	5.72	17.33	17.07	322	320
CH_3	90	77–78	...	...	...	...	...	...	...	...
t-C_4H_9	71	93–94	66.20	66.33	7.39	7.57	20.52	20.36	272	260

with diphenylcarbinol (benzhydrol) yielded diphenylmethane and the expected dimer, 1,1,2,2-tetraphenylethane in approximately equal yields (~30–40% each).

Experimental[32]

Ferrocenyl Ketones.—Acetylferrocene, benzoylferrocene, p-anisoylferrocene,[33] and p-toluoylferrocene were obtained in high yields by carrying out the Friedel–Crafts acylations using methylene chloride as solvent and aluminum chloride as catalyst.

Preparation of Ferrocenylcarbinols. General Procedure.—A solution of excess sodium borohydride (2.5 mmoles) in 2 ml. of ethanol–dioxane (4:1) was added to a solution of the ferrocenylketone (2.5 mmoles) in 25 ml. of ethanol–dioxane (4:1). After stirring for 1 hr. at room temperature the reaction mixture was poured into water (150 ml.) and the mixture extracted with four 25-ml. portions of ether. After washing the ether layer with three 25-ml. portions of water, drying (magnesium sulfate), and evaporation *in vacuo* (water pump), the residue was crystallized from hexane to obtain the pure carbinol (purity was determined by thin layer chromatography). The yields and properties are summarized in Table II.

Preparation of Ferrocenyl-*t*-butylcarbinol.—To the Grignard reagent[34] prepared from 560 mg. (6 mmoles) of t-butyl chloride and 290 mg. (12 g.-atoms) of magnesium turnings in 15 ml. of ether there was added 450 mg. (3 mmoles) of ferrocenylcarboxaldehyde[35] in 10 ml. of ether.

The reaction mixture was stirred overnight, under reflux, and then worked up as usual. The organic residue after evaporation of the ether extracts was chromatographed on neutral alumina (20 g.). Elution with hexane–benzene (3:2, 200 ml.) gave 300 mg. of crystalline material, m.p. 93–94°, which remained unchanged after recrystallization from hexane and showed a single spot on thin layer chromatography.

Further elution with chloroform (60 ml.) yielded 135 mg. of starting material, ferrocenylcarboxaldehyde.

Reductive Dimerization Reaction after Solvolysis of Ferrocenylcarbinols (5-Min. Solvolysis). General Procedure.—To a solution of the ferrocenylcarbinol (0.4–1 g.) in a minimum volume of glacial acetic acid (2–4 ml.) there was added 1 molar equiv. of hydrobromic acid in glacial acetic acid (30–32% HBr–HOAc solution). After stirring for exactly 5 min., excess zinc dust was added and stirring was continued for another 30 min. The reaction mixture was then diluted with water (25 ml.) and extracted with six 20-ml. portions of methylene chloride. The methylene chloride extracts were washed with two 20-ml. portions of water then once with saturated sodium bicarbonate aqueous solution and finally with water. After drying (magnesium sulfate) the organic layer was evaporated *in vacuo* (water pump) and the residue chromatographed on neutral alumina.

The following is a description of the work-up and chromatography of the reaction product from 1 g. of ferrocenylphenylcarbinol. The residue (936 mg.) from the evaporation of the organic solvent was triturated with ether and the mixture was filtered to give 458 mg. of yellow-orange crystalline material which was recrystallized from petroleum ether (100–120°) to give crystals in the form of leaflets, m.p. 214–216° (lit.[16] m.p. 218–220° for one of the diastereoisomers of VIII).

Anal. Found: C, 73.87; H, 5.48.

The filtrate was evaporated to yield a yellow-orange solid (478 mg.) which was chromatographed on neutral alumina (20 g.). (a) Elution with hexane–benzene (2:1) yielded a crystalline material (24 mg.), m.p. 70–74°, which presumably is ferrocenylphenylmethane (lit.[9] m.p. 70–74°); (b) this was followed by crystals (117 mg.), m.p. 194–197°.

Anal. Calcd. for $C_{34}H_{30}Fe_2$: C, 74.20; H, 5.49; Fe, 20.29; mol. wt., 550. Found: C, 74.32; H, 5.62; Fe, 20.17; mol. wt., 520.

Trituration of this material with hot acetone and filtration yielded crystals, m.p. 270° dec., from petroleum ether (lit.[16] m.p. 276–278° for second diastereoisomer of VIII). The acetone-soluble fraction had, after evaporation, m.p. 218–220°; ultraviolet spectrum (in ethanol), λ_{max} 193 mμ (log ϵ 4.90), 207 (4.95), 255 (3.74). This gives a total yield of 575 mg. of the diastereoisomeric dimer, 1,2-diferrocenyl-1,2-diphenylethane.

(c) Elution with hexane–benzene (1:1) yielded a powdery yellow material (93 mg.), m.p. 92–97° (hexane–ethanol).

Anal. Found: C, 74.46; H, 5.50; Fe, 20.08; mol. wt., 588.

Thin layer chromatography of this compound shows a single spot with an R_f value lower than that of the diastereoisomeric dimer VIII. The infrared spectrum of this dimer is similar but not identical with the spectrum of either of the two diastereoisomers. The structure ascribed to this dimer is that which would be obtained *via* electrophilic attack of the carbonium ion II on the ferrocene nucleous of another molecule. The ultraviolet spectrum (in ethanol) showed λ_{max} 192 mμ (log ϵ 4.96), 206 (4.89), 262 (3.86), 336 (1.59), and 440 (1.08).

(d) Elution with benzene gave a material (100 mg.) which upon rechromatography and repeated crystallizations (hexane–ethanol) gave a pure material with softening at 104–108°.

Anal. Calcd. for $(C_{17}H_{15}Fe)_n$: C, 74.2; H, 5.49; Fe, 20.29. Found: C, 75.12; H, 5.39; Fe, 19.36.

The infrared spectrum was practically identical with that of the previous fraction c and this is probably a higher oligomer of c.

Further elution with methylene chloride–methanol (9:1) yielded a dark brown powder (142 mg.). The infrared spectrum of this material is also practically identical with that of the previous fractions c and d and the thin layer chromatogram shows it to be a mixture of several compounds, probably oligomers of (c).

Solvolysis of Ferrocenylphenylcarbinol (20-Hr. Reaction) Followed by Zinc Dust Reduction.—The solvolysis reaction of 800 mg. of ferrocenylphenyl carbinol was carried out as described in the general procedure except that the zinc dust was added 20 hr. after the start of solvolysis.

Work-up was as described in the general procedure. The residue (790 mg.) upon chromatography on neutral alumina (25 g.) gave the compounds a–g: (a) ferrocenylphenylmethane (18 mg.), (b) the diasteroisomeric dimer VIII (62 mg.), (c) the dimer c (65 mg.), (d) a mixture (100 mg.) of the compound found in (c) and (d) in the previous experiment, (e) a material (150 mg.) which appeared to contain a small amount of (d) in addition to a new compound (e). Crystallization (hexane–ethanol) gave a material with m.p. 120–128° (softening point). Thin layer chromatography showed this to contain in addition to (e) some material of fraction d.

Anal. Calcd. for $(C_{17}H_{15}Fe)_4$: C, 74.20; H, 5.49; Fe, 20.29; mol. wt., 1100. Found: C, 74.39; H, 5.63; Fe, 20.28; mol. wt., 1043.

The infrared spectrum was practically identical with that of the dimer of fraction c.

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[32] (a) All melting points were determined on a Kofler block-type instrument. (b) The n.m.r. spectra were measured on Varian Model HR 60 spectrometer, in deuteriochloroform as solvent and with tetramethylsilane as internal standard.

[33] Weliky and Gould[9] report a 26% yield. We have obtained yields higher than 85% (based on reacted ferrocene, with 85% conversion).

[34] S. V. Puntambeker and E. A. Zoellner "Organic Syntheses" Coll. Vol. I, H. Gilman and A. H. Blatt, Ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p. 524.

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

(f) A material (150 mg.) also was isolated which contained in addition to some of the compound of fraction e at least three more compounds. This mixture of oligomers was purified for analysis by dissolving in hexane and reprecipitating with ethanol to give a material with softening at 135–145°. The analysis still fit the general formula $(C_{17}H_{15}Fe)_n$ and the infrared spectrum was identical with that of compound e.

Anal. Found: C, 75.24; H, 5.43; Fe, 19.38; mol. wt., 1161.

(g) A dark brown material (225 mg.) was isolated which appeared to be the same mixture as the last fraction obtained on the chromatography of the 5-min. solvolysis reaction.

Products of Reductive Dimerization of Ferrocenylmethylcarbinol.—The solvolysis and reduction were carried out on 1 g. of ferrocenylmethylcarbinol as described in the general procedure for the 5-min. reaction. After work-up and chromatography the following products (a–c) were isolated.

(a) Ethylferrocene (40 mg., 4% yield) had b.p. 80° (0.2 mm.) (lit.[36] b.p. 74–76° at 0.2 mm).

Anal. Calcd. for $C_{12}H_{14}Fe$: C, 67.30; H, 6.59; mol. wt., 214. Found: C, 67.51; H, 6.72; mol. wt., 230.

(b) 1,2-Diferrocenyl-1,2-dimethylethane (2,3-diferrocenylbutane) (175 mg., 10% yield) had m.p. 100–103° (lit.[23] m.p. 144–146°).

Anal. Calcd. for $C_{24}H_{26}Fe_2$: C, 67.64; H, 6.15; Fe, 26.20; mol. wt., 426. Found: C, 67.49; H, 6.21; Fe, 26.15; mol. wt., 440.

(c) A mixture of oligomers (760 mg.) was shown by infrared spectra. This mixture was not characterized any further.

Products of Reductive Dimerization of Ferrocenyl-*t*-butylcarbinol.—The solvolysis and reduction were carried out on 80 mg. of ferrocenyl-*t*-butylcarbinol as described in the general procedure for the 5-min. reaction.

The crude product, after work-up, was in the form of yellowish crystals (67 mg.) and consisted of only one compound (as shown by t.l.c.). Chromatography on neutral alumina (2 g.) gave on elution with hexane (20 ml.) 54 mg. of crystalline material, m.p. 61–62°. Sublimation *in vacuo* (80° at 0.01 mm.) produced the analytical sample, m.p. 61–62°.

Anal. Calcd. for $C_{15}H_{20}Fe$: C, 70.31; H, 7.87; Fe, 21.80; mol. wt., 256. Found: C, 70.48; H, 8.07; Fe, 21.75; mol. wt., 250.

This compound was shown to be ferrocenyl-*t*-butylmethane (2,2-dimethyl-3-ferrocenylpropane) by an independent synthesis through the reduction of ferrocenyl-*t*-butylcarbinol with a mixture of $LiAlH_4$–$AlCl_3$ (1:1). The melting point, mixture melting point, and infrared spectra of the two compounds were identical.

Products of Reductive Dimerization of Ferrocenylanisylcarbinol.—The solvolysis and reduction were carried out on 910 mg. of ferrocenylanisyl carbinol as described in the general procedure for the 5-min. reaction. After work-up there were obtained 910 mg. of crude product which was chromatographed on neutral alumina (30 g.) to yield the compounds a–c.

(a) Ferrocenylanisylmethane (23 mg.) had m.p. 72–75° (from hexane).

Anal. Calcd. for $C_{18}H_{18}FeO$: C, 70.61; H, 5.92; Fe, 18.23; mol. wt., 306. Found: C, 70.79; H, 6.48; Fe, 18.07; mol. wt., 298.

(b) A crystalline material (570 mg., 67%) was isolated which showed two contiguous spots on t.l.c. On repeated chromatography only one of the two components (the less polar one) was obtained completely pure, while the second component was always contaminated with some of the first one. We consider these to be the diastereoisomers of the dimer, 1,2-diferrocenyl-1,2-dianisylethane. The pure component, recrystallized from hexane, had m.p. 190–192°.

Anal. Calcd. for $C_{36}H_{34}Fe_2O_2$: C, 70.85; H, 5.61; Fe, 18.30; mol. wt., 610. Found: C, 70.72; H, 5.87; Fe, 18.07; mol. wt., 589.

The mixture of the two components, recrystallized from hexane, had m.p. 162–164°.

Anal. Found: C, 70.68; H, 5.97; Fe, 18.08; mol. wt., 593.

(c) A reddish-orange oil (300 mg.) was isolated which consisted of a mixture of several compounds (as shown by t.l.c.) and was not characterized any further, it being assumed to consist of a mixture of nuclear-substituted oligomers.

Products of Reductive Dimerization of Ferrocenyltolylcarbinol.—The solvolysis and reduction were carried out on 550 mg. of ferrocenyltolylcarbinol as described in the general procedure for the 5-min. reaction. After work-up there were obtained 520 mg. of crude product which was chromatographed on basic alumina (20 g.) to produce (a) an orange oil (20 mg.) which on the basis of its infrared spectrum appears to be ferrocenyltolylmethane, and (b) a crystalline material (480 mg., 80%) which showed (t.l.c.) one major component and traces of a second, slightly more polar, compound. Crystallization from hexane gave a pure compound (single spot on t.l.c.) which had m.p. 210 dec. This is 1,2-diferrocenyl-1,2-ditolylethane.

Anal. Calcd. for $C_{36}H_{34}Fe_2$: C, 74.78; H, 5.92; Fe, 19.31; mol. wt., 578. Found: C, 74.76; H, 5.78; Fe, 19.25; mol. wt., 609.

Products of Reductive Dimerization of Diphenylcarbinol (Benzhydrol).—The solvolysis and reduction were carried out on 670 mg. of diphenylcarbinol as described in the general procedure for the 5-min. reaction. After work-up there were obtained 630 mg. of crude crystalline product whose infrared spectrum showed the presence of an acetate group and the absence of a hydroxyl group. This was crystallized from hexane to give 134 mg. of white crystals, m.p. 209–211° (lit.[37] m.p. 209–211° for 1,1,2,2-tetraphenylethane). The mother liquor from the filtration of the above crystallization was passed through an alumina (20 g.) column. (a) Elution with hexane–benzene (9:1) gave 214 mg. (35%) of material (single spot in t.l.c.), m.p. 26–27° (lit.[37] m.p. 26–27° for diphenylmethane). (b) Elution with hexane–benzene (9:1) gave 100 mg. of the dimer 1,1,2,2-tetraphenylethane, m.p. 209–211°. This gives a total of 234 mg. (32% yield) of the dimer. (c) Elution with methylene chloride–methanol (95:5) gave 90 mg. (12%) of the starting material, benzhydrol. This arose from the hydrolysis, during chromatography, of diphenylcarbinyl acetate, present in the crude reaction product.

When the above solvolysis was carried out with 600 mg. of benzhydrol and allowed to stand for 1 hr., before addition of zinc dust, and then work-up and chromatography as described above, the following results were obtained: (a) 195 mg. (32%) of diphenylmethane, (b) 268 mg. (44%) of 1,1,2,2-2-tetraphenylethane, and (c) 100 mg. (16%) of benzhydrol.

Isolation of Ferrocenylphenylmethylcarbonium Ion as the Fluoroborate and Mercuric Tribromide Salts. A.—To a solution of ferrocenylphenyl carbinol (205 mg.) in acetic anhydride (2 ml.) there was added 0.5 ml. of a solution of fluoroboric acid in acetic anhydride [prepared by dissolving 1.5 ml. of aqueous fluoroboric acid solution (42%) in 4 ml. of acetic anhydride]. After stirring for 5 min., dry ether (25 ml.) was added and the blue-black precipitate formed was filtered, washed with dry ether, and dried *in vacuo* at room temperature.

Anal. Calcd. for $C_{17}H_{15}BF_4Fe$: C, 56.40; H, 4.18; F, 20.96. Found: C, 56.31; H, 4.22; F, 20.77.

The infrared spectrum (KBr) shows the typical absorption of the BF_4 group between 1110–1030 cm.$^{-1}$.

B.—To a solution of ferrocenylphenylcarbinol (57 mg.) in glacial acetic (1 ml.) there was added 1 drop of hydrobromic acid–acetic acid solution (32%). After stirring for 2 min. there was added 2 ml. of a saturated solution of mercuric bromide in glacial acetic acid. A black viscous oil separated out immediately. After decantation of the liquid phase, the oil was triturated with dry ether whereupon it solidified. The dark powder (80 mg.) was collected through filtration, washed with dry ether, and dried *in vacuo* at room temperature. The infrared spectrum was very similar to that of the fluoborate salt except for the absence of the BF_4 band.

Preparation of Ferrocenylphenylcarbinyl Methyl Ether. A.—The mercuric tribromide salt[25] (80 mg.) obtained in the previous experiment, suspended in methanol (2 ml.), was stirred overnight. After filtration and washing the precipitate with methanol the methanolic filtrates were evaporated to dryness (water pump vacuum) to produce 45 mg. (70%) of orange-brown crystals, m.p. 100–102°. The infrared spectrum of this material was identical with that of ferrocenylphenylcarbinyl methyl ether prepared in the experiment described below.

B.—To a solution of ferrocenylphenylcarbinol (400 mg.) in glacial acetic acid (4 ml.) there were added 0.36 ml. of hydrobromic acid–acetic acid solution (32%). After stirring for 5 min. a large excess of sodium methoxide was added. Stirring was continued for 30 min. and then the reaction mixture was poured into water and extracted with five 30-ml. portions of diethyl ether.

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(36) F. S. Arimoto and A. C. Haven, Jr., *J. Am. Chem. Soc.*, **77**, 6296 (1955).

(37) "Handbook of Chemistry and Physics," 44th Ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1962.

After drying (magnesium sulfate) and evaporation of the solvent there were obtained 400 mg. of crystalline material which appeared to consist (t.l.c.) of one major component and traces of a second compound. The crude product was chromatographed on basic alumina (20 g.). Elution with hexane–benzene (9:1) gave 8 mg. of crystalline material, m.p. 230°, which on the basis of comparative thin layer chromatography appears to be the diastereoisomeric dimer VIII. Elution with hexane–benzene (4:1) gave 342 mg. (80%) of crystals, m.p. 112° (lit.[9] m.p. 111–112° for ferrocenylphenylcarbinyl methyl ether). Further elution with benzene (50 ml.) gave 42 mg. of crystalline material whose infrared spectrum showed it to be benzoylferrocene.

Electrochemical Reduction of 1-Methyl-3-carbamidopyridinium Chloride[1a]

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1-Methyl-3-carbamidopyridinium chloride exhibits one polarographic wave at pH values below 7 ($E_{1/2} = -1.08$ v. *vs.* s.c.e. independent of pH), while a second, pH-dependent wave appears in basic solution ($E_{1/2} = -1.68$ to -1.78 v. *vs.* s.c.e.). The limiting currents for both waves are diffusion controlled. Coulometry during macroelectrolysis with controlled cathode potential on the second wave gives a value of two electrons for the reduction process. The product is 1-methyl-3-carbamido-1,4-dihydropyridine, proved by comparing ultraviolet and infrared spectra with those of authentic material. Electrolysis at a potential on the first wave involves the uptake of one electron and leads to the formation of a dimeric product. Its ultraviolet spectrum and other evidence strongly suggest that dimerization is at the 6-position. The dimer does not function as an intermediate in the formation of the 1,4-dihydro compound but is further reducible to a product which is still dimeric.

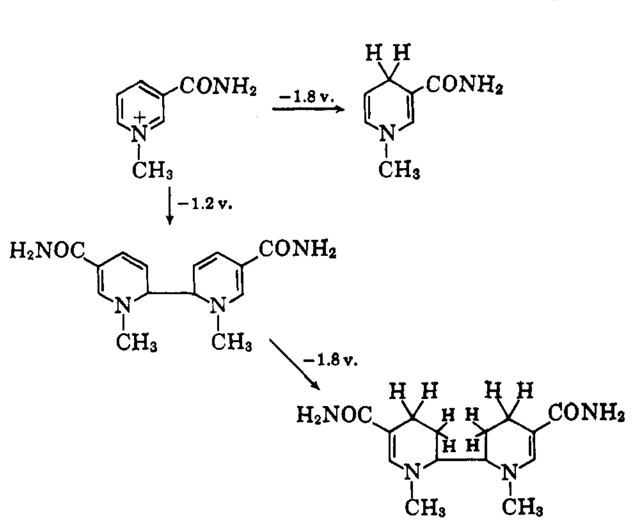
Several workers have attempted with varying success to prepare reduced nicotinamide adenine dinucleotide (NADH, DPNH) by electrolytic reduction of NAD at a cathode of controlled potential.[2–7] The reduction products varied in their coenzyme activity; the worst preparations were totally inactive,[3,4] while the best exhibited only 65–76% of the expected NADH activity.[7] Because electrode potentials may be precisely controlled and because no excess reducing agent is introduced, superior preparations were anticipated electrochemically; thus, even the best results were disappointing. It is apparent that a reduction product (or products) other than biologically active NADH may form in varying amount depending upon conditions, but neither its nature nor the manner of its formation has been elucidated. It is desirable to clarify the literature in this regard, if not indeed to circumvent the factors preventing exclusive reduction to NADH, by studying in detail the electrochemical behavior of NAD.

Although the remainder of the molecule is important to its biological activity, the reduction of NAD to NADH involves only the nicotinamide moiety. Thus it is reasonable to begin an electrochemical study of NAD by investigating the reduction of simple 1-alkylnicotinamides. The chemical reduction of NAD was elucidated in a similar fashion, beginning with Karrer's study of the dithionite reduction of the model compound 1-methyl-3-carbamidopyridinium chloride.[8]

Results

Polarography.—One reduction wave is exhibited by 1-Methyl-3-carbamidopyridinium chloride at *ca.* −1.1 v.[9] in the pH range of 4–7, while in more alkaline solutions a second wave at −1.7 to −1.8 v. is seen in addition to the first one. The two waves are of about equal height. The first is independent of pH, while the half-wave potential for the second is shifted about −27 mv. per pH unit, not far from the expected value (59/2) for a 2-electron process involving one H⁺. The heights of both waves vary directly with the square root of the mercury height, indicating that the limiting currents for both processes are diffusion controlled. Both reduction processes are irreversible under polarographic conditions. In strongly basic solution (*e.g.*, pH 13), the 1-methyl-3-carbamidopyridinium ion is quite rapidly altered, and the two waves give way to one wave at −1.5 v. as the solution stands. Catalytic hydrogen waves and adsorption waves, which frequently distort the polarograms of nitrogen heterocycles, are not encountered in the present case. The polarographic data are summarized in Table I.

Macroelectrolyses.—The electrochemical reduction processes of 1-methyl-3-carbamidopyridinium chloride are formulated as follows on the basis of large-scale



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[1] (a) Presented at the Southeastern Regional Meeting of the American Chemical Society, Charlotte, N. C., Nov. 1963. (b) Taken from a thesis presented by J. N. Burnett in partial fulfillment of the requirements for the M.S. degree, Emory University, 1963.

[2] B. Ke, *Biochim. Biophys. Acta*, **20**, 547 (1956).

[3] B. Ke, *J. Am. Chem. Soc.*, **78**, 3649 (1956).

[4] B. Ke, *Arch. Biochem. Biophys.*, **60**, 505 (1956).

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[6] T. Kono, *Bull. Agr. Chem. Soc. Japan*, **21**, 115 (1957).

[7] T. Kono and S. Nakamura, *ibid.*, **22**, 399 (1958).

[8] P. Karrer, G. Schwarzenbach, F. Benz, and U. Solmssen, *Helv. Chim. Acta*, **19**, 811 (1936).

[9] All potentials mentioned in this paper are referred to an aqueous saturated calomel electrode (s.c.e.).