

3060, 3020 cm^{-1} (cyclopropane, CH); nmr (CCl_4) δ 3.77 (d, $\text{H}_{2,3}$), 3.4 (m, 2 H), 1.8 (m, 2 H), 0.8 (m, 2 H), 0.35 (m, 1 H).

Anal. Calcd for $\text{C}_9\text{H}_{10}\text{O}$: C, 73.42; H, 10.27; O, 16.30. Found: C, 73.11; H, 10.18; O, 16.43.

Registry No.—1a, 27024-90-4; 1c, 17879-78-6; 1d, 17879-77-5; 1e, 17879-76-4; 1f, 17879-75-3; 1g, 17879-74-2; 1h, 27024-96-0; 1i, 18022-11-2; 2d, 27024-98-2; 2e, 27024-99-3; 2f, 27025-00-9; 2g, 27062-09-5; 2h, 27025-01-0; 3, 27025-02-1; 4, 27025-03-2; 6a, 27025-04-3; 6c, 27025-05-4; 6d, 27025-06-5; 6e, 27025-

07-6; 6f, 27025-08-7; 7a, 932-61-6; 7c, 27193-01-7; 7d, 27193-02-8; 8a, 931-28-2; 8c, 27025-11-2; 8d, 27025-12-3; 10, 286-10-2.

Acknowledgment.—The authors acknowledge some helpful nmr discussions with Dr. J. C. Deck, and partial financial support from the College of Arts and Sciences Research Committee, University of Louisville. The Varian A60-A nmr spectrometer was purchased with funds provided by the National Science Foundation.

2-Metalation of Dimethylaminoethylferrocene with Butyllithium and Condensations with Electrophilic Reagents. Synthesis of 2-Substituted Vinylferrocenes^{1a}

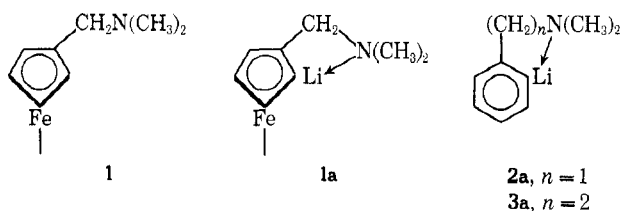
D. W. SLOCUM,*^{1b} C. A. JENNINGS,^{1c} T. R. ENGELMANN,^{1d} B. W. ROCKETT,^{1e} AND C. R. HAUSER^{1f}

Departments of Chemistry, Southern Illinois University, Carbondale, Illinois 62901, and Duke University, Durham, North Carolina 27706

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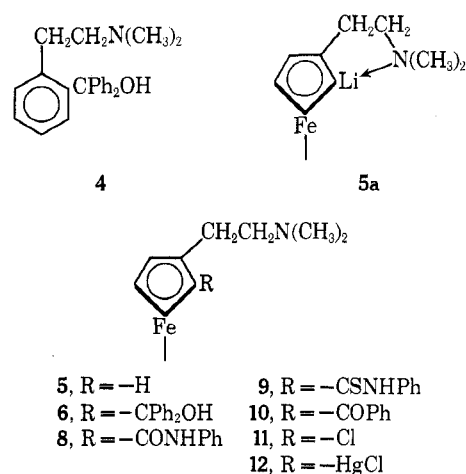
N,N-Dimethylaminoethylferrocene (DMAEF) was metalated in good yield with *n*-butyllithium in ether-hexane, and the intermediate 2-lithioamine was condensed with benzophenone, benzonitrile, phenyl isocyanate, phenyl isothiocyanate, hexachloroethane, and mercuric chloride to form the corresponding 2 derivatives. Methiodides of the above 2 derivatives were formed and converted to the corresponding 2-substituted vinylferrocene derivatives by treatment with potassium hydroxide. Metalation of DMAEF for extended time with excess *n*-butyllithium gave fair yields of the 2,1'-dilithioamine intermediate. That metalation occurred at the 2 position was established by converting the 2-benzoyldimethylaminomethylferrocene methiodide salt with $\text{KNH}_2\text{-NH}_3$ to give *via* a Stevens rearrangement the identical phenone derivative obtained from metalation of DMAEF. The successful 2-lithiation reported here for dimethylaminoethylferrocene is in direct contrast to the poor yield of lithiation found in the analogous benzene derivative, *N,N*-dimethyl- β -phenethylamine. The difference in behavior is attributed to the relative acidities of the 2 position and α protons in the respective systems.

Recently, we reported that metalation of dimethylaminomethylferrocene (DMAMF) (1) with *n*-BuLi apparently proceeded *via* the cyclic 2-lithiated species 1a.² The analogous 2 position lithiation of benzyldimethylamine (2) to give the lithio intermediate 2a had



been reported earlier.³ Hauser and other coworkers also published a study of the metalation of the homologous β -phenethyldimethylamine system but record only a tarry product from the reaction of β -phenethyldimethylamine (3) with *n*-BuLi followed by treatment with benzophenone.⁴ In contrast to this are two recent observations⁵ that metalation of β -phenethyldimethylamine (3) with *n*-BuLi apparently does proceed through

the six-membered cyclic lithioamine intermediate (3a) to give the anticipated carbinolamine 4 when treated with benzophenone, although the yield of such an intermediate must be very low. In a noteworthy extension of this method, the oxygen analog of amine 1, namely, ferrocenylmethyl methyl ether, has been found to undergo the 2-lithiation reaction.⁶



We would now like to report that metalation of dimethylaminoethylferrocene (DMAEF) (5) with *n*-BuLi for 2 hr gave an optimum yield of 68% of the 2-lithio intermediate 5a as demonstrated by its condensation with benzophenone to produce carbinolamine 6 (*cf.* Table I). Longer metalation periods brought considerable concentration of dilithio intermediate 5b. Struc-

(1) (a) Parts of this work were supported by the Office of Army Research (Durham) and by the Petroleum Research Fund; (b) Southern Illinois University, author to whom requests for reprints should be directed; (c) NSF Undergraduate Research participant; (d) NASA Fellow, Southern Illinois University, 1966-1969; (e) Wolverhampton College of Technology, Wolverhampton, England; (f) Duke University, deceased Jan 6, 1970.

(2) D. W. Slocum, B. W. Rockett, and C. R. Hauser, *J. Amer. Chem. Soc.*, **87**, 1241 (1965).

(3) (a) F. N. Jones, M. F. Zinn, and C. R. Hauser, *J. Org. Chem.*, **28**, 663 (1963); (b) F. N. Jones, R. L. Vaulx, and C. R. Hauser, *ibid.*, **28**, 3461 (1963).

(4) R. L. Vaulx, F. N. Jones, and C. R. Hauser, *ibid.*, **30**, 58 (1965).

(5) (a) N. S. Narasimhan and A. C. Ranade, *Tetrahedron Lett.*, 603 (1966); (b) D. W. Slocum, T. R. Engelmann, and C. A. Jennings, *Aust. J. Chem.*, **21**, 2319 (1968).

(6) D. W. Slocum and B. P. Koonsvitsky, *Chem. Commun.*, 846 (1969).

TABLE I

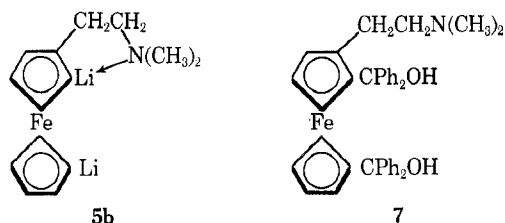
METALATION OF DIMETHYLAMINOETHYLFERROCENE (5) WITH *n*-BUTYLLITHIUM IN A MIXTURE OF HEXANE AND ETHER. CONDENSATION WITH BENZOPHENONE TO GIVE CARBINOLAMINE 6 AND DICARBINOLAMINE 7^a

Mol ratio, 5: <i>n</i> -BuLi	Lithiation period, hr	Yield, %	
		6	7
1:1.5	1	36 ^b	
1:1.5	2	68 ^b	4 ^b
1:1.5	10	32, ^b 36 ^c	16, ^b 18 ^c
1:1.5	14	36 ^d	21 ^c
1:1.5	20	13, ^b 16 ^c	28, ^b 36 ^c
1:3.0	20	45 ^b	28 ^b

^a Each condensation period 4 hr. ^b Purified by column chromatography. ^c Yield based on unrecovered starting material. ^d Recrystallized from 95% ethanol.

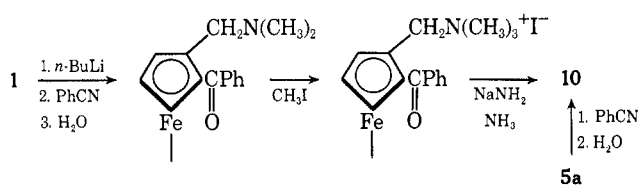
ture 6 for the benzophenone adduct was supported by elemental analysis and absorption spectra. In the infrared spectrum absorption bands were evident at 9.08 and 10.0 μ ; such bands are indicative of an unsubstituted cyclopentadienyl ring in a ferrocene (*cf.* Table II).⁷ An nmr spectrum of 6 in CDCl₃ exhibited a 5-proton singlet at τ 5.86 (unsubstituted cyclopentadienyl ring) and a 6-proton singlet at τ 8.02 [N(CH₃)₂]. Broad unresolved absorption from τ 7.4 to 8 integrated as 4.1 protons and was assigned to the -CH₂CH₂- portion of the molecule (*cf.* Table III).

Metalation with *n*-BuLi of DMAEF (5) over extended periods of time gave dilithiated species 5b; condensation with benzophenone led to dicarbinolamine 7 (Table I). That two benzophenone molecules had been substituted into dicarbinolamine 7 was supported by its elemental analysis. In addition, its infrared spectrum failed to show the characteristic absorptions of an unsubstituted cyclopentadienyl ring.⁷



Demonstration That the Site of Lithiation of DMAEF Is the 2 Position.—The 1,2 disposition of substituents in the DMAEF series was demonstrated by rearrangement of the methiodide of the 2-substituted phenone in the dimethylaminomethylferrocene (DMAMF) series² with NaNH₂-NH₃ (Stevens rearrangement) to give the identical phenone (10) as prepared in the DMAEF series. These paths are outlined in Scheme I. Inas-

SCHEME I



(7) M. Rosenblum, Ph.D. Thesis, Harvard University, 1953; M. Rosenblum, *Chem. Ind. (London)*, 953 (1958); P. L. Pauson, *Quart. Rev. (London)*, 391 (1955).

Compd	Calcd., %				Found, %				ANALYTICAL AND SPECTRAL DATA						
	C	H	N	Other	C	H	N	Other	Infrared absorptions, μ ^{a,b}		Chemical shifts ^c of pertinent nmr absorptions ^{d-f}				
									9-10- μ rule ^e	Substituent absorption	-N(CH ₃) ₂	Unsubstituted C ₅ H ₅	H _a ^g	H _b ^g	H _c ^g
6	73.79	6.65	3.19		73.73	6.70	3.09		9.08 (s)	10.00 (s)	8.02 (s)	5.86 (s)			
7	77.29	6.32	2.25		77.62	6.57	2.40		9.01 (m) ^h	9.95 (m) ^h	7.83 (s)	5.88 (s)			
8	67.03	6.43	7.45	14.85	66.85	6.51	7.34	14.26	9.02 (m)	9.96 (m)	7.92 (s)	5.82 (s)			
9	64.29	6.16	7.14	S, 8.17	64.55	6.01	7.30	S, 8.04	9.03 (m)	9.96 (m)	7.83 (s)	5.97 (s)			
10	69.82	6.42	3.88	15.46	69.82	6.68	3.69	15.25	9.02 (m)	9.96 (m)	7.79 (s)	5.89 (s)			
11	57.66	6.22	4.80	19.15	58.84 ⁱ	6.66	4.45	17.90	9.02 (m)	9.95 (m)	7.75 (s)	5.85 (s)			
12	34.16	3.68	2.85		34.42	3.51	2.89		9.03 (m)	9.94 (m)	7.92 (s)	5.82 (s)			
20	76.15	5.62	14.16		76.46	5.78	14.34		9.04 (m)	9.98 (s)	7.83 (s)	5.97 (s)			
21	68.90	5.17	4.23	16.86	68.54	5.26	4.36	16.46	9.04 (m)	10.01 (s)	7.79 (s)	5.89 (s)			
22	72.18	5.10	17.66	O, 5.06	72.15	5.50	17.46	O, 5.15	9.01 (m)	9.95 (m)	7.75 (s)	5.83 (s)			
23	58.47	4.50	22.65	Cl, 14.38	56.21 ⁱ	4.56	22.03	Cl, 13.66	9.03 (m)	9.97 (m)	7.75 (s)	5.85 (s)			
									9.04 (m)	9.98 (s)	7.79 (s)	5.89 (s)			
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									9.03 (m)	9.94 (m)	7.75 (s)	5.85 (s)			

TABLE III
 2-SUBSTITUTED METHIODIDES AND 2-SUBSTITUTED VINYL COMPOUNDS OF CONDENSATION PRODUCTS 6 AND 8-11

Methiodide ^a	Mp, °C ^{b,c}	Vinyl compd	Mp, °C ^c	Yield, %
15	239-246	Vinylcarbinol 20	163-164.5	96
16	220-225	Vinylcarboxamide 21	97.5-99.0 ^d	82
17	223-226	...	127.0-130.0 ^d	..
18	196-208.5	Vinylphenone 22	Oil	80
19		Vinylchloro compound 23	Oil	83

^a Methiodides were formed from parent amines in essentially quantitative yields. ^b Melts with decomposition. ^c All melting points are corrected. ^d These two samples gave superimposable infrared spectra. ^e Attempted elimination of the elements of trimethylammonium iodide from the methiodide 17 of the thiocarboxamide 9 apparently led to decomposition.

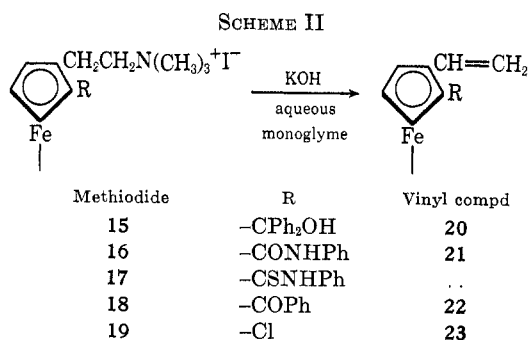
much as 2-lithiation has been unequivocally demonstrated in the DMAMF series,² the fact that a product from this series can be transformed into a product from the DMAEF series means that the *site of lithiation in DMAEF (5) must also be the 2 position.*

Attempts to cyclize carbinolamine 6 to the six-membered ring cyclic ether in a manner similar to that utilized in the DMAMF series² proved fruitless.

Condensations of Lithioamine 5a with Electrophilic Compounds.—In addition to benzophenone, 2-lithioamine 5a has been condensed with phenyl isocyanate, phenyl isothiocyanate, benzonitrile, and hexachloroethane⁸ to afford the carboxamide 8 (35%), thiocarboxamide 9 (33%), phenone 10 (62%), and chloro derivative 11 (30%), respectively. Infrared spectra of each of these compounds possessed adsorption at 9 and 10 μ in accord with their assigned structures (Table II).

Lithioamine 5a underwent a transmetalation reaction with mercuric chloride to produce the chloromercuri derivative 12 (12%). This compound is of interest because it contains both a σ - and a π -bonded metal atom. It also represents a potentially useful intermediate from which a number of other 1,2-disubstituted ferrocenes might be prepared.

Reaction of Methiodides of 2-Substituted DMAEF's with Base. Formation of 2-Substituted Vinylferrocenes.—The methiodides of each of the condensation products described in the preceding section were prepared using methyl iodide (Table III). Elimination of the elements of trimethylammonium iodide from the respective molecules was effected with an aqueous KOH-monoglyme system to afford the 2-substituted vinyl compound (Tables II and III). The reaction is illustrated for the conversion of the methiodide 18 of phenone 10 to the 2-substituted vinyl compound 22 (Scheme II).

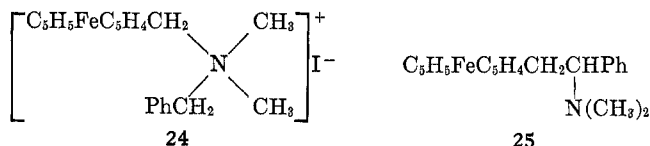


(8) R. L. Gay, T. F. Crimmins, and C. R. Hauser, *Chem. Ind. (London)*, 1635 (1966).

Discussion

It is of interest to compare the lithiation of dimethylaminoethylferrocene (5) with that of dimethylaminomethylferrocene (1). Whereas maximum lithiation of amine 1 took place within 1 hr,² that of amine 5 required at least 2 hr; both ferrocene derivatives were metalated much more rapidly than benzyldimethylamine (2) which requires 20-30 hr.³ That amine 1 is metalated faster than amine 5 is apparently a reflection of the well-known greater stability of the five-membered chelate ring in lithioamine 1a. Longer metalation periods for 5 appear to allow significant formation of dilithiated species such as 5b. Similar behavior was reported for lithiation of the dimethylaminomethyl compound 1,² but only to the extent of a very few per cent. Possibly, random lithiation competes much more efficiently in the case of 5.

Some suggestion is in order as to why the dimethylaminoethyl derivative of ferrocene can be significantly lithiated in the 2 position while that of benzene evidently cannot.^{4,5} An explanation of this difference may lie in the relative acidities of the ring protons and the methylene protons α to the ring in β -phenethyldimethylamine (3) and dimethylaminoethylferrocene (5). Lithiation of amine 3 apparently involves a competing E₂ reaction which results in the formation of styrene and thence polystyrene.^{4,5} No comparable material was found among the products from the lithiation of amine 5 followed by various condensations. It must be concluded that the methylene protons α to the benzene system are much more acidic than those α to the ferrocene system. Some support for this statement can be found in the observations of Ustynyuk and Perevalova.⁹ These authors have demonstrated that benzyl(ferrocenylmethyl)dimethylammonium chloride (24) rearranged exclusively to *N,N*-dimethyl- α -phenylferrocene ethylamine (25) under Stevens rearrangement condi-



tions; *i.e.*, ionization with strong base apparently took place at the benzyl methylene protons. Interestingly enough, the Stevens rearrangement of the methiodide of DMAMF which was used to prepare the DMAEF utilized in this study brings out the fact that a -CH₃ group must be ionized in preference to the methylene protons adjacent to the ring system. A recent study

(9) Yu. A. Ustynyuk and E. G. Perevalova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 62 (1964).

has shown that ferrocene acting as a substituent is electron donating.¹⁰ One other point might be made: the fact that ferrocene ring protons are more acidic than benzene ring protons should allow lithiation of the aromatic ring in the ferrocene system (5) to compete much more effectively with the elimination reaction. Thus relative acidity of the ring protons and relative nonacidity of the α protons in DMAEF seem to offer a fair explanation for the coordinate directed lithiation reaction being observed in this ferrocene system.

These results continue our studies of synthetic routes to produce 1,2-disubstituted ferrocenes. Not only can a variety of 1,2-disubstituted derivatives be prepared by this method, but it is also evident that 1,2,1'-trisubstituted ferrocenes can be prepared in fair yield when longer metalation periods are employed.

Curiously, attempts to effect addition reactions at the double bond of vinylcarbinol 20 were fruitless. Several such reactions for vinyl ferrocene itself have been recorded in the literature.¹¹ This may be a simple steric effect caused by the substituent in the 2 position of compound 20.

Experimental Section

Elemental analyses were performed by Alfred Bernhardt, Microanalytical Laboratories, Mülheim, West Germany, and by Galbraith Laboratories, Nashville, Tenn. Melting points were determined on a Hoover melting point apparatus and are corrected. Chromatograms were obtained using Fisher alumina. All infrared spectra were run on a Perkin-Elmer 137 sodium chloride spectrophotometer and are standardized against polystyrene unless otherwise indicated. All nmr spectra were run on a Varian A-56/60 spectrometer.

Metalated Dimethylaminoethylferrocene (5a) Solution.—In general, 10–20 mmol of amine 5a in ether was treated with 1.5 equiv (condition A) or 2.4 equiv (condition B) of *n*-butyllithium for 1.5–2 hr. The metalation reaction was carried out with stirring under argon at room temperature.

Carbinolamine 6 and Dicarbinolamine 7.—A solution of 7.2 g (40 mmol) of benzophenone in 20 ml of dry ether was slowly added to a solution of 20 mmol of lithioamine 5a metalated by condition A. Water (10 ml) was added and the solution stirred for 2 hr. The ether layer and ether extracts of the aqueous layer were combined and stripped. The resulting brown oil was chromatographed on alumina III. The fraction eluted with 50% petroleum ether–benzene contained 6.0 g of dark oil which crystallized on standing. Recrystallization from 95% ethanol gave 4.9 g (68%) of carbinolamine 6, orange crystals, mp 122–125°. Repeated recrystallization of 6 produced an analytical sample, mp 125–126°.

A fraction eluted with benzene(80%)–ether (20%) gave a small amount of crystals (4%) of dicarbinolamine 7, mp 156–160°. Recrystallization of 7 from ether–hexane produced an analytical sample, mp 163–166°. Higher yields of 7 were obtained using much longer lithiation periods (cf. Table I).

Carboxamide 8.—A solution of 4.3 ml (40 mmol) of phenyl isocyanate in 10 ml of dry ether was slowly added to a mixture of 10 mmol of lithioamine 5a metalated by condition B. The resulting suspension was hydrolyzed after 4 hr with 10 ml of water. The aqueous and ether phases were separated and the aqueous layer was extracted with benzene. The organic layers were combined and extracted with 1:10 H₃PO₄. These extracts were combined and made basic with solid Na₂CO₃. An oil separate which was extracted into benzene, stripped again to an oil, and chromatographed on alumina III. A dark orange oil representing a 33% yield of carboxamide 8 was eluted with benzene. This oil could not be induced to crystallize. Elemental analysis and spectral data supported assignment of its structure (cf. Table II).

Thiocarboxamide 9.—A solution of 4.3 ml (36 mmol) of phenyl

isocyanate in 10 ml of ether was added to a mixture of lithioamine 5a metalated under condition A. This product solution was hydrolyzed with water after stirring for 4 hr, the ether layer was separated, and the aqueous layer extracted with ether several times. The ether layer and ether extracts of the aqueous layer were combined, stripped, and chromatographed on alumina III. A red band which was eluted with petroleum ether (30%)–benzene(70%) solution was collected. Recrystallization from hexane–benzene gave a 33% yield of red crystals of thiocarboxamide 9, mp 147.5–149.5°. Elemental analysis and spectral data are recorded in Table II.

Phenone 10.—A solution of 4.12 g (40 mmol) of benzonitrile in 25 ml of dry ether was added to a mixture of 20 mmol of lithioamine 5a metalated by condition B. The resulting dark solution was stirred 12 hr and hydrolyzed with 10 ml of water. The ether layer and ether extracts of the aqueous layer were combined, stripped, and chromatographed on alumina III. A dark red oil was eluted with 20% ether–benzene. A yield of 62% of phenone 10 was obtained. This material seemed somewhat sensitive to light. Elemental analysis and various spectral data supported assignment of its structure (cf. Table II).

Chloroamine 11.—A solution of 4.8 g (20 mmol) of hexachloroethane in 50 ml of dry ether was added to a mixture of 10 mmol of lithioamine 5a metalated by condition A. After stirring for 16 hr, the mixture was hydrolyzed with water. The ether layer and ether extracts were combined, stripped, and chromatographed on alumina III. A yellow band was eluted with 50% petroleum ether–benzene and stripped to give 0.87 g (30%) of a dark red oil which was chloroamine 11, bp 135–145° (0.25 mm). Chloroamine 11 appeared to be contaminated with dimethylaminoethylferrocene. Elemental analysis of this compound were not totally acceptable (cf. Table II). Evidence for the presence of DMAEF in this product is presented in the experimental section on the vinyl derivatives.

Chloromercuriamine 12.—Solid mercuric chloride (27.2 g, 10 mmol) was added to 10 mmol of lithioamine 5a metalated under condition A. After stirring for 15 hr, 20 ml of water was added and the solution stirred for 2 hr. The ether layer and ether extracts were combined, dried over MgSO₄, and stripped. The crude product was taken up in petroleum ether and excess mercuric chloride filtered off. Chromatography on alumina yielded 5.8 g (12%) chloromercuriamine 12 upon elution with benzene. Recrystallization from hexane gave analytical material having mp 122.5–124.0°. Spectral and analytical data are recorded in Table II.

Formation of the Methiodide Salt of 2-(Dimethylaminomethyl)ferrocenylphenone.³ Treatment of Methiodide with KNH₂–NH₃ to Give Phenone 10.—2-(Dimethylaminomethyl)ferrocenylphenone was treated with methyl iodide (5 equiv) in ether with stirring for 4 hr to afford an orange precipitate of the methiodide salt. After washing several times with dry ether and drying in a vacuum desiccator orange crystals, mp 160–166° dec, were obtained in 94% yield.

The above methiodide (9.8 g, 20 mmol) was added to a solution obtained by adding 3.9 g of potassium metal (100 g-atoms) to 150 ml of liquid NH₃ and stirring with a trace of Fe(NO₃)₃ for 1 hr. After addition of the methiodide, the mixture was stirred for 6 hr (150 ml additional NH₃ added after 3 hr). Ether (350 ml) and 30 g of NH₄Cl were added and the mixture was stirred until all the NH₃ had evaporated. The ether layer and ether extracts of the aqueous layer were combined, dried over MgSO₄, stripped, and chromatographed on alumina III. A dark red oil was eluted with 20% ether–benzene in 20% yield. The spectral, physical, and chemical properties of the compound were identical with those of phenone 10 prepared *via* condensation of lithioamine 5a with benzonitrile.

Formation of Methiodide Salts of Amines 6 and 8–11.—The above 2-substituted amine derivatives were treated for 1 hr with a 5–10 *M* excess of methyl iodide in ether. The methiodide salts were recrystallized from ether–methanol (cf. Table III).

Treatment of Methiodides 15–19 with Base to Give Vinyl Derivatives 20–23.—The above methiodide salts were treated with excess 10–25% aqueous KOH–monoglyme (1:1 volume ratio) for 3 days at reflux temperature to give the crude vinyl materials. Each product was chromatographed on alumina III. The chlorovinyl product was analyzed in a benzene solution on a Varian Model 90-P gas chromatograph using a column of 3% silicon rubber SE-30 on Chromosorb P operating at 178° with a gas flow of 60 cc/min. Two peaks besides benzene appeared at 4.0 and 5.0 min with relative integration of 3–5% and 95–97%, respec-

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tively. The first peak was shown to be vinylferrocene by enrichment of the mixture with an authentic sample of vinylferrocene. Apparently this impurity resulted from contamination of chloroamine 11 with amine 5. The method of formation and the analytical data identify the main chromatographic component to be 2-chlorovinylferrocene. For melting point and analytical and spectral data, see Table II.

Registry No.—Butyllithium, 109-72-8; 1, 1271-86-9; 6, 12441-23-5; 7, 12441-25-7; 8, 12441-17-7; 9, 12441-18-8; 10, 12441-16-6; 11, 12441-13-3; 12, 12441-12-2; 15, 12441-24-6; 16, 12441-20-2; 17, 12441-21-3; 18, 12441-19-9; 20, 12441-22-4; 21, 12441-15-5; 22, 12441-14-4; 23, 12441-11-1.

The Reaction of Triisobutylaluminum with 1,5-Cyclooctadiene¹

E. MARCUS,*² D. L. MACPEEK, AND S. W. TINSLEY

Research and Development Department, Union Carbide Corporation,
Chemicals and Plastics, South Charleston, West Virginia 25303

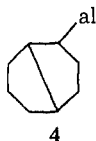
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Hydrolysis of the reaction product derived from triisobutylaluminum and 1,5-cyclooctadiene gave rise to *cis*- and *trans*-1-ethyl-2-methylcyclopentane as well as some cyclooctene, but no cyclooctane. Treatment of the reaction product with ethylene in the presence of nickel acetylacetonate afforded 1-methylene-2-vinylcyclopentane.

The unexpected results obtained from the investigation of the triisobutylaluminum-butadiene reaction³ prompted us to study reactions of other diolefins with triisobutylaluminum (TIBA). 1,5-Cyclooctadiene (1) looked like an especially interesting case, because its two double bonds would not necessarily be expected to behave as independent units in this type of reaction.

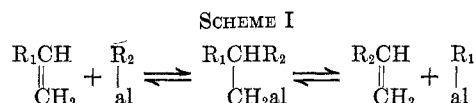
Isobutylene was not displaced efficiently until a reaction temperature of about 145° was reached. After hydrolysis of the reaction product, a saturated C₈H₁₆ hydrocarbon boiling at about 120–125° was obtained in 60% yield based on TIBA. Gas chromatography showed the presence of two peaks. The major component of this cut was proven to be *cis*-1-ethyl-2-methylcyclopentane (2) by comparison with a National Bureau of Standards sample. Although a similar reference sample of *trans*-1-ethyl-2-methylcyclopentane (3) is not available, there is little doubt that the other component is the *trans* isomer; besides, hydrogenation of 1-methylene-2-vinylcyclopentane gave the same two 1-ethyl-2-methylcyclopentanes, one of which was the *cis* isomer and the other one was identical with the *trans* isomer in question. Furthermore, the infrared spectrum of 3 was identical with the spectrum of *trans*-1-ethyl-2-methylcyclopentane published by Natalis.⁴ No cyclooctane was observed and only a small amount of cyclooctene was obtained.

Formation of the ethylmethylcyclopentanes was unexpected. The unusual step is the breakage of a carbon-carbon single bond at some stage. Initial formation of aluminobicyclo[3.3.0]octane (4) appeared at first sight a likely possibility (al = ¹/₃Al).

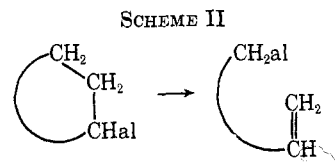


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The reversibility of the following reaction, where R₁ and R₂ are alkyl, has been proven (Scheme I).⁵ How-



ever, this type of reaction with an aluminocycloalkane has never been reported (Scheme II). Therefore, it



would have been interesting to subject bicyclo[3.3.0]oct-2-ene to the reaction with TIBA. Since this material was not available, the structurally related tricyclo[5.2.1.0^{2,6}]dec-3-ene was treated with TIBA at 150–190°. However, the desired ring opening did not occur; tricyclo[5.2.1.0^{2,6}]decane was the only product we could detect after hydrolysis of the reaction product. We also attempted unsuccessfully the conversion of cyclooctene with an excess of TIBA at 150–190° into 1,8-dialaminoctane; cyclooctane was the only product formed after hydrolysis. Hence, it is unlikely that aluminobicyclooctane (4) is involved in the formation of 2 and 3.

Although we do not have experimental support for a satisfactory explanation of the observed results, Scheme III may be looked upon as an alternative interesting speculation. The critical step in Scheme III involves, of course, the intermediacy of 3-alumino-1,7-octadiene. The pyrolysis of cyclooctene to 1,7-octadiene can be accomplished in high efficiencies at 500°. This reaction depends on the rupture of a carbon-hydrogen bond in the 5 position of cyclooctene.^{7,8} The con-

(1) A part of this work has been described by E. Marcus and D. L. MacPeek, U. S. Patent 3,388,180 (June 11, 1968).

(2) Author to whom correspondence should be directed.

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