ternary iminium system of **2** would afford the four-membered cyclic species **3**. Rearrangement of **3** by shift of two pairs of electrons would thus afford the observed benzenediazonium nitrate and benzaldehyde.

Experimental

A solution of 1.0 g. (0.0055 mole) of N-benzylideneaniline in 20 ml. of ether was added to a solution of about 1 ml. (at 20°, 1.5 g., 0.03 mole) of nitrogen tetroxide[9] in 20 ml. of ether cooled in an ice bath. After being stirred in the cold for 0.5 hr., the mixture was allowed to stand, without stirring, at room temperature overnight. The voluminous precipitate which had appeared by the next morning was collected by filtration and rinsed with fresh ether (Caution![10]). After air drying, the crude benzenediazonium nitrate[10] weighed 0.85 g. (90%) and dissolved completely in water. An analytical sample, prepared by dissolving a portion of the crude salt in cold methanol and reprecipitating it with ether, melted at about 100° when placed on a melting point block at about 90°, although occasionally detonation occurred before melting.[10] The salt could also be detonated by a gentle tap from a hammer.

Anal. Calcd. for $C_6H_5N_3O_3$: C, 43.12; H, 3.03; N, 25.15. Found: C, 43.37; H, 3.49; N, 24.87.

The major bands in the infrared spectrum (Nujol) were at 2273 (diazonium); 1563 and 1456 (phenyl C=C); 1408 (nitrate); 1316, 1302, 1068, 826 (nitrate); and 757 (phenyl CH) cm.$^{-1}$.

The ethereal filtrate remaining from collection of the insoluble diazonium salt was washed with two 25-ml. portions of water and with saturated sodium chloride, and then dried over sodium sulfate. Evaporation of the ether under slightly reduced pressure at room temperature gave an oil which was taken up in 5 ml. of ethanol. Addition of this solution to a solution of 1.2 g. of 2,4-dinitrophenylhydrazine, 6 ml. of concentrated sulfuric acid, and 9 ml. of water in 30 ml. of ethanol[11] gave the 2,4-dinitrophenylhydrazone of benzaldehyde which, after crystallization from ethanol–ethyl acetate, weighed 0.93 g. (59%) and melted at 243–244° (uncor.), lit.[11] m.p. 237°.

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[9] Commercial grade, obtained from the Matheson Co., Inc., East Rutherford, N. J.

[10] P. Griess, *J. Chem. Soc.*, **20**, 40 (1867), reported that benzenediazonium nitrate explodes violently when heated.

[11] R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 219.

Ferrocenes. VII. Ferrocenes from Monofunctional Cyclopentadienes

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One phase of an investigation toward the synthesis of difunctional ferrocenes as polymer intermediates and additives[1,2] involved the reaction of cyclopentadienylsodium with functionally substituted alkyl halides and conversion of the products to ferrocenes. Although reactions of alkali metal derivatives of cyclopentadiene with alkyl halides to form alkylcyclopentadienes have been known for some time,[3] investigation of the preparation of cyclopentadienes containing reactive functional groups by this method has been very limited. In particular, no information was available on the site of attack by cyclopentadienylsodium on alkyl halides with ester, nitrile, and acetal substituents.

Since completion of the present work, Kresze, *et al.*, described the reactions of this reagent with CH_3OCH_2Cl and CH_3OOCCH_2Cl to give the cyclopentadienyl derivatives in 62 and 30% yields, while $CH_3OCH_2CH_2I$ gave both mono- and bis(β-methoxyethyl)cyclopentadienes in a 1:2 to 1:3 ratio.[4] The recently reported reaction of cyclopentadienylsodium with epichlorohydrin involved attack of the epoxy group.[5] A functional group survived in the reaction of the *acyl* halide, methyl chloroformate, and both carbomethoxycyclopentadiene and bis(carbomethoxy)cyclopentadiene were obtained.[6]

In the present work, addition of methyl 3-bromopropionate to cyclopentadienylsodium at −70° afforded 51% β-carbomethoxyethylcyclopentadiene and 15% bis(β-carbomethoxyethyl)cyclopentadiene.[7] The bis compound undoubtedly arose *via* transmetalation of the mono compounds by cyclopentadienylsodium. Similarly, (cyanomethyl)cyclopentadiene was obtained from chloroacetonitrile in 43% yield; in this case no bis compound was isolated, and there was considerable distillation residue.

A mixture of chloroacetal and cyclopentadienylsodium in tetrahydrofuran refluxed for several hours furnished 29% β,β-diethoxyethylcyclopentadiene. Despite the lengthy heating period, the product had not dimerized but distilled at pot temperatures well below the usual depolymerization temperatures of cyclopentadienes.[8] It is interesting to note that reactions of phenyllithium and butyllithium in ether with chloroacetal failed to yield the desired acetals.[9]

$$C_5H_5Na \xrightarrow{RX} C_5H_5R$$

$$R = CH_2CH_2COOCH_3,\ CH_2CN,\ \text{and}\ CH_2CH(OCH_2CH_3)_2$$

Treatment of a mixture of cyclopentadienyllithium and cyclopentadiene in tetrahydrofuran with excess ethylene oxide and work-up 1 hr. after the exotherm began near 40° yielded 5% β-hydroxyethylcyclopentadiene and 13.5% bis(β-hydroxyethyl)cyclopentadiene. The reaction of cyclopentadienylsodium with ethylene oxide during 0.5-hr. reflux in ether was described by Boberg and Schultz, who obtained dimeric β-hydroxyethylcyclopentadiene in 12.5% yield.[10]

That the above-mentioned cyclopentadienyl compounds did indeed contain the cyclopentadiene ring was shown by ultraviolet and infrared spectra. All the

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[1] Paper VI: R. L. Schaaf and C. T. Lenk, *J. Org. Chem.*, **28**, 3238 (1963); Paper V: R. L. Schaaf and C. T. Lenk, *J. Chem. Eng. Data*, **9**, 103 (1964).

[2] This investigation was conducted under Air Force Contract AF 33(616)-7214, monitored by the AF Materials Laboratory, Research and Technology Division, U. S. Air Force.

[3] K. Alder and H. Holzrichter, *Ann.*, **524**, 145 (1936).

[4] G. Kresze, G. Schultz, and H. Walz, *ibid.*, **666**, 45 (1963).

[5] H. Schaltegger, *Helv. Chim. Acta*, **45**, 1368 (1962); K. F. Bangert and V. Boekelheide, *Tetrahedron Letters*, **17**, 1119 (1963).

[6] D. Peters, *J. Chem. Soc.*, 1757 (1959).

[7] Compounds containing a monosubstituted cyclopentadiene ring are referred to here without designation of the relative positions of substituents and double bonds in the ring. The position was not critical to the investigation, inasmuch as the final products were ferrocenes, in which the ring positions are equivalent.

[8] A complication encountered with most work on cyclopentadiene compounds is the tendency of cyclopentadienes to self-condense in Diels-Alder fashion to give dimers and higher polymers. Depolymerization to the monomers above 150° can sometimes be accomplished even with dicyclopentadienes containing functional groups; *cf.* D. Peters, *J. Chem. Soc.*, 1832 (1960).

[9] G. Jones and H. D. Law, *ibid.*, 3631 (1958).

[10] F. Boberg and G. R. Schultze, *Z. Naturforsch.*, **10b**, 721 (1955); *cf.* H. K. Wiese and C. A. Cohen, *Am. Chem. Soc. Div. Petrol. Chem. Symposia*, **35-S**, 27 (1955); *Chem. Abstr.*, **51**, 8664 (1957).

TABLE I

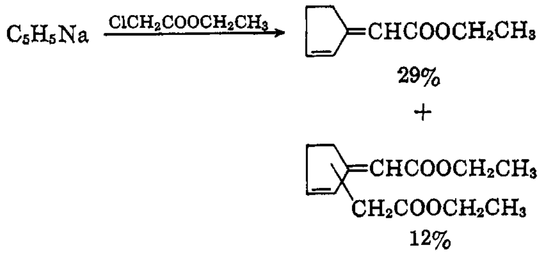
SUBSTITUTED CYCLOPENTADIENES, C_5H_5–R

No.	R	Formula	B.p., °C. (mm.)	λ_{max}, mμ (log ε)[a]	$n^{25}D$	Carbon, %		Hydrogen, %	
						Calcd.	Found	Calcd.	Found
1	$CH_2CH_2COOCH_3$	$C_9H_{12}O_2$	51–51.5 (0.7)	249 (3.43)	1.4719	71.02	71.19	7.95	7.90
2	$CH_2CH_2COOCH_3$[b]	$C_{13}H_{18}O_4$	112–122 (0.7)	246 (2.63)	1.4779	65.53	65.59	7.61	7.60
3	CH_2CN	C_7H_7N	32–34 (0.6)	244 (3.55)	1.4851	79.95	79.99	6.71 13.34[c]	6.78 13.50[c]
4	$CH_2CH(OCH_2CH_3)_2$	$C_{11}H_{18}O_2$	43 (0.3)	248 (3.59)	1.4542	72.49	72.23	9.95	9.84
5	CH_2CH_2OH	$C_7H_{10}O$	33–34 (0.3)	246 (3.10)	1.4917	76.32	76.46	9.15	9.24
6	CH_2CH_2OH[b]	$C_9H_{14}O_2$	118–150 (0.4)	252 (3.37)	. . .	70.10	69.69	9.15	8.94

[a] In cyclohexane for compounds 1, 2, and 4, and in ethanol for compounds 3, 5, and 6. [b] R in $C_5H_4R_2$, a disubstituted cyclopentadiene. [c] Nitrogen, %.

cyclopentadienes showed strong absorption in the ultraviolet at 244–252 mμ (Table I), as would be expected of "alkyl" cyclopentadienes (cyclopentadiene, λ_{max} 238 mμ; a 1-methyl group contributed 7 mμ[11]; 5,5-dimethylcyclopentadiene, λ_{max} 250 mμ[12]). In addition, all showed strong absorption in the infrared at 11–11.3 μ, a region known to be characteristic of a double bond in a cyclopentyl ring[13]; the absorption for bis(β-carbomethoxyethyl)cyclopentadiene was medium weak. Strong bands in this region readily differentiated the monomers from the dimers, which showed weak absorption at most, in the three cases examined, *viz.*, dicyclopentadiene, di(β-hydroxyethylcyclopentadiene), and di(cyanomethylcyclopentadiene).

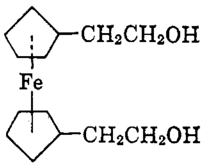
From a reaction of ethyl chloroacetate and cyclopentadienylsodium, the two products isolated showed maximum absorption in the ultraviolet at 268 mμ, well above the maxima of the cyclopentadienes but coincident with the region for dienes conjugated with an ester carbonyl group.[11] Evidently, double bond migration occurred to give 6-carbethoxy-3,4-dihydrofulvene (29%) and carbethoxymethyl-6-carbethoxy-3,4-dihydrofulvene (12%).

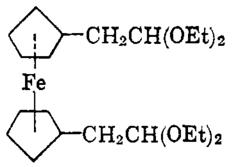


The preparation of difunctional ferrocenes *via* monofunctional cyclopentadienyl intermediates has been described in a number of publications. Thus, in particular instances sandwiching has been successful in the presence of the following groups: carbomethoxy,[14] acetyl,[14,15] diethylaminoalkyl,[16] phenylazo,[17] methyldiethoxysilyl,[18] piperidinodimethylsilyl,[18] hexamethyldisiloxanyl,[19] and the sodium salt of an alcohol.[20]

Treatment of β,β-diethoxyethylcyclopentadiene in tetrahydrofuran with isopropylmagnesium chloride at −10° followed 0.5 hr. later by ferrous chloride yielded (upon addition of water) up to 39% of 1,1′-bis(β,β-diethoxyethyl)ferrocene and 2% of an oil, $C_{33}H_{52}FeO_6$; 24–27% of the starting acetal was recovered. When isopropylmagnesium chloride and the acetal were in contact for 2 hr. instead of 0.5 hr. before addition of ferrous chloride, 61% of the starting acetal was recovered after hydrolysis 2 days later.

When β-hydroxyethylcyclopentadiene (1 equiv.) was treated with butyllithium (1.4 equiv.) followed by ferrous chloride, 19% 1,1′-bis(β-hydroxyethyl)ferrocene was isolated and 14% of the starting cyclopentadienyl compound was recovered. In addition, an oil, $C_{28}H_{38}FeO_4$, was obtained in 13% yield. The ultraviolet and visible spectra of this oil, which were very similar to those of the material $C_{33}H_{52}FeO_6$ mentioned above, showed maxima near 440 mμ (log ε 2.25), characteristic of ferrocenes, but both showed absorption in the 240–440-mμ region greater than that of ferrocene. Because of the high probability that these oils were a mixture of a number of position isomers, they were not investigated further.[21]





In a total of four experiments, attempts to convert compounds 1, 3, and 6, Table I, to ferrocenes were unsuccessful. For example, treatment of (cyanomethyl)cyclopentadiene in tetrahydrofuran with methyllithium in ether at −70° caused gas evolution, which would indicate formation of the desired lithium derivative, but stirring the mixture with ferrous chloride at −20° for 8 hr. and subsequent hydrolysis gave no ferrocenes.

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[11] D. Peters, *J. Chem. Soc.*, 1761 (1959).

[12] R. S. Rouse and W. E. Tyler, III, *J. Org. Chem.*, **26**, 3535 (1961).

[13] J. Thiec and J. Wiemann, *Bull. soc. chim. France*, 207 (1958).

[14] J. M. Osgerby and P. L. Pauson, *J. Chem. Soc.*, 4604 (1961).

[15] M. A. Lynch, Jr., and T. C. Brantley, British Patent 785,760 (Nov. 6, 1957).

[16] G. R. Knox, J. D. Munro, P. L. Pauson, G. H. Smith, and W. E. Watts, *J. Chem. Soc.*, 4619 (1961).

[17] G. R. Knox and P. L. Pauson, *ibid.*, 4615 (1961).

[18] R. L. Schaaf, P. T. Kan, and C. T. Lenk, *J. Org. Chem.*, **26**, 1790 (1961).

[19] R. L. Schaaf, P. T. Kan, C. T. Lenk, and E. P. Deck, *ibid.*, **25**, 1986 (1960).

[20] R. E. Benson and R. V. Lindsey, Jr., *J. Am. Chem. Soc.*, **79**, 5471 (1957).

[21] That the compounds are not mixtures of ferrocenes and iron-free compounds is suggested by their compositions. Thus, $C_{33}H_{52}FeO_6$ = $3(C_5H_5CH_2CH(OCH_2CH_3)_2) + Fe - 2H$, and $C_{28}H_{38}FeO_4 = 4(C_5H_5CH_2CH_2OH) + Fe - 2H$. Another oil that contained three units of precursor per iron atom less two hydrogen atoms was obtained in a related reaction but not described because the structure of the precursor was not sufficiently established. All three oils were sharp chromatography fractions.

Experimental[22]

β-Carbomethoxyethylcyclopentadiene and Bis(β-carbomethoxyethyl)cyclopentadiene.—Under a nitrogen stream, 11.5 g. (0.5 g.-atom) of sodium was added to 500 ml. of tetrahydrofuran[23], followed by 50 ml. of cyclopentadiene. After the mixture was stirred for 45 min. at room temperature and refluxed for 2 hr. without nitrogen flow, an additional 6 ml. of cyclopentadiene was added through the condenser and the mixture was refluxed until the sodium was gone (30 min.). The colorless solution of cyclopentadienylsodium[24] was cooled in a −70° bath under a nitrogen stream, and 83.5 g. (0.5 mole) of methyl 3-bromopropionate was added in one portion; the temperature rose to about 25°. After the mixture was stirred for 10 min. without the bath, 150 ml. of petroleum ether (30–60°) was added, the mixture was poured into water, and the aqueous layer was extracted with ether. The organic layers were combined, dried with magnesium sulfate, and solvent was removed *in vacuo* at or below room temperature. Distillation of the residue under nitrogen through a short Vigreux column gave 34.1 g. (45%) of β-carbomethoxyethylcyclopentadiene, b.p. 46–48° (0.2 mm.), 15.7 g. of material, b.p. 104–110° (0.3 mm.), and left essentially no residue. Redistillation of the first fraction furnished compound 1, Table I. Redistillation of the second fraction gave 4.2 g. (6%) of additional β-carbomethoxyethylcyclopentadiene, b.p. 51–58° (0.7 mm.), and 8.91 g. (15% based on the halide) of bis(β-carbomethoxyethyl)cyclopentadiene (compound 2, Table I).

(Cyanomethyl)cyclopentadiene.—In the manner of the preceding experiment, 37.8 g. (0.5 mole) of chloroacetonitrile was added to cyclopentadienylsodium in tetrahydrofuran at −50°, the mixture was maintained at 5–12° for 10 min., after an exotherm near −20°, and 50 ml. of petroleum ether was added. The mixture was then worked up as above, the organic material was distilled,[25] and the distillate was collected in a receiver in a −70° bath to give 21.2 g. (40%) of (cyanomethyl)cyclopentadiene, b.p. mainly 35–38° (0.8 mm.; later fractions as low as 28°). The residue (16 g.) was a soluble tar. Material trapped at −70° beyond the receiver was redistilled to give an additional 1.4 g. (3%) of the nitrile, b.p. 33° (0.6 mm.). Combination and redistillation gave compound 3, Table I.

In an initial run, in which distillation was too rapid for complete depolymerization, a sharp fraction, b.p. 142° (0.13 mm.), was obtained and assumed to be dimerized (cyanomethyl)cyclopentadiene. Infrared bands at 11 to 11.3 μ were medium-weak.

β,β-Diethoxyethylcyclopentadiene.—A mixture of 1.97 moles each of chloroacetal and cyclopentadienylsodium in tetrahydrofuran refluxed for 15 hr. furnished 105 g. (29%) of β,β-diethoxyethylcyclopentadiene (compound 4, Table I) after two distillations. In addition, 168 g. of other substituted cyclopentadienes were obtained, b.p. 80–143° (0.13–0.3 mm.), λ_{max} 246–248 mμ (log ε 3.3–3.6), two fractions.

β-Hydroxyethylcyclopentadiene and Bis(β-hydroxyethyl)cyclopentadiene.—To 132 g. (2 moles) of cyclopentadiene in 1000 ml. of dry tetrahydrofuran in an ice bath was added 840 ml. (1.35 moles) of 15% butyllithium in hexane below 15° under nitrogen, and the mixture was stirred for 1 hr. Ethylene oxide (150 ml., 3 moles) was added in one portion under a −70° condenser and the ice bath was replaced by a hot water bath until the temperature reached 30°. The temperature continued to rise, and near 40° it rose rapidly. Quick application of an ice bath lowered the temperature from 50 to about 40°; the mixture became lumpy. After an additional hour at 36–43° without external heating, the mixture was treated with 1 l. of water under nitrogen, the aqueous phase was extracted with ether, and the combined organic layers were dried and evaporated *in vacuo* to low volume. Distillation gave a 13.3-g. fraction, b.p. 25–44° (0.3–0.6 mm.), which upon redistillation furnished β-hydroxyethylcyclopentadiene (compound 5, Table I). Continuation of the first distillation yielded bis(β-hydroxyethyl)cyclopentadiene (compound 6, Table I).

In a second run, 2 moles of butyllithium was employed, with all other quantities unchanged, but the amount of β-hydroxyethylcyclopentadiene isolated was negligible.

6-Carbethoxy-3,4-dihydrofulvene and Carbethoxymethyl-6-carbethoxy-3,4-dihydrofulvene.—Ethyl chloroacetate was substituted for methyl 3-bromopropionate in the above procedure for β-carbomethoxyethylcyclopentadiene and the reaction mixture was stirred overnight at room temperature; an exotherm occurred near −10°. After two distillations, 21.2 g. (28%) of 6-carbethoxy-3,4-dihydrofulvene was obtained, b.p. 45–47° (0.3–0.4 mm.), n^{25}_{D} 1.5049, λ_{max} 268 mμ (log ε 4.22, ethanol). Absorption in the infrared at 5.85 μ (medium) suggested that the product was contaminated with a singly conjugated ester. The infrared spectrum also showed strong bands at 5.95, 6.24, 8.36, and 8.93 μ.

Anal. Calcd. for $C_9H_{12}O_2$: C, 71.02; H, 7.95. Found: C, 70.94; H, 7.85.

Redistillation of a fraction, b.p. 85–180° (1.3 mm.), furnished 0.5 g. (0.7%) of additional diene, b.p. 40–45° (0.3 mm.), and 7.2 g. (12%) of liquid, b.p. 118–121° (0.2 mm.), n^{25}_{D} 1.4944, λ_{max} 268 mμ (log ε 4.17, ethanol). The infrared spectrum showed strong bands at 5.83, 5.94, 6.23, and 7.8–8.9 μ, and a medium weak band at 11.2 μ. The spectral data and analyses indicated that the liquid was carbethoxymethyl-6-carbethoxy-3,4-dihydrofulvene.

Anal. Calcd. for $C_{13}H_{18}O_4$: C, 65.53; H, 7.61. Found: C, 65.70; H, 7.63.

1,1′-Bis(β,β-diethoxyethyl)ferrocene and $C_{33}H_{52}FeO_6$. Run 1.—Isopropylmagnesium chloride solution was prepared by dropwise addition of 3.2 ml. of isopropylmagnesium chloride to 0.91 g. (0.0374 g.-atom) of magnesium in 9 ml. of dry ether, after the reaction had been initiated by a drop of ethyl bromide and 1.0 ml. of isopropyl chloride. The solution was added in 5 min. to 6.16 g. (0.0338 mole) of β,β-diethoxyethylcyclopentadiene in 40 ml. of dry tetrahydrofuran at −10° under nitrogen, the mixture was stirred for 25 min. at −10°, and 2.14 g. (0.0169 mole) of ferrous chloride was added in one portion. The cooling bath was removed but applied again after about 10 min. to prevent loss by frothing. After the mixture was stirred overnight without the bath, it was added to water along with 50 ml. of petroleum ether. The aqueous layer was extracted with chloroform, filtered, and the combined organic layers were dried. Removal of solvent and rapid distillation of the residue gave 1.50 g. (24%) of recovered acetal, b.p. 32–37° (0.12 mm.), and 2.75 g. (39%) of 1,1′-bis(β,β-diethoxyethyl)ferrocene, b.p. 156–162° (0.12–0.2 mm.), n^{25}_{D} 1.5096.

Anal. Calcd. for $C_{22}H_{34}FeO_4$: C, 63.16; H, 8.19; Fe, 13.35. Found: C, 63.36; H, 8.35; Fe, 13.43.

Run 2.—The procedure used in run 1 was repeated except that the mixture, after addition of isopropylmagnesium chloride, was stirred for 2 hr. at −10 to −20° instead of 25 min. After ferrous chloride was added, the mixture was stirred for 2 days. Distillation gave 3.73 g. (61%) of starting acetal (infrared comparison), b.p. 39–42° (0.3 mm.).

Run 3.—The procedure of run 1 was employed with 0.5 mole of acetal and 0.555 g.-atom of magnesium. Distillation of an aliquot gave 25% starting acetal, b.p. 28–34° (0.14 mm.). Slow continued distillation resulted in decomposition, and no ferrocenes were isolated. A second aliquot was chromatographed on Florisil in petroleum ether by elution with petroleum ether, benzene, and 2:1 benzene–ether. Material eluted with the last eluent was kept in a bath at 85° (0.5 mm.) to remove starting material; the infrared spectrum of the residue was the same as that of the desired ferrocene (14% yield). A third aliquot was filtered through a column of Florisil in chloroform and eluted with chloroform and with ether. Material eluted with chloroform was distilled to give 24% starting acetal and 13% 1,1′-bis(β,β-diethoxyethyl)ferrocene, b.p. 152° (0.45 mm.) to 172° (1.0 mm.) Material eluted with ether was removed as a small sharp band, elemental analyses on which agreed fairly well for a compound containing three units of starting acetal (less two hydrogen atoms) per iron atom (2% yield).

Anal. Calcd. for $C_{33}H_{52}FeO_6$: C, 65.99; H, 8.73; Fe, 9.30. Found: C, 65.29; H, 8.77; Fe, 9.02.

1,1′-Bis(β-hydroxyethyl)ferrocene and $C_{28}H_{38}FeO_4$.—A solution of 9.75 g. (0.0885 mole) of β-hydroxyethylcyclopentadiene in 75 ml. of dry tetrahydrofuran under nitrogen in an ice bath was treated with 77 ml. (0.124 mole) of 15% butyllithium in hexane during a 30-min. period. After 1.5 hr., 5.60 g. (0.0443 mole) of

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[22] All distillations of cyclopentadienyl or ferrocenyl compounds were conducted under nitrogen, and cyclopentadienyl compounds were stored below 0°. Melting points and boiling points are uncorrected. Analyses were performed by Galbraith Laboratories, Inc., Knoxville 21, Tenn. Ultraviolet and visible spectra were determined on a Perkin-Elmer spectracord Model 4000 and a Beckman Model DU quartz spectrophotometer. Infrared spectra were obtained with a Baird infrared recording spectrophotometer.

[23] Freshly distilled into the reaction flask from lithium aluminum hydride under nitrogen.

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

[25] The distillation was in part a slow depolymerization with the pot temperature finally at 210°.

ferrous chloride was added to the slightly opaque solution and the mixture was stirred overnight without the bath. It was then added to a solution of 10 ml. of concentrated hydrochloric acid in 100 ml. of water, the aqueous layer and oil were extracted with chloroform, and the combined organic layers were dried and taken to dryness. The residue was distilled to remove unreacted β-hydroxyethylcyclopentadiene [1.35 g. (14%), b.p. 25–30° (0.2 mm.)], the distillation residue (6.52 g.) was dissolved in chloroform, and one-fourth of the solution was chromatographed on Florisil in benzene. Elution with benzene and benzene–ether was unfruitful, but subsequent elution with ether slowly removed 0.89 g. of colored material, which after two crystallizations from ether gave 0.59 g. (19%) of 1,1'-bis(β-hydroxyethyl)ferrocene, m.p. 43–45°.

Anal. Calcd. for $C_{14}H_{18}FeO_2$: C, 61.34; H, 6.62; Fe, 20.37. Found: C, 61.31; H, 6.76; Fe, 20.52.

Subsequent elution with acetone removed 0.45 g. of liquid, which was extracted with dry ether, the extract was taken to dryness, and the residue was extracted with 20 ml. of dry ether. Removal of solvent from the extract left 0.35 g. (13%) of amber oil, elemental analyses on which agreed fairly well for a compound containing four units of starting material (less two hydrogen atoms) per iron atom.

Anal. Calcd. for $C_{28}H_{38}FeO_4$: C, 68.01; H, 7.75; Fe, 11.30. Found: C, 67.48; H, 7.78; Fe, 10.83, 11.15.

Acknowledgment.—We wish to thank Mr. Richard Thivierge for technical assistance and Mr. Arthur Raymond for the ultraviolet spectra.

Pyrolytic Conversion of 7,7-Dichloronorcarane to Cycloheptatriene

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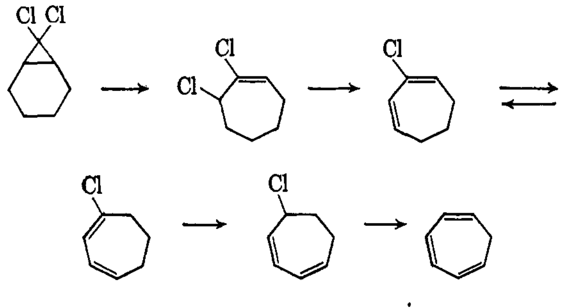
1,3,5-Cycloheptatriene is a versatile chemical intermediate used as a starting material for preparation of tropolone,[1] tropone,[2] and tropylium[3] salts. A convenient synthesis of high purity cycloheptatriene would facilitate work on these aromatic ring systems and on seven-membered ring compounds generally. Recent methods of synthesis of cycloheptatriene have involved reaction of diazomethane with benzene,[4] pyrolysis of 7,7-dichloronorcarane,[5] and pyrolysis of bicycloheptadiene.[6] The latter procedure is presently the most useful for large-scale preparations but gives a product contaminated with 7% toluene which is difficult to remove. Furthermore, the maximum yield is 45%.

The synthesis reported here is a modification of the 7,7-dichloronorcarane pyrolysis procedure of Winberg. Winberg passed 7,7-dichloronorcarane through a pyrolysis tube packed with short lengths of glass tubing heated at 490–520°. He obtained a 57% yield of hydrocarbon consisting of 35% cycloheptatriene and 65% toluene. The over-all cycloheptatriene yield was 14%. The origin of the toluene formed under Winberg's conditions was not established. It might have been a coproduct formed at the same time as the cycloheptatriene or it might have resulted from isomerization of cycloheptatriene.

The conditions chosen for our study of the pyrolysis of 7,7-dichloronorcarane were 444° over lump calcium oxide. These conditions were chosen to minimize any thermal or hydrogen chloride catalyzed isomerization of cycloheptatriene to toluene. Aerosol formation was a problem and some product was lost by entrainment during condensation of the pyrolysate. Examination of the crude condensate by gas–liquid chromatography showed a single hydrocarbon peak, a peak for unreacted dichloronorcarane, and twin peaks at an intermediate retention time. Separation of cycloheptriene by distillation gave 63% of a product having no toluene bands in its infrared spectrum. No toluene was detectable on gas–liquid chromatography. The procedure used would have detected 2% toluene. The distillation fraction corresponding to the twin peaks at intermediate retention time appeared from its infrared spectrum to be a mixture of chlorocycloheptadienes. This identification is consistent with the observed boiling point.

The mechanism by which cycloheptatriene is formed from 7,7-dichloronorcarane was not studied. The presence of two chlorocycloheptadienes in the crude product would be consistent with chlorocycloheptadienes serving as intermediates. The work of Kloosterziel[7] makes reasonable the occurrence of 1,5-hydrogen shifts in 1- and 2-chlorocycloheptadiene-1,3. This would permit isomerization of chlorine from a stable vinylic position to an allylic position where it could be readily eliminated as hydrogen chloride. The reaction sequence



is consistent with the known facts.

The effect of calcium oxide on the pyrolysis of bicycloheptadiene was studied qualitatively to see if the toluene content of the pyrolysate was reduced. No change in toluene content was detected. Since pyrolysis of 7,7-dichloronorcarane under identical conditions yielded toluene-free cycloheptatriene, the toluene in bicycloheptadiene pyrolysate must arise independently of cycloheptatriene. Klump and Chesick came to this same conclusion from comparing the pyrolysis rate of bicycloheptadiene with the rate of thermal rearrangement of cycloheptatriene to toluene.[8]

Experimental

Cycloheptatriene.—The apparatus consisted of a dropping funnel and a nitrogen inlet atop a Pyrex tube (30 × 2.8 cm.) charged with 140 g. of lump calcium oxide. The receiver train was an ice-cooled 50-ml. filter flask followed by a Dry Ice cooled U-tube. The calcium oxide was heated to 444° by a tube furnace. Then 50 g. (0.30 mole) of 7,7-dichloronorcarane was added from the dropping funnel during 1.5 hr., while maintaining a nitrogen

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