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Fig. 1. Absorption spectra in the ultraviolet of ferrocene (A), ethylferrocene (), isopropylferrocene (), and tert-butylferrocene (). Solvent—isoctane; $C_{\text{mol}} = 1 \cdot 10^{-n}$; $d = 0.5$ cm

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Abstract

Full Text

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HOMOLOGS OF FERROCENE WITH A TERTIARY ALKYL RADICAL

The alkylation of ferrocene by the Friedel–Crafts reaction, carried out by us for the first time ^{1,2}, made it possible to obtain a series of monoalkyl homologs of ferrocene from C_1 to C_5 , as well as dialkylferrocenes and several polyalkylated homologs. Measurement of the IR spectra established ^{2,4} that the dialkylferrocenes thus obtained contain both alkyl substituents in one cyclopentadiene ring.

In the present work it proved possible to use, as the alkylating agent, in addition to alkyl halides, also isobutylene, and to obtain, depending on the selected conditions, up to 50% mono-tert-butylferrocene with an overall yield of alkylation products of 30% (see Table 2). tert-Butylferrocene, di-tert-butylferrocene, and di-tert-amylferrocene, like all the alkylation products previously obtained by us, contain one free cyclopentadiene ring and have characteristic frequencies in the region of 1003 and 1107 cm^{-1} . Comparison of the found values of the molecular refraction shows that in the homologous series of alkylferrocenes the usual additivity of molecular refraction is observed (see Table 1); this agrees with the almost complete identity of the absorption curves in the ultraviolet region of ferrocene itself and its homologs* (see Fig. 1).

Fig. 1. Absorption spectra in the ultraviolet of ferrocene (A), ethylferrocene (), isopropylferrocene (), and tert-butylferrocene (). Solvent—isoctane; $C_{\text{mol}} = 1 \cdot 10^{-n}$; $d = 0.5$ cm.

* Measurement of the UV spectra was carried out by I. Ya. Kakurova in the laboratory of Corresponding Member of the Academy of Sciences of the USSR I. V. Obreimov, to whom the authors express their deep gratitude.

The difference between the molecular refraction found and the sum of the atomic

refractions of C and H in the ferrocene homologs we investigated ranges from 13.58 to 13.89 and averages 13.74. It includes the atomic refraction of iron and the structural increment of ferrocene (π -bonds, etc.) and may conventionally be called the ferrocene increment. This value gives for ferrocene a calculated molecular refraction of 48.91, not 46.8 (as given in the work of Richmond and Frizerey⁽³⁾, with reference to a private communication from Woodward). It is as yet impossible to say to what extent this value will remain constant in other ferrocene derivatives.

Table 1

	n_D^{20}	d_4^{20}	M	MR_{found}	Sum* of atomic refrac- tions of C and H	Ferrocene in- cre- ment, includ- ing the atomic refrac- tion of iron	Homologous differ- ence "CH ₂ " , found	Homologous differ- ence "CH ₂ " , calc.
$\text{C}_2\text{H}_5\text{C}_{10}\text{H}_9\text{Fe}$ (²)	1,5897	1,2628	214,08	58,06	44,316	13,74	—	—
$(\text{C}_2\text{H}_5)_2\text{C}_8\text{H}_8\text{FeI}$, 2002 (²)	1,5822	1,2002	242,13	67,35	54,652	13,70	4,64	4,618
$(\text{C}_2\text{H}_5)_2\text{C}_8\text{H}_8\text{FeII}$, 2041 (²)	1,5851	1,2041	242,13	67,39	53,652	13,74	4,66	4,618
<i>i</i> - $\text{C}_3\text{H}_7\text{C}_{10}\text{H}_9\text{Fe}$	1,5897	1,2230	228,11	62,92	49,034	13,89	4,86	4,618
<i>t</i> - $\text{C}_3\text{H}_7\text{C}_{10}\text{H}_9\text{Fe}$	1,5790	1,2013	242,13	67,54	53,652	13,89	4,62	4,618
<i>t</i> - $\text{C}_4\text{H}_9\text{C}_{10}\text{H}_9\text{Fe}$	1,5760	1,1798	256,16	71,85	58,270	13,58	4,31	4,618
$\text{C}_5\text{H}_{11}\text{C}_{10}\text{H}_9\text{Fe}$ Average						13,74	4,62	

* Atomic refractions are taken according to Eisenlohr.

Experimental Part

tert-Butylferrocenes from ferrocene and tert-butyl chloride. To a solution of 40 g of ferrocene in 300 ml of absolute petroleum ether, 7.5 g of tert-butyl chloride was added over the course of an hour as a solution of tert-butyl chloride in 20 ml of absolute petroleum ether. After heating for 5 h at 50°, the reaction mixture was decomposed in the usual manner⁽¹⁾. Ferrocene was recovered, 17 g (m.p. 172–173°); 14.8 g of liquid reaction products was obtained.

tert-Butylferrocene was obtained, 5.3 g, $n_D^{20} = 1,5790$; $d_4^{20} = 1,2013$, b.p. 103–105°/4 mm. $MR_{\text{found}} = 67,54$.

Found, %: C 69,54; 69,46; H 7,42; 7,50; Fe 22,90; 22,98
 $C_{14}H_{18}Fe$. Calculated, %: C 69,51; H 7,40; Fe 23,09

Di-tert-butylferrocene was also obtained, 6.8 g, $n_D^{20} = 1,5581$, $d_4^{20} = 1,1336$, b.p. 124.5–125°/3 mm, $MR_{\text{found}} = 85,51$.

Found, %: C 72,56; 72,40; H 8,46; 8,42; Fe 19,04; 18,73
 $C_{18}H_{26}Fe$. Calculated, %: C 72,98; H 8,69; Fe 18,43

In addition, a high-boiling fraction was obtained, b.p. 130–180°/4 mm, which was not subjected to further study. According to the results of analysis, the polyalkylation products contain on average 4 butyl residues per one ferrocene residue.

Found, %: C 76,67; 76,55; H 8,96; 9,00; Fe 13,75; 13,58
 $C_{26}H_{42}Fe$. Calculated, %: C 76,25; H 10,10; Fe 13,65

tert-Butylferrocenes from isobutylene. A suspension of 20 g of ferrocene, 200 ml of absolute *n*-heptane, various amounts of cooled liquid isobutylene, and dry aluminum chloride (see Table 2) was charged into a steel autoclave of 0.5 l capacity and heated with continuous stirring for various periods of time. After

After decomposition in the usual manner and distillation of the solvent, a certain amount of ferrocene was recovered and dark-red liquid products were obtained (see Table 2).

Table 2

Ferrocene, g	$CH_2=Al(CH_3)_2CH_3$, ml	g	°C	Time, h	Recovered, g	Obtained, g	Reaction products, g	Fraction I, 110°/5 mm, $n_D^{20} = 1,5790$		Fraction II, 110°/5 mm, $n_D^{20} = 1,5580$		Fraction III, 130°/5 mm, $n_D^{20} < 1,54$	
								yield, %	Fraction I, %	Fraction II, %	Fraction III, %		
20	30	—	50–60	5	16	0.8	2	0.15	18.8	0.07	8.7	0.16	20
20	30	0.5	50–60	5	6.8	2	5	0.16	8	0.2	10	0.48	24
20	30	1.0	50–60	5	11.4	1.6	4	0.22	13.7	0.32	20	—	—
20	30	7.5	50–60	5	—	31	—	—	—	—	—	7.3*	20**
20	30	7.5	20	24	8	6.3	30	3.2	51	2.35	37.3	—	—

Reaction	Temperature, °C	Time, h	Ferrocene, g	Liquid, g	Yield, %	Fraction I, Average		Fraction II, Average		Fraction III, Average		
						110°/5 mm, $n_D^{20} = 1.5760$	110°/5 mm, $n_D^{20} = 1.5790$	120°/5 mm, $n_D^{20} = 1.5550$	120°/5 mm, $n_D^{20} = 1.5580$	130°/5 mm, $n_D^{20} < 1.54$	130°/5 mm, $n_D^{20} < 1.54$	
Ferrocene + 2-chlorobutane	20	24	20	7.5	92	100	—	—	—	—	12*	40**

* And higher-boiling products.

** Yield calculated in % based on the ferrocene taken.

tert-Amylferrocenes from 2-methyl-2-chlorobutane.

Similarly, from 40 g of ferrocene and 30 ml of 2-methyl-2-chlorobutane, 1.9 g (13.7%) of tert-amylferrocene was obtained, $n_D^{20} = 1.5760$, $d_4^{20} = 1.1798$. $MR_{\text{found}} = 71.85$, b.p. 135–136°/4 mm.

Found, %: C 70.44; 70.40; H 7.85; 7.87; Fe 21.69; 21.51
 $C_{15}H_{20}Fe$. Calculated, %: C 70.327; H 7.870; Fe 21.813

Di-tert-amylferrocene was obtained in a yield of 2.6 g (15.2%), $n_D^{20} = 1.5602$, $d_4^{20} = 1.1469$, b.p. 162–163°/4 mm.

Found, %: C 73.95; 73.65; H 8.86; 8.73; Fe 18.37; 16.80
 $C_{20}H_{30}Fe$. Calculated, %: C 73.61; H 9.267; Fe 17.123

30 g of unreacted ferrocene was recovered.

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REFERENCES CITED

1. A. N. Nesmeyanov, N. S. Kochetkova, DAN, **109**, No. 3, 545 (1956).
2. A. N. Nesmeyanov, N. S. Kochetkova, DAN, **114**, No. 4, 800 (1957).
3. H. N. Richmond, H. Freiser, J. Am. Chem. Soc., **77**, 2022 (1955).
4. A. N. Nesmeyanov, L. A. Kozitsina, B. V. Lokshin, I. I. Kritskaya, DAN **117**, No. 3 (1957).

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