Tetrahedron. Vol. 25, pp. 5245 to 5253. Pergamon Press 1969. Printed in Great Britain

BRIDGED FERROCENES—V[1]

STERIC AND CONFORMATIONAL EFFECTS IN THE ACETYLATION OF [*m*]FERROCENOPHANES

T. H. BARR, E. S. BOLTON, H. L. LENTZNER and W. E. WATTS

Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, Scotland

(*Received in the UK 4 July 1969; Accepted for publication 11 July 1969*)

Abstract—The Friedel-Crafts acetylation of a series of [*m*]ferrocenophanes has been carried out and the results compared with those for non-bridged analogues. Steric effects predominate. In each case studied, substitution at cyclopentadienyl ring positions β- to the interannular bridge is favoured by a factor which varies markedly with the nature of the bridge. The PMR and electronic spectra of the products are discussed.

INTRODUCTION

THE directive influence exerted by a substituent attached to the ferrocene nucleus upon the pattern of electrophilic substitution has been a subject of much interest.[2] Studies have shown that the activating or deactivating effect of a substituent is felt not only by the ring to which it is attached but also, to a lesser extent, by the other ring in the molecule. In consequence, electrophilic substitution of derivatives containing an electron-withdrawing group (e.g. acylferrocenes) occurs predominantly in the unsubstituted ring whereas the presence of an electron-releasing group (e.g. alkylferrocenes) favours homoannular substitution.

Simplified MO calculations predict[3] that, irrespective of the electronic character of the substituent, the electrophilic substitution of a substituted ring in a ferrocene derivative should occur more readily at positions α- to the substituent rather than the corresponding β-positions. Experimental support for this conclusion has been provided by a study[3b] of the acetylation of a series of arylferrocenes. The acylation of 1,1′-dialkylferrocenes, on the other hand, occurs preferentially at the β-positions to an extent which increases with increase in the steric bulk of the substituent or the attacking electrophile.[4] In these reactions, therefore, there exists a delicate balance between steric and electronic effects when in opposition.

In order to assess more fully the relative importance of steric effects, we have carried out the acetylation of a series of [*m*]ferrocenophanes (I) and determined the relative proportions of the isomeric ketones formed in each case. Due to the conformational constraints imposed upon the interannular bridges in compounds of this type,[3] more subtle variations in steric shielding of the cyclopentadienyl rings is possible than for non-bridged analogues. In order to permit a direct comparison with the corresponding substitution patterns for non-bridged derivatives, we have repeated the acetylation of 1,1′-dimethyl- and 1,1′-diethylferrocene under comparable reaction conditions.

RESULTS AND DISCUSSION

All of the acetylation reactions were carried out under standardized conditions in methylene chloride solution using acetyl chloride in the presence of aluminium chloride. Each experiment was carried out at least twice and reproducible results were obtained. The total yields of monoacetylated products were high (Table 1) and relatively insignificant amounts of diacetylated products were formed. These were not examined. The α- and β- acetyl isomers were cleanly separated from each other and from unchanged starting material by chromatography on alumina. As found in previous studies,[6–11] the α-isomers eluted first in each case. Structural assignments were based upon spectral evidence which is discussed fully in a later section. The results of these experiments are summarized in Table 1.

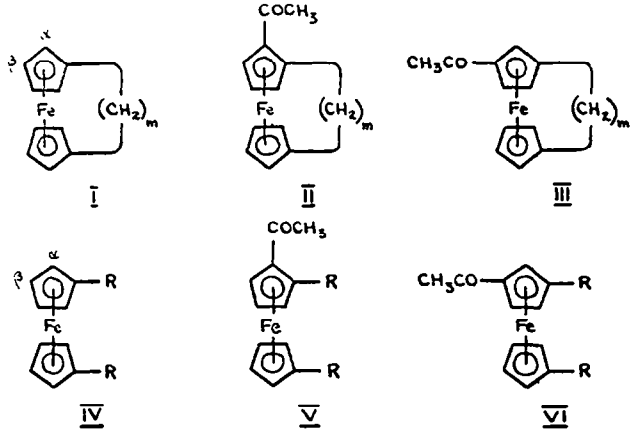


TABLE 1. EXPERIMENTAL DATA

No.	Compound	Yield (%)[a]	M.p. (b.p.)	Lit. m.p. (b.p.)[b]	Formulae	Found (%) C	Found (%) H	Calc. (%) C	Calc. (%) H	Refs.
1	II ($m = 3$)	32	75–77°	78–78·5°	$C_{15}H_{16}FeO$	—	—	—	—	5,7,8
2	III ($m = 3$)	51	99–101	103–104	$C_{15}H_{16}FeO$	—	—	—	—	5,7,8
3	II ($m = 4$)	33	(120/0·2)	—	$C_{16}H_{18}FeO$	68·3	6·2	68·1	6·4	—
4	III ($m = 4$)	56	81–82	—	$C_{16}H_{18}FeO$	68·7	6·5	68·1	6·4	—
5	II ($m = 5$)	25	98–99	—	$C_{17}H_{20}FeO$	69·2	6·6	68·9	6·8	—
6	III ($m = 5$)	55	66–68	—	$C_{17}H_{20}FeO$	68·8	6·8	68·9	6·8	—
7	V (R = Me)	24	(170/0·1)	15–16	$C_{14}H_{16}FeO$	—	—	—	—	6,11
8	VI (R = Me)	47	48–49	48·4–48·6	$C_{14}H_{16}FeO$	—	—	—	—	6,11
9	V (R = Et)	10[c]	(120/0·05)	(150/3)	$C_{16}H_{20}FeO$	—	—	—	—	9,10
10	VI (R = Et)	29[c]	(122/0·05)	(152/3)	$C_{16}H_{20}FeO$	—	—	—	—	9,10
11	VIII	8	(260/0·1)	—	$C_{23}H_{24}FeO$	74·5	6·7	74·3	6·5	—
12	IX	13	101–102	—	$C_{23}H_{24}FeO$	74·7	6·3	74·3	6·5	—
13	X or XI[d]	55	(300/0·1)	—	$C_{23}H_{24}FeO$	74·1	6·4	74·3	6·5	—
14	X or XI[d]		120–122	—	$C_{23}H_{24}FeO$	74·2	6·2	74·3	6·5	—

[a] Based on unrecovered starting material; results taken from a typical experiment.
[b] Highest reported value is given.
[c] Starting material not recovered.
[d] Structures not assigned (see text).

TABLE 2. PRODUCT RATIOS

Precursor	Products[a]	Reaction conditions	β/α Ratio	Refs[b]
I ($m = 3$)	1 and 2	$AcCl/AlCl_3/CH_2Cl_2$	1·57	—
		$AcCl/AlCl_3/CH_2Cl_2$	1·65	8
		$Ac_2O/AlCl_3/CH_2Cl_2$	1·60	9
I ($m = 4$)	3 and 4	$AcCl/AlCl_3/CH_2Cl_2$	1·65	—
I ($m = 5$)	5 and 6	$AcCl/AlCl_3/CH_2Cl_2$	2·19	—
IV (R = Me)	7 and 8	$AcCl/AlCl_3/CH_2Cl_2$	1·95	—
		not specified	1·7	4
		$Ac_2O/AlCl_3/CH_2Cl_2$	2·33	7
		$Ac_2O/BF_3.Et_2O$	1·38	12
IV (R = Et)	9 and 10	$AcCl/AlCl_3/CH_2Cl_2$	2·88	—
		$Ac_2O/AlCl_3/CH_2Cl_2$	2·60	10
		$AcCl/AlCl_3/CH_2Cl_2$	2·27	11
VII	11–14	$AcCl/AlCl_3/CH_2Cl_2$	2·62[c]	—

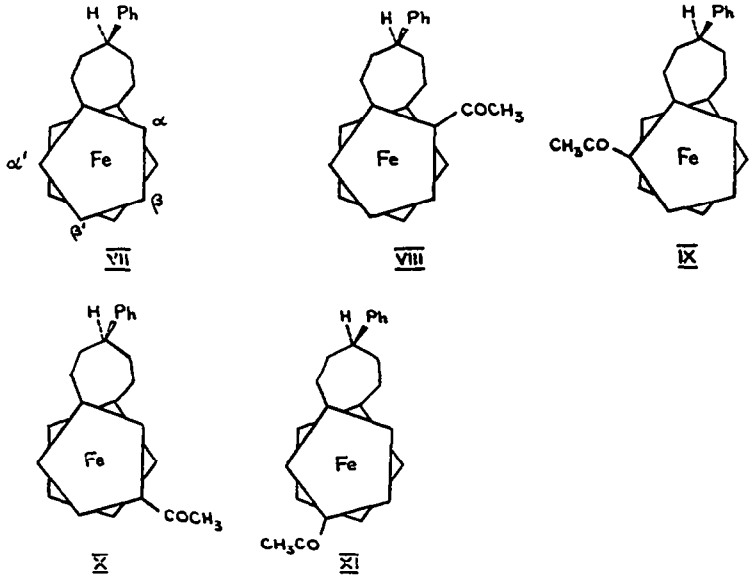
[a] See Table 1 for key.
[b] Unless present study
[c] (X + XI)/(VIII + IX).

In the case of the [*m*]ferrocenophanes (I) and the non-bridged compounds (IV), the four cyclopentadienyl ring positions α- to the substituent are equivalent as are the corresponding β-positions. The results are therefore conveniently expressed as β/α product ratios, the α-positions being assigned unit reactivity. These values are given in Table 2 together with those obtained by other groups for related investigations. Results previously published relative to other positions have been recalculated accordingly.

The acetylation of [3]ferrocenophane (I; $m = 3$) has previously been studied quantitatively by Rosenblum[8] and Rinehart[9] *et al.* Although different reaction conditions have been employed, there is good agreement between their results and those obtained in the present investigation. Substitution at the β-positions is favoured by a factor of ca. 1·6:1. As the length of the interannular bridge is successively increased by the incorporation of additional methylene groups in the chain (i.e. I; $m = 4$ and 5), however, the preference for β-substitution progressively increases. Since differences in the inductive or hyperconjugative characteristics of the individual polymethylene bridges should be insignificant, the variation of the β/α acetylation ratio with bridge length can be sensibly attributed to steric factors only.

We have previously shown[5] that the bridging groups in [*m*]ferrocenophanes (I) possess considerable flexibility and undergo rapid conformational exchange. Further, the PMR spectrum of [5]ferrocenophane (I; $m = 5$) was interpreted[5] to indicate that bridge flexing requires passage of the three central methylene groups close to the four α-ring positions in turn. Close interatomic approach of this nature is not possible in the case of [3]ferrocenophane (I; $m = 3$) whose α-positions are thereby sterically shielded to a smaller extent. Approach of an electrophile to these positions is subject to less steric hindrance than in the case of [5]ferrocenophane and the β/α product ratio is therefore lower. The β/α ratio found for [4]ferrocenophane (I; $m = 4$) is slightly higher but similar in magnitude to that found for the [3]-analogue. The α-ring positions in these derivatives are shielded by the bridges to a similar extent.

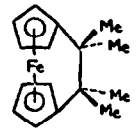
In order to compare the substitution patterns found for bridged ferrocenes with those for non-bridged analogues, we have also carried out the acetylation of 1,1′-dimethyl(IV; R = Me) and 1,1′-diethylferrocene (IV; R = Et). These reactions have been studied previously but widely differing values have been reported for the β/α product ratios (Table 2). These differences may arise from differences in the experimental conditions used. Under our conditions, values of 1·95 and 2·88 were found for the dimethyl and diethyl derivatives respectively. Since this ratio appears to be determined mainly by steric factors, it may be concluded that steric shielding of the α-ring positions by an interannular pentamethylene bridge is of the same order of magnitude as that introduced by a methyl substituent but considerably smaller than that of an ethyl group.



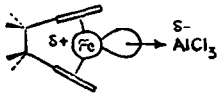
As discussed above, it was concluded that conformational flexing of the central portion of the pentamethylene chain in [5]ferrocenophane causes steric shielding of the α-ring positions. This conclusion is supported by the results obtained for the acetylation of the 3-phenyl derivative (VII). The presence of an asymmetric bridge carbon atom in this molecule renders non-equivalent the four unsubstituted positions of each cyclopentadienyl ring. Accordingly, four isomeric ketones were obtained from this reaction. The increase in the ratio of β/α substitution (2·62) compared with that found for [5]ferrocenophane itself (2·19) reflects the overall increase in steric shielding of ring positions adjacent to the bridge by the phenyl group attached to the central carbon atom.

The two α(α′)-isomers (VIII and IX), which were cleanly separated by chromatography, were formed in disparate proportions (ca. 1·7:1). Dreiding molecular models show that the Ph group can approach more closely to the α-positions than the corresponding α′-positions (see VII). The major of these products is therefore tentatively assigned the structure (IX), formed by electrophilic attack at the less hindered

α′-positions. Although pure samples of the β(β′)-isomers (X and XI) were obtained (their IR and PMR spectra are distinct), complete separation of these products was not achieved. Spectral evidence, however, suggested that they were formed in approximately equal amounts as expected.



XII



XIII

Finally, we report unsuccessful attempts to carry out acetylation of the [2]ferrocenophane derivative (XII). Even under mild conditions (Perrier complex; low temperatures), this reaction yielded only intractable decomposition products together with varying amounts of recovered starting material. This unexpected failure* stands in marked contrast to the relative ease of electrophilic substitution of other [*m*]ferrocenophanes. A possible explanation may be found in the formation of a coordination complex (XIII) between the ferrocenophane and the Lewis acid catalyst.

According to the orbital picture suggested[14] by Ballhausen and Dahl for ring-tilted[15] metallocenes of this type, three filled non-bonding orbitals are projected in the opening between the cyclopentadienyl rings as shown (XIII). Electronic reorganization of this nature should lead to an increase in Lewis basicity of the Fe atom compared with undistorted analogues in which the rings occupy parallel planes. Co-ordination of one of these electron pairs to aluminium chloride would cause a drainage of electron density towards the iron atom from the attached rings which would thereby be deactivated towards electrophilic attack. The broader implications of this hypothesis merit further study.

SPECTRAL CORRELATIONS

Assignment of structure to the products listed in Table 1 was decided on the basis of spectral evidence. The IR spectra of all of the ketones contained a strong carbonyl stretching absorption in the expected[9] region (ca. 1665 cm^{-1}). Although in each case the spectra of α- and β-acetyl isomers were distinct from each other, no regular differences were noted. The PMR and electronic spectra, on the other hand, showed a number of regularities which are discussed below.

PMR spectra. Details of the PMR spectra of the compounds prepared are given in Table 3. In all of these, the acetyl protons appear as a sharp singlet in a narrow spectral range (τ7·55–7·66). The protons of the alkyl groups attached to different rings in the non-bridged derivatives show chemical shift distinction. This is particularly noticeable in the case of α-acetyl-1,1′-dimethylferrocene (V; R = Me) where the difference in chemical shift (0·40 ppm) between the methyl groups is much larger than

* A report of the failure of this reaction has been mentioned in a patent.[13]

TABLE 3. PMR SPECTRA[a]

Compound[b]	Cyclopentadienyl protons[c, d] (τ)	Acetyl protons[e] (τ)	Alkyl protons[c] (τ)
1	5·37(t)(1H); 5·6–5·8(3H) 5·8–6·1(2H); 6·1–6·3(1H)	7·65	6·9–8·3
2	5·31(d)(2H); 5·6–5·8(3H) 5·9–6·1(2H)	7·64	7·8–8·2
3	5·38(t)(1H); 5·45–5·6(1H) 5·64(t)(1H); 5·8–6·2(4H)	7·60	6·6–8·3
4	5·2–5·35(2H); 5·45–5·6(1H) 5·6–5·8(2H); 5·85–6·15(2H)	7·62	7·3–8·3
5	5·3–5·5(1H); 5·5–5·9(4H) 6·0–6·3(2H)	7·63	7·0–8·6
6	5·25–5·5(2H); 5·6–5·9(3H) 6·0–6·3(2H)	7·66	7·3–8·6
7	5·44(t)(1H); 5·71(d)(2H) 5·98(bs)(4H)	7·61	7·71 (s) 8·11 (s)
8	5·36(d)(2H); 5·63(t)(1H) 5·97(bs)(4H)	7·63	7·96 (s) 8·10 (s)
9	5·4–5·5(1H); 5·55–5·75(2H) 5·95(bs)(4H)	7·58	7·0–8·0 8·85(t) 8·89 (t)
10	5·33(d)(2H); 5·60(t)(1H) 5·8–6·1(4H)	7·62	7·64(bq) 8·80 (t) 8·87 (t)
11[f]	5·34(t)(1H); 5·5–5·6(2H) 5·65–5·9(2H); 5·95–6·1(2H)	7·55	7·4–8·0
12[f]	5·3–5·4(1H); 5·45–5·6(2H) 5·65–5·8(2H); 5·9–6·1(2H)	7·60	7·3–8·2
13[f]	5·2–5·35(2H); 5·5–5·6(1H) 5·6–5·8(2H); 5·85–6·1(2H)	7·60	7·3–8·2
14[f]	5·1–5·3(2H); 5·5–5·7(2H) 5·9–6·0(1H); 6·1–6·25(2H)	7·55	7·2–8·2

[a] In $CDCl_3$
[b] See Table 1 for key
[c] Multiplets unless indicated otherwise; (s) singlet, (d) doublet, (t) triplet, (q) quartet.
[d] Relative intensities of signals are given.
[e] Singlet resonance.
[f] Phenyl protons give broadened singlet at τ2·5–2·6.

that (0·14 ppm) found for its isomer (VI; R = Me). The protons of the methyl group adjacent to the acetyl group in the former compound are therefore located in the deshielding zone of the carbonyl group.

It is also clear from the complexity of the signals due to the four methylene protons in the spectrum of α-acetyl-1,1′-diethylferrocene (V; R = Et) that the rotational freedom of one of the ethyl groups is considerably restricted by the vicinal acetyl group.[16] The corresponding protons in the spectrum of the isomer (VI; R = Et), on the other hand, appear as overlapping quartets as expected for freely rotating ethyl groups. We also note that the fortuitous coincidence[5] in chemical shift of the bridge protons of [3]ferrocenophane (I; m = 3) is removed upon introduction of an acetyl group into the cyclopentadienyl ring. In the spectra of all of the acetylferrocenophanes (II and III), the bridge protons give rise to broad structureless multiplets.

It is well recognised that the protons of an acylated ferrocene ring, and particularly those adjacent to the carbonyl function, experience a deshielding effect.[17] The signal appearing at lowest field in the ring proton patterns of acylferrocenes, therefore, can be assigned to protons adjacent to the CO group and the integrated relative intensity of this signal reveals the number of protons of this type in the molecule. Differentiation between the α- and β-acetyl isomers prepared in this study was decided on this basis. This effect is best demonstrated by the spectra of the non-bridged derivatives. The spectra of the α-acetyl compounds (V; R = Me or Et) contain a one-proton multiplet at lowest field (ca. τ5·4) for the unique proton adjacent to the CO group, the two remaining protons of the acylated ring appearing as a multiplet at higher field (ca. τ5·7). The situation is reversed for the β-acetyl derivatives (VI; R = Me or Et) whose spectra show a two-proton multiplet at lowest field.

As a consequence of free relative rotation of the cyclopentadienyl rings in these compounds, the magnetic environments of the protons of the non-acetylated ring are averaged relative to the CO group and they appear as broadened singlets or finely split multiplets at higher field than the protons of the other ring. In the case of the acetylferrocenophanes (II and III), however, ring-ring torsion is restricted to an extent which is controlled by the length of the interannular bridge.[5] In the spectra of these compounds, therefore, the protons of the non-acetylated ring give rise to an ABCD pattern which overlaps with the ABC pattern of the protons of the acetylated ring. Complete analysis of these spectra is difficult and the problem is further complicated by the uncertainty concerning the preferred conformation of the CO group, particularly when it is located adjacent to a bridge. An interpretation of the ring proton spectra of a range of acetylferrocenophanes including II and III (m = 3) has been given by Rinehart *et al.*[9] Somewhat different conclusions regarding the spectrum of the former compound have been reached[19] by Levenberg and Richards from a more detailed analysis.

TABLE 4. ELECTRONIC SPECTRA[a]

Compound[b]	Band I		Band II		Band III		Band IV	
	λ_{max}	ε	λ_{max}	ε	λ_{max}	ε	λ_{max}	ε
1	226 nm	15000	265 nm	6300	337 nm	1000	440 nm	540
2	230	14190	267	6950	338	1760	456	870
3	228	12900	268	5300	339	1070	455	420
4	233	14480	274	5670	338	1340	454	610
5	230	15370	269	6750	340	1020	464	420
6	235	14500	274[c]	6000[c]	340	1140	460	510
7	229	15700	271	6280	338	1140	460	450
8	233	14420	274	6050	341	1200	458	540
9	228	16030	270	6500	338	1130	459	450
10	232	14730	274	6280	341	1200	459	530
11	230	15100	269[c]	5800[c]	344	1050	470	425
12	229	16700	268[c]	6700[c]	341	1040	468	440
13	234	14170	277[c]	5310[c]	340	1000	463	460
14	233	16160	276[c]	5670[c]	341	1070	460	460

[a] In abs EtOH

[b] See Table 1 for key

[c] Shoulder.

Electronic spectra. The absorption bands appearing in the electronic spectra of the ketones prepared in this study are given in Table 4. The spectra of acylferrocenes contain four distinct maxima at ca. 230, 270, 340 and 460 nm. [19] For convenience, these are designated Bands I–IV respectively. For each isomeric pair, the position of maximum absorbance for Bands I and II occurs at longer wavelength for the β-acetyl derivatives. Since these bands most probably represent electronic transitions of the N → V type involving ring-CO molecular orbitals,[20] this bathochromic shift reflects the enhanced conjugation between the cyclopentadienyl ring and the attached CO group which is possible for the β-acetyl derivatives. With the α-acetyl isomers, steric interaction between the acetyl group and the adjacent bridge raises the energy of conformations in which the CO group is coplanar with the ring and conjugative interaction is thereby reduced.

This effect can also be seen in the behaviour of Band IV. We have previously demonstrated[19] that the intensity of this absorption is extremely sensitive to conjugation effects and is enhanced as conjugative interaction between the ferrocene nucleus and an attached π-system is increased. For each pair of isomeric ketones, the intensity of Band IV is greater for the β-acetyl derivatives, the differentiation being particularly marked for compounds of the [3]ferrocenophane series (II and III; $m = 3$). The position and intensity of Band III vary little throughout the series.

EXPERIMENTAL

The methods of preparation of the ferrocenophanes used have been described previously.[21] 1,1′-Dimethyl- and 1,1′-diethylferrocene were prepared by lit methods.[4] PMR spectra were recorded for $CDCl_3$ solns at 60 MHz on a Perkin–Elmer spectrometer using TMS as internal standard. Electronic spectra were obtained for abs EtOH solns on a Unicam SP800A spectrometer calibrated against holmium film. At least two determinations of each spectrum were carried out and reproducible results were obtained. Each acetylation reaction was carried out at least twice and consistent results for β/α product ratios were found. Only one such experiment is described in detail. All other reactions were carried out under exactly similar conditions and the results are summarized in Table 1.

Acetylation of 3-phenyl[5]ferrocenophane (VII). Freshly ground $AlCl_3$ (1·25 g; 9·4 mmole) was added portionwise to a stirred soln of VII[22] (2·47 g; 7·5 mmole) and acetyl chloride (0·86 g; 1·1 mmole) in CH_2Cl_2 (250 ml) under N_2 at room temp. The violet soln was stirred for 19 hr and then poured over crushed ice (1:1). The organic layer was separated and combined with three CH_2Cl_2 extracts of the aqueous phase. The total extract was washed twice with $NaHCO_3$ aq, thrice with water, dried (Na_2SO_4), and evaporated. The residual red gum was dissolved in ligroin (b.p. 40–60°)/ether (4:1) and chromatographed on partially deactivated alumina. Ligroin eluted unchanged starting material (60 mg; 2·5% recovery), m.p. and mixed m.p. 112–113°. Ligroin/ether (9:1) eluted two well-separated orange-red bands which afforded, in order of elution, a viscous liquid (VIII; 200 mg; 8%), and an orange solid (IX; 350 mg; 13%), m.p. 101–102° (from ligroin). Ligroin/ether (1:2) eluted a broad red band which afforded a viscous red oil (X + XI; 1·37 g; 55%). The first runnings of this band gave one pure isomer, a viscous red liquid, and the last portion the second isomer, a red solid, m.p. 120–122° (from ether). The IR and PMR spectra of these compounds were quite distinct from each other.

Acknowledgements—The authors thank Mr. R. G. Kinnley for preliminary experiments, Mr. J. Ritchie for PMR spectra, Mr. F. Daubney for microanalyses, and the Science Research Council for a maintenance grant (to T.H.B.).

REFERENCES

[1] Part IV; T. H. Barr and W. E. Watts, *Tetrahedron* **25**, 861 (1969).

[2] See: G. R. Knox, I. G. Morrison, P. L. Pauson, M. A. Sandhu and W. E. Watts, *J. Chem. Soc.* (C) 1853 (1967).

[3] [a] J. H. Richards and T. J. Curphy, *Chem. & Ind.* 1456 (1956).
[b] M. Rosenblum and W. G. Howells, *J. Am. Chem. Soc.* **84**, 1167 (1962).
[4] M. Rosenblum, *Chemistry of the Iron Group Metallocenes* Part 1; p. 72, Interscience, New York (1965).
[5] T. H. Barr and W. E. Watts, *Tetrahedron* **24**, 6111 (1968).
[6] E. A. Hill and J. H. Richards, *J. Am. Chem. Soc.* **83**, 4216 (1961).
[7] K. L. Rinehart, K. L. Motz and S. Moon, *Ibid.* **79**, 2749 (1957).
[8] M. Rosenblum, A. K. Banerjee, N. Danieli, R. W. Fish and V. Schlatter, *Ibid.* **85**, 316 (1963).
[9] K. L. Rinehart, D. E. Bublitz and D. H. Gustafson, *Ibid.* **85**, 970 (1963).
[10] D. E. Bublitz, *Canad. J. Chem.* **42**, 2381 (1964).
[11] G. Tainturier and J. Tirouflet, *Bull. Soc. Chim. Fr.* 600 (1966).
[12] K. Schlögl, H. Falk and G. Haller, *Monatsch.* **98**, 82 (1967).
[13] R. L. Pruett and E. L. Morehouse, U.S. Patent 3063974 (1962); See: *Chem. Abstr.* **58**, 11404 (1963).
[14] C. J. Ballhausen and J. P. Dahl, *Acta Chem. Scand.* **15**, 1333 (1961).
[15] M. B. Laing and K. N. Trueblood, *Acta Cryst.* **19**, 373 (1965).
[16] P. L. Pauson, M. A. Sandhu, W. E. Watts, R. C. Haley and G. R. Knox, *J. Chem. Soc.* (C) 1851 (1967).
[17] M. D. Rausch and A. Siegel, *J. Organometal. Chem.* **17**, 117 (1969).
[18] M. I. Levenberg and J. H. Richards, *J. Am. Chem. Soc.* **86**, 2634 (1964).
[19] T. H. Barr and W. E. Watts, *J. Organometal. Chem.* **15**, 177 (1968).
[20] Cf. K. Schlögl and H. Egger, *Liebigs Ann* **676**, 88 (1964).
[21] W. E. Watts, *Organometal. Chem. Revs* **2**, 231 (1967).
[22] T. H. Barr and W. E. Watts, *Tetrahedron* **24**, 3219 (1968).