

REACTION OF (BROMOMETHYL)NAPHTHALENES WITH IRON NONA-CARBONYL. A NOVEL ROUTE TO THE TRIMETHYLENEMETHANE COMPLEXES

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SUMMARY

The reaction of the (bromomethyl)naphthalene derivatives with iron nonacarbonyl has been investigated, and it has been shown that in some cases the trimethylenemethaneiron carbonyl complexes are formed. The PMR spectra of the compounds prepared are discussed.

INTRODUCTION

In attempting to synthesize π -benzyliron derivatives^{1,2} we have studied the reaction of iron nonacarbonyl with a series of aralkyl halides, including 2-(bromomethyl)naphthalene¹. In all the cases, other than that mentioned above, stable iron complexes were not obtained, the main course in these reactions being the dimerization of hydrocarbon fragments or the formation of the corresponding ketones. In the present paper additional data on the reactions of (bromomethyl)naphthalenes are submitted together with the structure of the resulting complexes.

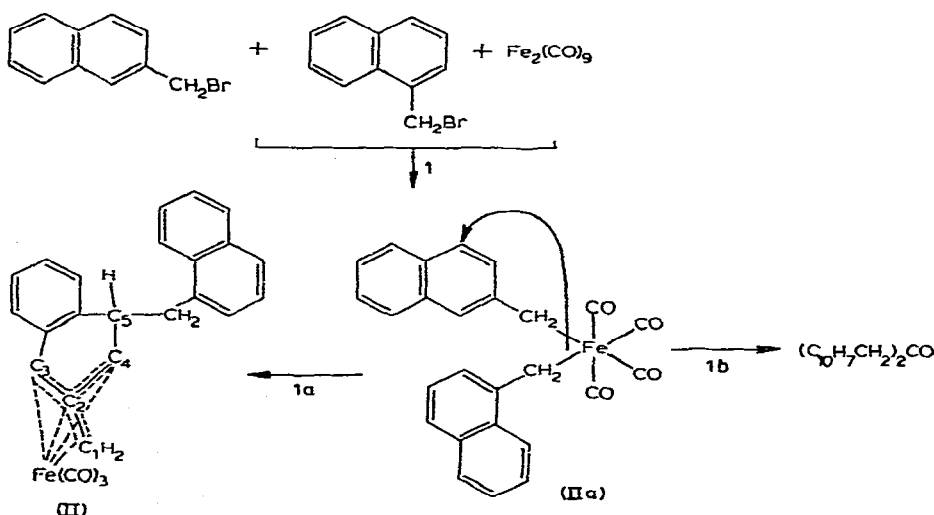
RESULTS AND DISCUSSION

Gentle heating of 2-(bromomethyl)naphthalene with $\text{Fe}_2(\text{CO})_9$ in hexane results in almost complete expulsion of the carbonyl group and yields reaction products containing the complex $(\text{C}_{10}\text{H}_7\text{CH}_2)_2\text{Fe}(\text{CO})_3$ (I) and 1,3-di-2-naphthylacetone. The mass-spectrum of complex (I) allows its composition to be established and show that besides molecular ion, almost all conceivable fragments of the complex are distinguishable in the spectrum. Of the ions formed, $(\text{C}_{10}\text{H}_7\text{CH}_2)_2\text{Fe}^+$ is the most stable. In the IR spectrum of the complex the symmetric CH_2 stretching frequencies appear as two bands which could be attributed to two differently hybridized methylene groups. The NMR data discussed in detail below led to a similar conclusion.

Polarographic reduction of complex (I), using a dropping mercury electrode in the presence of a buffer, occurs at $E_{1/2} = -1.6$ V, *i.e.* at the usual reduction potential for complexes with a σ -bonded group³. This information suggested that one naphthylmethyl group in this complex is combined with the iron atom through bonding of the

π -benzyl type, while the other group is involved in σ -bonding. However, the specificity of the NMR spectrum of (I) and the observation that the isomeric 1-(bromomethyl)naphthalene produced no complex with iron nonacarbonyl led us to undertake additional investigations. We have synthesized and have in addition studied the behaviour of the complexes containing deuterium and bromine in the 1-position of both naphthomethyl groups in (I), (III) and (IV) and also the complex (II) formed from the reaction of an equimolar mixture of 1- and 2-(bromomethyl)naphthalenes with $\text{Fe}_2(\text{CO})_9$. All these complexes are light yellow, crystalline (II), (IV) or amorphous (I), (III) substances having high m.p.'s and are stable against oxidation. Protection by an inert atmosphere is not necessary during the isolation and crystallization of the products, although the synthesis itself was carried out under argon. No oxidation of compound (I) was observed over the whole range of dropping mercury electrode potentials (up to +0.6 V)¹. All four compounds have identical infrared (Table 1) and NMR spectra. The mass spectra of (I) and (II) are also identical. X-ray study of (II)⁴ showed that it was a trimethylenemethane complex, the trimethylenemethane entity arising from the 2-naphthomethyl component after addition of one $\text{CH}_2\text{C}_{10}\text{H}_7$ group to position 4 of the ring. The preliminary data available from this work suggest that this may be an intra-molecular transformation occurring with formation of a σ -intermediate (IIa) (Scheme 1).

SCHEME 1



The measured C-C and Fe-C distances (C_1 - C_2 1.42, C_2 - C_3 1.37, C_2 - C_4 1.41, Fe- C_1 2.11, Fe- C_2 1.95, Fe- C_3 2.11, Fe- C_4 2.10 Å) are close to those present in (phenyltrimethylenemethane)iron tricarbonyl⁵.

As a result of such coordination a part of the naphthalene nucleus completely loses its aromaticity. This structure is supported by the IR spectrum of the compound and especially by its nuclear magnetic resonance spectrum. All four compounds exhibit three groups of the lines in their NMR spectra: a complex multiplet with a relative intensity of 11 or 10 (in the case of a substituted complex) observed in the

shifts at 1.7 and 1.57 ppm respectively are observed.

The integral intensities are related as $(L)/(M)/(N)/(P)/(Q)=7/4/5/1/1$. The spectrum pattern indicates that there are at least 11 aromatic protons in the compound which suggests the presence of at least two naphthyl fragments in the molecule. Seven protons belong to the $C_{10}H_7-CH_2$ fragment [multiplet (L)], as is evident from a comparison of the PMR spectra of (II) and the initial 1-(bromomethyl)naphthalene. Irradiation of any line in the region corresponding to aromatic protons with a second radiofrequency field does not change the multiplet (N) or the singlets (P) and (Q). There is also no spin-spin coupling between the multiplet (N) and other groups of signals in the spectrum. A more detailed study of the multiplet (N) indicated the existence of a doublet (E) at 3.94 ppm with a relative intensity corresponding to one proton and its components separated by 2.5 Hz. This doublet splitting is due to the spin-spin coupling with the proton, which give rise to signal (D) in the spectrum, at approximately 3.55 ppm, overlapping with other proton signals of the multiplet (N). Therefore, irradiation with a second radiofrequency corresponding to this chemical shift results in the collapse of the doublet (E) to a singlet.

The spectrum of compound (II) represents a complex spin system whose analysis in terms of a first order approximation is impossible. A subsequent interpretation of the spectrum has been made possible through the use of higher resonance frequencies (100 and 220 MHz).

Multiplet (N) recorded at slow scanning speed at 100 MHz is depicted in Fig. 2a. It can be shown that the signal (D) is a triplet with the components separated by 2.5 Hz. Four upfield lines with summary intensities corresponding to one proton (A)

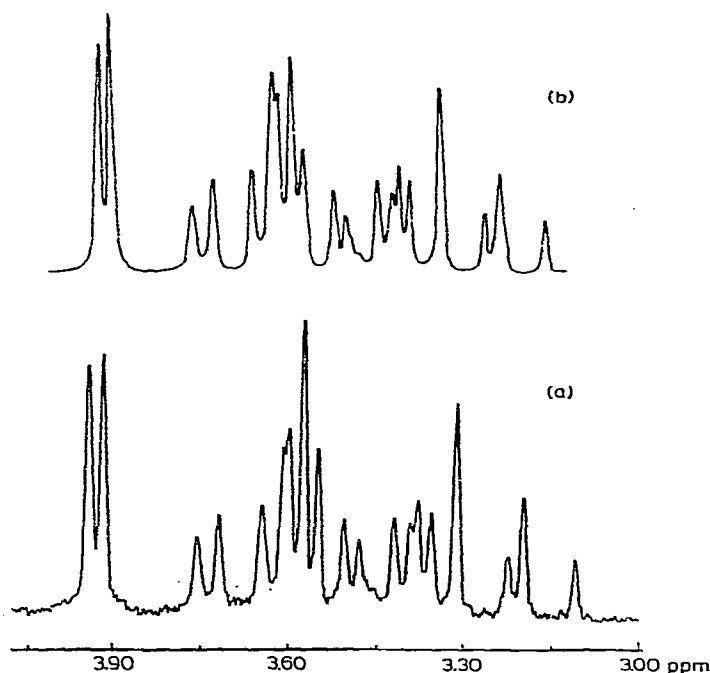
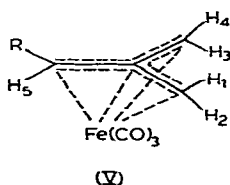


Fig. 2. The spectrum of compound (II) in CS_2 (multiplet N); a. experimental at 100 MHz, b. theoretical, calculated using parameters shown in Table 2.

could be also distinguished. On the basis of these data the following preliminary conclusions have been drawn regarding the nature of multiplet (N): it represents an ABCDE type spectrum, proton (E) interacts only with (D). The latter in turn has the same spin-spin coupling constant (2.5 Hz) with one of the (B) and (C) protons. From the shape of the signal, the spin-spin coupling constants of proton (A) with (B) and (C) are different.

The correctness of these conclusions is confirmed by the spectrum of (II) in benzene. Due to the ASIS effect, the chemical shifts in the multiplet (N) are now different, and in this spectrum a doublet (E) at 3.614 ppm, triplet (D) centered at 3.555 ppm, signal of proton (A) — the four lines at 3.136 ppm, and a complex multiplet in the region of 3.305–3.512 ppm relating to the protons (B) and (C) are observed. The singlets (P) and (Q) are located respectively at 1.70 and 1.57 (in CS_2) and at 1.302 and 1.24 ppm (in benzene). From the basis of their intensities and positions, these signals could only be assigned to the CH_2 group. This group, however, cannot belong to the $\text{C}_{10}\text{H}_7\text{CH}_2$ fragment which gives rise to the aromatic proton multiplet (L). If this were the case the resonance signal should be either a singlet in the lower field part of the spectrum or system AB (in the case of the non-equivalent protons) with its specific geminal spin-spin coupling constant of $\sim 12\text{--}15$ Hz. The absence of spin-spin coupling between the (P) and (Q) and other groups of signals was established by means of a double resonance experiment. When the operating frequency was increased the separation between the P and Q signals also increased. Some spin-spin coupling between these protons might be assumed to exist, but if so this is so great that the weak external components were lost in the background noise at large J/δ . However, a double resonance investigation showed the absence of these weak lines in the region of ± 40 Hz from the center of (P) and (Q) signals. Thus the (P) and (Q) protons are not equivalent and have a spin-spin coupling constant close to zero. These results suggest that this CH_2 group is a part of the fragment similar to that of the π -allyl or trimethylenemethane complexes⁶. For example, in complex (V) the H_1 and H_2 chemical shifts are 1.84 ppm and $J_{12} \simeq J_{34} \simeq 0$, which is rather close to the observe (P) and (Q) values in the spectrum of (II).



These conclusions have been entirely confirmed by the study of the spectrum of (II) at 220 MHz, which has enabled a detailed interpretation of this spectrum. The multiplet (N) is shown in Fig. 3. Although again in this case an exact calculation of the spectrum is impossible from the basis of a first order approximation, the five separate signal groups observed are sufficiently accurate to enable a determination of all the parameters, which were further improved by calculation on an M-20 electronic digital computer using the YaMR-1 program⁷. At an operating frequency of 220 MHz the spectrum has only a low sensitivity to the choice of constants (± 0.2 Hz) and to the variation of chemical shifts (± 1.5 Hz). For this reason the parameters were varied

TABLE 2

THE PROTON CHEMICAL SHIFTS AND SPIN-SPIN COUPLING CONSTANTS OF THE MULTIPLY (N) CALCULATED FOR COMPOUND (II)
(Solvent CS₂)

Proton	δ (ppm)	J(Hz)
H _A	3.220	$J_{AB} - 12.8$
H _B	3.675	$J_{AC} 9.00$
H _C	3.420	$J_{BC} 4.7$
H _D	3.579	$J_{CD} 2.5$
H _E	3.930	$J_{DE} 2.5$

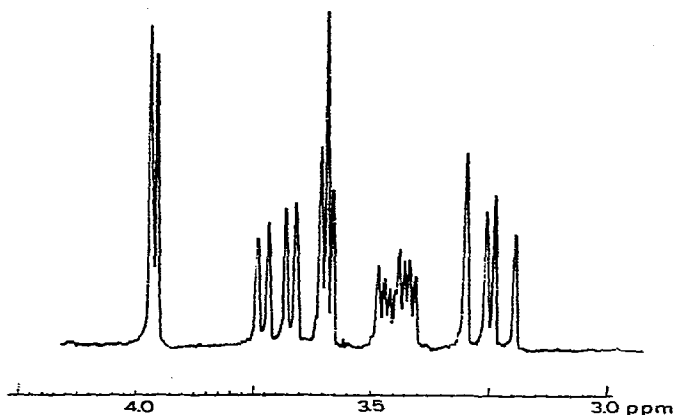


Fig. 3. The spectrum of compound (II) in CS₂ (multiplet N) at 220 MHz.

until a good fit was obtained with the 100 MHz spectrum (Fig. 2), which is much more sensitive to the choice of parameters. The calculated spectrum thus obtained is shown in Fig. 2b, the parameters of the ABCDE spectrum being listed in Table 2. Analysis of the multiplet (N) enabled an immediate decision to be made regarding the presence of the CH₂-CH-fragment in the molecule. The (A) and (B) signals of the CH₂ protons could be readily recognized from the geminal spin-spin coupling constant (-13 Hz), which is characteristic of an aliphatic series⁶. The chemical shifts of (A) and (B) show that the CH₂-group is joined to an aromatic ring and thus belongs to the C₁₀H₇CH₂ fragment. On the other hand, the (C) proton chemical shift also indicates that it is in the 1-position to an aromatic ring. A significant difference between the J_{AC} and J_{BC} constants indicates that the (A) proton occupies a predominantly *trans*- and the proton (B) a *gauche*-position with respect to (C) in C₁₀H₇CH₂CH. The proton (E) is spin-spin coupled only with (D) and, in addition, the same spin-spin coupling constant was observed with the (D) and (C) protons.

These data indicate that one of the nuclei of the second naphthyl fragment is not aromatic but has a tetrahedral carbon C₅ bonded with H_C and C₁₀H₇CH₂. The C₁, C₂, C₃ and C₄ carbons form the skeleton of the trimethylenemethane fragment which is π -bonded with the Fe(CO)₃ group. This is confirmed by a significant upfield

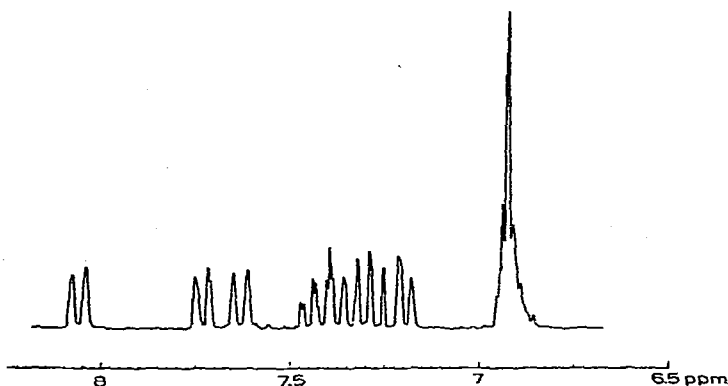


Fig. 4. The spectrum of compound (II) in CS_2 (multiplets L and M) at 220 MHz.

shift of the H_E and H_D signals with respect to those of the aromatic protons. The value of J_{ED} is close to that observed for the respective proton pair of trimethylenemethane-iron tricarbonyl. Thus the 2-naphthylmethyl group is coordinated to the iron atom, the four protons of the second six-membered ring retaining their aromaticity and giving rise to a singlet at 6.92 ppm in the 60 and 100 MHz spectra which resolves to an additional structure at 220 MHz (Fig. 4).

The structure of the C_{10}H_7 fragment giving a multiplet (L) in the aromatic proton region of the spectrum must now be determined. At 220 MHz this multiplet resolves into three doublets (centered at 7.62, 7.73 and 8.05 ppm with the components separated by 8 Hz), and a multiplet (within the region of 7.16–7.50 ppm; 1/1/1/4) which indicates the presence of three 1-protons in the naphthyl nucleus. The fourth 1-position is occupied by CH_2 .

Thus the structure of compound (II) may be confirmed from an analysis of the proton magnetic resonance spectra and their theoretical calculation. The NMR data for the solution are in agreement with the X-ray data.

The spectrum of compound (I) at 60 MHz in CS_2 is shown in Fig. 5. Its pattern is rather similar to that of compound (II). In the region of aromatic protons a complex multiplet (L) and a singlet (M) are found. A multiplet (N) within 3.85–2.90 ppm and two upfield singlets (P) and (Q) with chemical shifts 1.64 and 1.595 ppm, respectively are also observed. The integral intensities are related as $(L)/(M)/(N)/(P)/(Q) = 7/4/5/1/1$. From a double resonance experiment, it was established that the aromatic protons have no spin-spin coupling with the protons which give rise to multiplet (N) and singlets (P) and (Q) in the spectrum. The multiplet (N) also does not couple with other groups of signals in the spectrum. In a similar fashion to compound (II), the multiplet (L) may be assigned immediately to the aromatic fragment $\text{C}_{10}\text{H}_7\text{CH}_2$, and singlet (M) to the four protons of that six-membered ring of the second naphthyl group which retains its aromaticity. The singlets (P) and (Q) are due to the protons at the C_1 carbon of the trimethylenemethane skeleton which is π -bonded with the $\text{Fe}(\text{CO})_3$ group. Again, similarly to compound (II), the multiplet (N) contains the signals from five protons. This multiplet, recorded at a slow scanning speed at 100 MHz, is shown in Fig. 6a. This spectrum contains a doublet (E) at 3.816 ppm separated by 2.5 Hz, and a triplet (D) centered at 3.635 ppm with a similar separation of components. These results allow the direct assignment of the (E) signal to the H_E proton at C_3 and the

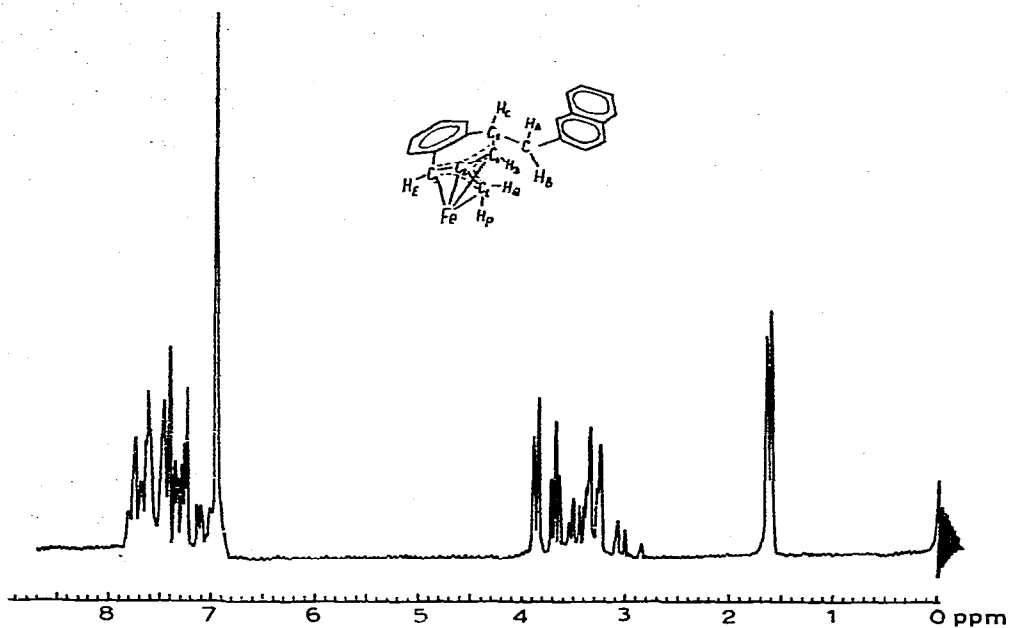


Fig. 5. The spectrum of compound (I) in CS_2 , at 60 MHz.

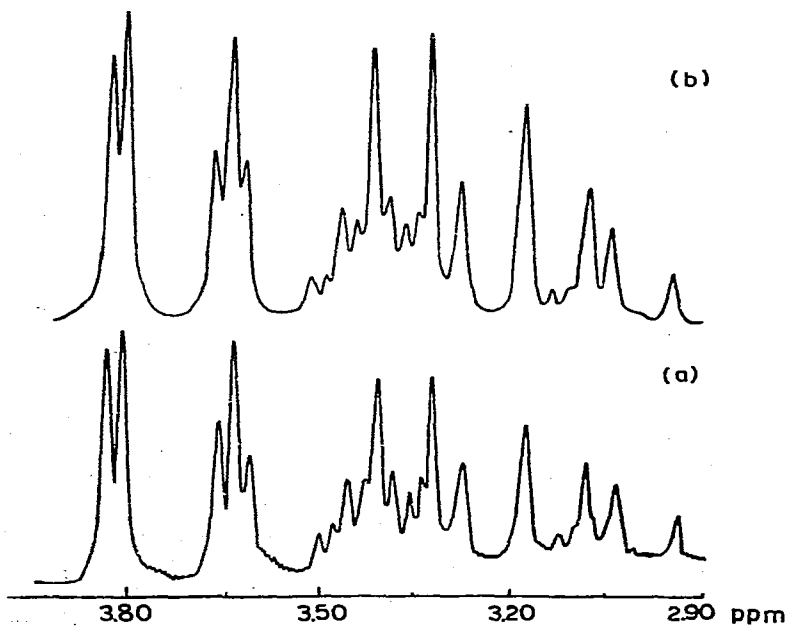


Fig. 6. The spectrum of compound (I) in CS_2 (multiplet N); a. experimental at 100 MHz, b. theoretical, calculated using parameters shown in Table 3.

signal (D) to the H_D proton at C_4 , in a similar fashion to compound (II). The four up-field lines may be assigned to one proton (A). The H_C and H_B proton signals superimpose.

In the 100 MHz spectrum of (I) in benzene the chemical shifts of the multiplet change due to the ASIS-effect. The H_D triplet (δ 3.42 ppm) is now located at a lower field strength than the H^E proton doublet (δ 3.35 ppm). On selective deuteration of the 1-position, the signal (E) disappears while (D) is transformed into a doublet separated by 2.5 Hz. The four H_A proton signals are found at the high field strengths, and from the four H_B lines three signals are observed, the fourth being concealed by multiplet H_C .

A theoretical calculation of the spectrum of (I) in CS_2 using the YaMR-1 program has also been undertaken (Fig. 6b). The spin-spin coupling constants of compound (II) were used in this calculation while chemical shifts were subjected to a variation analysis. The best fit between the experimental and theoretical spectra was attained using the parameters listed in Table 3. By comparing the calculated chemical

TABLE 3

THE PROTON CHEMICAL SHIFTS AND SPIN-SPIN COUPLING CONSTANTS OF THE MULTIPLET (N) CALCULATED FOR COMPOUND (I)
(Solvent CS_2)

Proton	δ (ppm)	J (Hz)
H_A	3.085	$J_{AB} - 13.2$
H_B	3.355	$J_{AC} \quad 9.00$
H_C	3.421	$J_{BC} \quad 5.00$
H_D	3.641	$J_{CD} \quad 2.5$
H_E	3.817	$J_{DE} \quad 2.5$

shifts for the ABCDE protons of (I) with those for compound (II) in CS_2 , it is possible to see that although the H_E , H_D and H_C proton chemical shifts change only slightly from one compound to the other, there is a considerable difference in the CH_2 proton shifts of $\text{C}_{10}\text{H}_7\text{CH}_2\text{CH}$ (H_A and H_B). This is probably due to a change in the contribution of the magnetic anisotropy of the 2-naphthyl fragment to the H_E and H_B proton shielding with respect to that in an 1-substituted naphthyl.

The spectrum of (I) in benzene also shows some changes with increasing temperature (Fig. 7). The H_P and H_Q proton signals approach each other and collapse at 100° , while the H_D proton signal shifts upfield and interferes with the H_E signal at this temperature. Although all these changes are reversible this cannot be taken as evidence of a dynamic process, since the changes in chemical shift are not accompanied by a characteristic broadening and collapsing of the spin multiplets. It is possible that these effects may be due to complex formation between benzene and (I), although such effects are not observed with other solvents, *e.g.*, carbon disulfide and chloroform.

Thus the complexes formed in the reactions investigated in this study contain two differently bonded naphthomethyl groups. Their bonding is, however, the exact reverse of that initially suggested. Transformation of the aromatic system to a trimethylenemethane system upon coordination with iron (+2) is more apparent preferred to bonding in the π -benzyl form.

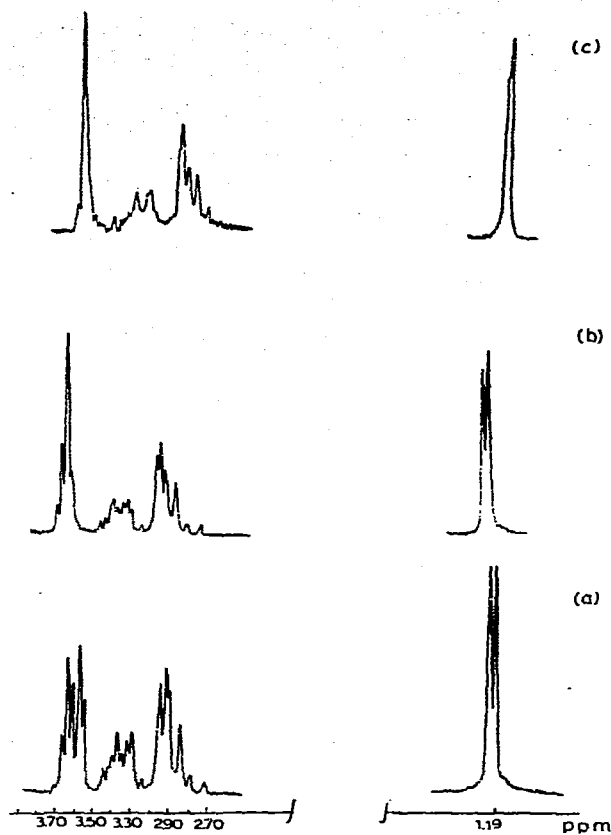


Fig. 7. The spectrum of compound (I) in C_6H_6 at 100 MHz; a. 20° , b. 56° , c. 97° .

EXPERIMENTAL

The NMR spectra were measured on JNM-C-60HL and JNM-4H-100 JEOL Model, HA-100D and HP-220 Varian Model instruments. Hexamethyldisiloxane was used as an internal standard. In the double resonance experiments the frequency sweep and the external lock were employed. The IR spectra were recorded on an UR-10 spectrometer. The mass-spectra were measured on an MX-1306 instrument at 115° , 10^{-7} mm, ionizing voltage 50 V, emission current 1.5 amp and accelerating voltage 2 kV.

The solvents employed were purified by general methods and distilled under an argon stream before use.

Reaction of 2-(bromomethyl)naphthalene with iron nonacarbonyl, synthesis of complex (I)

An equimolar mixture (0.027 mole) of 2-(bromomethyl)naphthalene (m.p. $53-54^\circ$), obtained by bromination of 2-methylnaphthalene with *N*-bromosuccinimide, and iron nonacarbonyl in 70 ml of hexane was stirred for 3.5–4 h at 45° under an argon atmosphere. The reaction was accompanied by complete dissolution of the carbonyl,

evolution of CO and precipitation of an orange-brown solid. The solution above the solid became yellow-orange in colour. The solid was filtered off and washed several times with hot hexane. The combined filtrate was evaporated *in vacuo* under stream of argon to remove the solvent and $\text{Fe}(\text{CO})_5$, and the residue subjected to thin layer chromatography on alumina (II activity grade) using petroleum ether/benzene (9/1) as the eluant. The complex (I) was eluted in the first yellow band and further crystallized from hexane or alcohol prior to subsequent analysis. The yield was 10.5% (accordingly Scheme 1(1a)). The second product, which was strongly retained in the chromatogram, was 1,3-di-2-naphthylacetone (30%, Scheme 1(1b)), m.p. 133–134° (from heptane). (Found: C, 88.88; H, 5.75. $\text{C}_{23}\text{H}_{18}\text{O}$ calcd.: C, 88.96; H, 5.84%) 2,4-dinitrophenylhydrazone, m.p. 132° (from glacial CH_3COOH).

Complexes (II), (III) and (IV) were prepared and isolated (~10%) in a similar fashion. Their analyses and other characteristics are shown in Table 1. 1-(Bromomethyl)naphthalene (m.p. 49–50°), required for the synthesis of (II), was prepared by bromomethylation of naphthalene. 1-Deuterated 2-(bromomethyl)naphthalene was obtained by bromination of 2-methylnaphthalene (1-Br-2- $\text{CH}_3\text{C}_{10}\text{H}_6$, b.p. 146–147°/10 mm), followed by further conversion of this compound to an organomagnesium derivative and decomposition of the latter by D_2O . The introduction of bromine into the side chains of 1-D-2- $\text{CH}_3\text{C}_{10}\text{H}_6$ and 1-Br-2- $\text{CH}_3\text{C}_{10}\text{H}_6$ was performed via bromosuccinimide. 1-D-2-Br $\text{CH}_2\text{C}_{10}\text{H}_6$, m.p. 53–54° (from heptane); 1-Br-2-Br $\text{CH}_2\text{C}_{10}\text{H}_6$, m.p. 106–107° (from CCl_4).

In a similar manner to compound (I), the respective ketones were prepared at the same time as the complexes in approximately the same yields (25–30%). The structure of the ketone obtained in a run with a mixture of 1- and 2-(bromomethyl)naphthalenes was not identified, m.p. 110° (from alcohol), (Found: C, 88.87; H, 5.80. $\text{C}_{23}\text{H}_{18}\text{O}$ calcd.: C, 88.96; H, 5.84%), 2,4-dinitrophenylhydrazone, m.p. 177–178° (from glacial CH_3COOH). The ketone of composition ($\text{C}_{10}\text{H}_6\text{BrCH}_2$) $_2\text{CO}$ had a m.p. 190° (from alcohol). (Found: C, 58.66; H, 3.50; Br, 33.13. $\text{C}_{23}\text{H}_{16}\text{Br}_2\text{O}$ calcd.: C, 58.99; H, 3.44; Br, 34.13%). The yields and structures of the carbonylation products are at present under investigation.

The mass-spectra of compounds (I) and (II) are quite similar and contain the following ion peaks: 422 (C_{11}H_9) $_2\text{Fe}(\text{CO})_3^+$; 394 (C_{11}H_9) $_2\text{Fe}(\text{CO})_2^+$; 366 (C_{11}H_9) $_2\text{Fe}(\text{CO})^+$; 338 (C_{11}H_9) $_2\text{Fe}^+$; 282 (C_{11}H_9) $_2^+$; 268 $\text{C}_{21}\text{H}_{16}^+$; 254 $\text{C}_{20}\text{H}_{14}^+$; 197 $\text{C}_{11}\text{H}_9\text{Fe}^+$; 141 $\text{C}_{11}\text{H}_9^+$; 28 CO^+ .

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