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SUBSTITUTION IN THE CYCLOPENTADIENIDE ANION SERIES

METHYLATION OF THE CYCLOPENTADIENIDE AND METHYLCYCLOPENTADIENIDE ANIONS[1]

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Abstract—It is shown that the cyclopentadienide anion can undergo an electrophilic substitution. In methylation reactions it was possible to stop the reaction at the intermediate 5-substituted cyclopentadiene stage. In the methylcyclopentadienide anion, the methyl group directs an electrophile to the adjacent carbon atom.

ALTHOUGH it is generally conceded that the presence of six π-electorns in a single ring[3] endows the cyclopentadienide anion with "aromatic" character, and this contention is supported by the calculated "resonance stabilization" of the system[4] and by the ability of the anion to "sustain an induced ring current"[5] (because it is negatively-charged and associated with a cation, the extent to which it can do so is difficult to estimate,[6] nevertheless, most commentators[7] have seriously doubted the possibility of demonstrating the aromaticity of the cyclopentadienenide anion in the classical sense, that is by the nature of its reactions. However, it appears obvious that it should be possible to demonstrate an electrophilic substitution, the most characteristic class of reactions of aromatic species, in the cyclopentadienide system by allowing the anion (I) to react with an electrophile (which, because of the charge on the anion, need only be weakly active) in a basic medium;[8] the anticipated sequence of events (I→II→III)

[1] Part of this work was reported at the XIXth *Congress of Pure and Applied Chemistry*. London, July (1963); cf. Abstract A 1–84.

[2] Holder of National Research Council (Canada) Scholarship 1963–64.

[3] E. Hückel, *Z. Phyzik.* **70**, 204 (1931).

[4] J. D. Roberts, A. Streitwieser and C. M. Regan, *J. Amer. Chem. Soc.* **74**, 4579 (1952); F. Combert-Farnoux and G. Berthier, *C.R. Acad. Sci., Paris* **248**, 688 (1959).

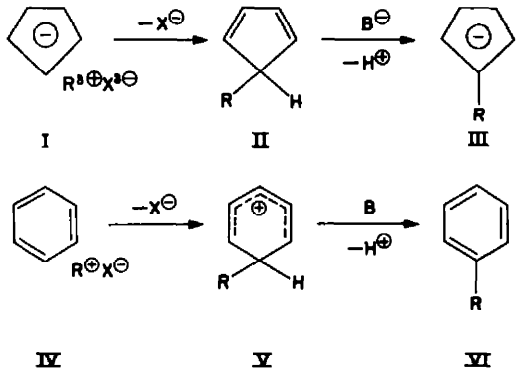
[5] J. A. Elvidge and L. M. Jackson, *J. Chem. Soc.* 859 (1961).

[6a] G. Fraenkel, R. E. Carter, A. McLachlan and J. H. Richards, *J. Amer. Chem. Soc.* **82**, 5846 (1960); [b] T. Schaefer and W. G. Schneider, *Canad. J. Chem.* **41**, 966 (1963); [c] S. McLean and P. Haynes, *Ibid.* **41**, 1231 (1963).

[7] e.g. E. S. Gould, *Mechanism and Structure in Organic Chemistry* p. 415. Holt, Rinehart and Winston, New York (1959); P. L. Pauson in *Non-benzenoid Aromatic Compounds* (Edited by D. Ginsburg) p. 113. Interscience, New York, N.Y., (1959); however, for an example of the opposite view, see M. E. Vol'pin, *Russ. Chem. Rev.* **29**, 129 (1960).

[8a] As the basicity of the cyclopentadienide species is reduced by appropriate substitution (e.g. D. Peters, *J. Chem. Soc.* 1757 (1959); R. C. Cookson, J. Hudec and B. Whitear, *Proc. Chem. Soc.* 117 (1961)) it should be possible to make the reaction conditions resemble more and more those used for a system such as benzene (or at least one of its more reactive derivatives); [b] It has already been demonstrated that in certain special cases, e.g. triphenylphosphoniumcyclopentadienylide (cf. F. Ramirez and S. Levy, *J. Amer. Chem. Soc.* **79**, 6167 (1957)) and diazocyclopentadiene (the analog is this system of the benzenediazonium ion) (cf. D. J. Cram and R. D. Partos, *Ibid.* **85**, 1273 (1963)), common aromatic substitution reactions can be effected.

is clearly the complete analog in a charged system of an electrophilic substitution on benzene (IV→V→VI).



While it is true that a similar reaction sequence may be predicted for a number of other carbanions for which there can be no suggestion of aromatic character, it was still of interest to us to establish experimentally that a reaction parallel to an electrophilic substitution on benzene could take place on the cyclopentadienide ring. It is clear that such an experiment really only reflects the general nature of electrophilic substitution: electrophilic attack on a substrate (e.g. I or IV) will lead to a substitution when the species (e.g. II or V) resulting from the attack has a path available which can lead, by ejection of a leaving group, to a product (e.g. III or VI) that is more stable than the intermediate in the environment produced. Nevertheless, if the analogy with the reactions in the benzene series can be established, it should be possible to compare the course of corresponding reactions in the charged and in the uncharged systems. How substituents already present on the ring influence the rate and direction of attack of an electrophile has been the first problem of this sort to engage our attention. Our immediate objective has been a study of reactions in which a weakly electrophilic methyl group (e.g. in CH_3I) was the attacking species and the substrate was first the cyclopentadienide anion and then the methylcyclopentadienide anion. It was also of interest to determine whether reactions could be terminated at the intermediate (e.g. II); this was particularly intriguing since there appeared to be no well-authenticated examples of 5-mono-substituted cyclopentadienes reported in the literature at the start of this work (several have now been reported[9]).

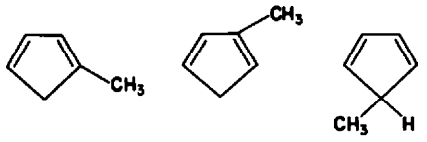
RESULTS

Methylation of sodium cyclopentadienide

The anticipated reaction of sodium cyclopentadienide with methyl iodide in the presence of base should lead to sodium methylcyclopentadienide (and other products). Although it has been possible to examine reactants and products spectroscopically,[6] it was experimentally convenient to protonate the products at the end of the reaction

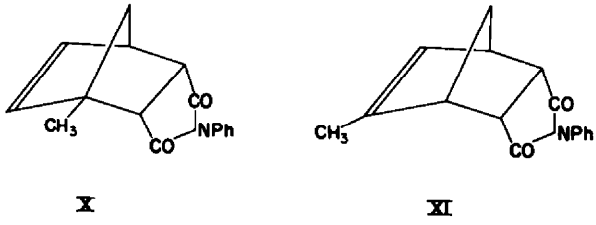
[6a] V. A. Mironov, E. V. Sobolev, and A. N. Elizarova, *Tetrahedron* **19**, 1939 (1963); [b] V. A. Mironov, E. V. Sobolev and A. N. Elizarova, *Dokl. Akad. Nauk. S.S.S.R.* **146**, 1098 (1962); [c] V. A. Mironov, M. V. Mavrov and A. N. Elizarova, *Zh. Obshch. Khim.* **32**, 2723 (1962) (*J. Gen. Chem.* **32**, 2680 (1962)); V. A. Mironov and A. N. Elizarova, *Zh. Obshch. Khim.* **32**, 2731 (1962) (*J. Gen. Chem.* **32**, 2688 (1962)); [d] G. Kresze, G. Schulz and H. Walz, *Liebigs Ann.* **666**, 45 (1963).

and examine the dienes produced. The methylcyclopentadienide anion (III; R = Me) can, in principle, lead to three methylcyclopentadienes, the 1-, 2-, and 5-isomers (VII, VIII and IX respectively). We have shown,[6,10] by allowing the mixture of

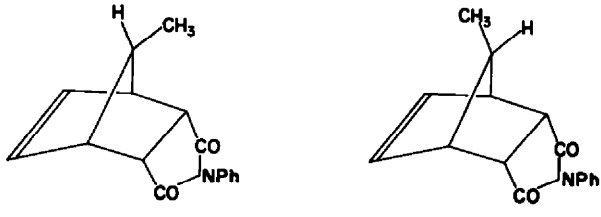


VII VIII IX

methylcyclopentadienes obtained from the commercial dimer to equilibrate in the presence of a small amount of sodium methylcyclopentadienide, that the equilibrium distribution of methylcyclopentadienes contains VII and VIII in the ratio 0·82:1 and IX constitutes 1% or less of the equilibrium mixtures. Prior to this study attempts had been made to identify the isomeric methylcyclopentadienes either as the free dienes[11] or their Diels-Alder adducts,[12] but none was completely satisfactory. In the present study we have separated the isomers using Csicsery's[11] conditions of vapour phase chromatography on dimethylsulpholane. The diene (λ_{max} 249 mμ) with retention time[13] 2·71 was shown to be 1-methylcyclopentadiene (VII); in the NMR it showed a doublet (J = 1·7 c/s) at 8·04τ (CH_3), a multiplet at 7·30τ (2 methylene protons), and a complex pattern from 3·6 to 4·0τ (3 vinyl protons). With N-phenylmaleimide it formed an adduct (X), m.p. 179–180°, the NMR spectrum of which included an unsplit CH_3 signal (8·40τ) and signals arising from two non-equivalent



X XI



XII XIII

[10] S. McLean and P. Haynes, *Tetrahedron* (21, 2329 (1965) *with this paper*); *Tetrahedron Letters* 2385 (1964).

[11] S. M. Csicsery, *J. Org. Chem.* 25, 518 (1960).

[12a] W. J. Craven, Ph.D. Dissertation, Cornell University (1955); [b] S. McLean, Ph.D. Dissertation, Cornell University (1958).

[13] Throughout this paper retention times for methyl- and dimethylcyclopentadienes are given relative to cyclopentadiene = 1·00; cf. Experimental section.

vinyl protons, one of which was split by a third proton (3·93τ; an AB quartet, J = 6·0 c/s, with internal chemical shift of 11·4 c/s; the low field half of the quartet was split further into a pair of doublets, J = 2·5 c/s). It was not possible to isolate enough of the second diene (λ_{max} 242 mμ) with retention time[13] 2·42 to obtain an NMR spectrum. However, its spectrum could be deduced by subtracting the spectrum of VII from that of the mixture of isomers; the spectrum that remained consisted of a multiplet at about 8·05τ (CH_3), a multiplet at 7·20τ (2 methylene protons), and a complex pattern (3 protons) in the vinyl region, consisting of two closely-spaced peaks (1·7 c/s spacing) at 3·69τ and a multiplet (at least six lines with 1·7 c/s spacing) at 4·10τ. The NMR spectrum of its N-phenylmalemide adduct (XI), m.p. 128–129·5°, established that this was 2-methylcyclopentadiene (VIII) since the spectrum showed a doublet (J = 1·8 c/s) at 8·18τ (CH_3 at a double bond) and the signal for only one vinyl proton as an unresolved multiplet at 4·24τ. The adducts formed by each diene with maleimide served to corroborate the assignments. These results confirm the structural assignments made for the components isolated by fractional crystallization of the mixture of adducts obtained from commercial methylcyclopentadiene[12,14] and for the parent dienes on the basis of their UV spectra.[11] The third isomeric diene (λ_{max} 245 mμ) with retention time[13] 1·36 (Csicsery's assignment[11] is in error in this case) was shown unequivocally to be 5-methylcyclopentadiene (IX); its NMR spectrum showed a doublet (J = 7·8 c/s) at 8·92τ (CH_3), two broad peaks at 6·97τ (the spacing was 7·8 c/s and the signal was presumably part of a quartet but the inevitable appearance in this region of signals from rearrangement products[10] obscured the rest of the pattern), and a single unresolved peak at 3·65τ (4 vinyl protons). With N-phenylmaleimide it formed two isomeric adducts (XII and XIII) which were extremely difficult to separate from each other. The NMR spectrum of the mixture of adducts (m.p. 110–119°) in $CHCl_3$ included a doublet at 9·11τ (J = 6·3 c/s) and two sets of signals in the vinyl proton region, a triplet at 3·71τ and a triplet which showed further splitting at 3·87τ. It became clear that the 9·11τ signal was composed of two coincident but distinguishable methyl signals since gradual addition of benzene to the solution caused both signals to move to higher field, but they did so at different rates, and consequently resolved into two distinct doublets (each with J = 6·3 c/s). Changes were apparent in other parts of the spectrum also, and we hope to be able to comment on them in detail in a later paper; they are closely similar to those recorded recently by Laszlo and Schleyer[15] for other bicycloheptene derivatives. The spectrum of the mixture showed that the two isomers were present in about equal amounts, suggesting that the 5-methyl group of IX had little steric influence on the course of the Diels-Alder reaction, and it was possible to obtain a pure sample of one of them by fractional crystallization. This adduct, m.p. 130–132°, showed the more complex 3·87τ vinyl signal (two protons) and its methyl signal was less affected than that of its isomer by the addition of benzene. On the basis of these observations it is possible to assign tentatively structure XIII to the isolable adduct and structure XII to its isomer; the mother liquors were considerably enriched in the latter, but it was not possible to isolate XII uncontaminated

[14] Direct comparison showed that the "116° N-phenylmaleimide adduct" reported consisted of XI contaminated with some X. It appears to be generally true that adducts of this class are difficult to separate by fractional crystallization, and pairs of isomers frequently form constant-melting mixtures.

[15] P. Laszlo and P. von R. Schleyer, *J. Amer. Chem. Soc.* **86**, 1171 (1964).

by XIII. Our results confirm the assignments of structure of methylcyclopentadienes made by Mironov using IR and Raman spectroscopy.[9a,b] In our present study we have identified the products of methylation reactions by their characteristic retention times on dimethylsulpholane, and, when necessary, we have used UV, mass spectrometry, and conversion to a characterized N-phenylmaleimide adduct for confirmation.

Methyl iodide (or methyl sulphate) was allowed to react with an equivalent amount of sodium cyclopentadienide (prepared from cyclopentadiene and sodium amide) dissolved in liquid ammonia containing an excess of sodium amide; the anionic products were converted to dienes, which separated as a second phase, by the addition of ammonium chloride. The diene mixture consisted of cyclopentadiene, the equilibrium distribution of isomeric methylcyclopentadienes, and more highly methylated cyclopentadienes.[16,17] This experiment alone establishes that the cyclopentadienide anion has undergone electrophilic substitution (as in I→III) under these reaction conditions and that the product anion (III; R = Me) was susceptible to further substitution.

It was of interest to observe how product composition varied under different reaction conditions, and in particular to determine what conditions were necessary to stop the reaction at II. In liquid ammonia in the absence of excess sodium amide, product dienes separated directly as a second phase; by increasing the proportion of methyl iodide to sodium cyclopentadienide the yield of cyclopentadiene could be reduced and that of polymethylcyclopentadienes increased, but the isomeric methylcyclopentadienes were always obtained in their equilibrium proportions. Similar results were obtained when methyl iodide (or methyl sulphate) was added to sodium cyclopentadienide in ether solvents such as tetrahydrofuran or dimethoxyethane, or in dimethylsulphoxide. These observations provide evidence that the substitution reaction (I→III) can take place even in the absence of added base; the base required to convert II to III and thus allow further substitution to take place is presumably unchanged cyclopentadienide anion.[6c,18] Under various conditions of temperature and concentration for reactions in dimethoxyethane and dimethylsulphoxide ratios of VII to VIII other than the equilibrium value were sometimes found, but the variations did not follow a consistent pattern. When inverse addition was employed, that is, a solution of sodium cyclopentadienide in dimethoxyethane was added slowly to methyl iodide, ratios of VII to VIII much larger than the equilibrium value were obtained, but no appreciable increase in IX was observed until extreme care was taken, particularly in the control of temperature during reaction and work-up. If sodium cyclopentadienide in an ether solvent was slowly added to excess methyl iodide (or

[16] S. McLean and P. Haynes, *Tetrahedron* **21**, 2343 (1965).

[17] A study of alkylations of cyclopentadiene by methods similar to ours has been reported, but isomer distributions were generally not determined. Our results relating to the polysubstitution reactions and the conclusions drawn from them are at variance with those reported previously, cf. R. Riemschneider and E. B. Grabitz, *Monatsh*, **89**, 748 (1958); R. Riemschneider and R. Nehrin, *Ibid.* **91**, 824 (1960), and other papers in the series.

[18] Riemschneider has observed alkylation of cyclopentadiene in liquid ammonia even in the absence of $NaNH_2$ and has proposed the intermediacy of ammonium cyclopentadienide; cf. R. Riemschneider and R. Schonfelder, *Z. Naturforsch.* **18b**, 979 (1963). Thus, it is possible in liquid ammonia that the solvent is a strong enough base to account for polymethylation; this should not apply to the other solvents.

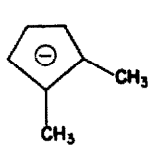
methyl sulphate) in the same solvent at −10 to −15° and the reaction mixture carefully distilled under reduced pressure at the same temperature, the distillate consisted of solvent, methyl iodide, and 5-methylcyclopentadiene (IX); the latter was identified by converting it to its N-phenylmaleimide adducts (XII and XIII). The best experimental conditions found for synthesis of IX simply used diglyme (diethylene glycol dimethyl ether) as the solvent and methyl sulphate as methylating agent; the distillate was then almost pure 5-methylcyclopentadiene[9a,b] and a trace of diglyme.

It was then shown, in agreement with Mironov's report[9a,b] that 5-methylcyclopentadiene (IX) rearranged very rapidly to VII which then rearranged more slowly to VIII, both steps being accelerated in the presence of a strong base; the rate of rearrangement is strongly temperature dependent, IX being quite stable below 0° in the absence of base, but rearranging rapidly at room temperature.[10] We found that IX rearranged under even the most gentle VPC conditions we could employ; this partially vitiates some of our earlier results[1] regarding the detailed nature of the isomer distribution among methylcyclopentadiene products, but the results are not worthless since we had established at an early stage that both VII and VIII showed no sign of rearranging on the column and kept their own characteristic retention times when injected separately or together. It follows that those chromatograms showing a large VII to VIII ratio reflected a reaction that produced mainly IX which rearranged subsequently, while those showing an equilibrium distribution of VII and VIII reflected a reaction in which IX rearranged during the reaction.

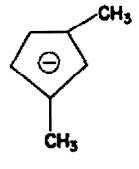
These data allow us to explain rationally what had been previously a very perplexing series of results.[1] Sodium cyclopentadienide reacts with methyl iodide to form IX which can rearrange by an intramolecular hydrogen shift[9a,b,10] to VII, which can rearrange further more slowly and ultimately lead to the equilibrium distribution of isomers. In the presence of base (sodium cyclopentadienide) the formation of III (R = Me) becomes possible and the rearrangement is accelerated; III can in turn revert to the equilibrium mixture of methylcyclopentadienes, or react further to give polymethylcyclopentadienes. The isolation of small yields of a polymethylcyclopentadiene fraction even in some reactions employing inverse addition presumably shows that the sodium cyclopentadienide persisted in the reaction mixture long enough to react with some of the methylcyclopentadiene product. We are at present studying the kinetics of the methylation reaction and our results should help to resolve this question.

Methylation of sodium methylcyclopentadienide

Substitution on the methylcyclopentadienide anion (III; R = Me) under the conditions described above can lead to two isomeric dimethylcyclopentadienide anions (XIV and XV) of equal statistical probability; the observed composition of the product mixture should, therefore, reflect the directing influence of the substituent

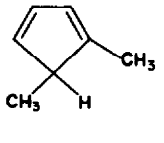


XIV

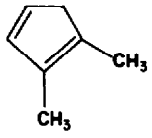


XV

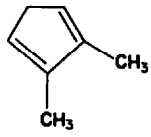
initially present. Protonation of XIV could lead to three isomeric dienes, XVI (which is also the intermediate analogous to II in the substitution reaction), XVII and XVIII; in a similar way, XV could give rise to XIX (the substitution intermediate), XX and XXI.



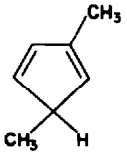
XVI



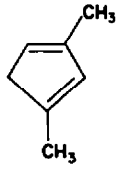
XVII



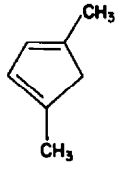
XVIII



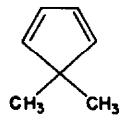
XIX



XX



XXI



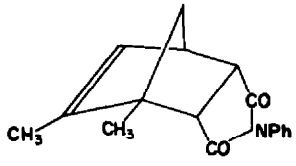
XXII

A seventh possible diene, XXII, could arise from electrophilic attack at C-1 in III (R = Me), a process that could not resolve effectively into a substitution

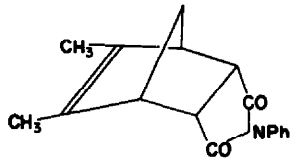
The reaction of sodium methylcyclopentadienide with methyl iodide in the presence of excess sodium amide gave, after the reaction mixture had been treated with ammonium chloride, a methylcyclopentadiene fraction (5·5%), dimethylcyclopentadienes XVII, XVIII, XX and XXII in the ratio 2·0:1·5:1·0:0·1 (total yield 40%), and more highly substituted products. The dimethylcyclopentadiene fraction reflected a substitution reaction resulting in the formation of XIV and XV in the ratio 3·5:1, accompanied by a non-substitution reaction leading to XXII. Varying the solvent, ratios of reactants, mode of addition, and other reaction conditions produced changes in product composition closely analogous with those observed in the reactions of sodium cyclopentadienide; that is, the composition showed the extent to which isomerization by hydrogen migration had taken place. However, in every case, if one considers only the positions of the methyl substituents relative to each other, the isomer distribution showed that electrophilic attack on III (R = Me) took place predominantly at the β carbon, less effectively at the γ carbon, and to only a small extent at the α carbon. When the conditions required to stop the reaction of sodium cyclopentadienide at IX were recognized, they could be adapted to the isolation of a mixture of XVI, XIX and XXII in the corresponding reaction of sodium methylcyclopentadienide. The isomer distribution, XVI:XIX:XXII = 3·45:1·0:0·45, showed the positional selectivity of electrophilic attack on III under the conditions used; the rather high proportion of XXII obtained probably resulted from some fractionation during distillation of products from the reaction mixture, but it might be expected that the XVI:XIX ratio would not change appreciably during this process.

The products of these reactions were again recognized by their VPC characteristics and assignments were confirmed where possible by converting the dienes to their

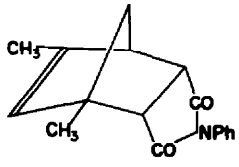
N-phenylmaleimide adducts. 1,2-Dimethylcyclopentadiene[9a,19] (XVII), λ_{max} 250·5 mμ, with relative retention time[13] 6·59, was carefully isolated by VPC; it formed an N-phenylmaleimide adduct (XXIII), the NMR spectrum of which included a singlet at 8·44τ (bridgehead CH_3), a doublet (J = 1·8 c/s) at 8·28τ (CH_3 at a double bond), and an unresolved multiplet at 4·18τ (one vinyl proton). 2,3-Dimethylcyclopentadiene[9a,19] (XVIII), λ_{max} 241·5 mμ, with relative retention time[13] 7·27, was isolated in a similar manner and converted to its N-phenylmaleimide adduct (XXIV), the NMR spectrum



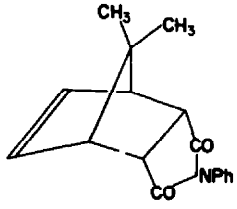
XXIII



XXIV



XXV



XXVI

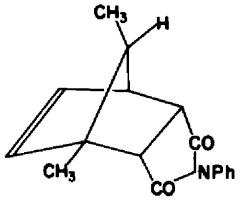
of which included a singlet at 8·31τ (two equivalent CH_3 groups at a double bond) but showed no signal attributable to vinyl protons. It was necessary to exercise a considerable amount of care in isolating XVII and XVIII since they underwent isomerization on heating to form, eventually, an equilibrium mixture of XVII and XVIII (1·4:1).[10] This mixture of XVII andXVIII was also formed when 2,3-dimethyl-2-cyclopentenol was dehydrated; the 1,2 relationship of the methyl substituents was therefore confirmed. It was not possible to isolate 1,3-dimethylcyclopentadiene (XX), in satisfactory amounts from the methylation reactions to characterize it completely: material from the peak of retention time[13] 6·08 in the chromatogram had a mol. wt. of 94 (mass spectrometry[20]); its retention time corresponded exactly with that of synthetic XX,[12b] and its UV spectrum (λ_{max} 247·5 mμ) agreed closely with that of the synthetic material which had λ_{max} 248·5 mμ. Synthetic XX was prepared by the reaction of 3-methyl-2-cyclopentenone with methyl magnesium bromide followed by dehydration of the alcohol;[12b] it formed an N-phenylmaleimide adduct (XXV), the NMR spectrum of which included a singlet at 8·44τ (bridgehead CH_3), a doublet (J = 1·5 c/s) at 8·20τ (CH_3 at a double bond), and an unresolved multiplet at 4·43τ (one vinyl proton). 5,5-Dimethylcyclopentadiene (XXII), λ_{max} 250 mμ, retention time[13] 1·32 formed an N-phenylmaleimide adduct (XXVI) identical in every respect

[19] K. Alder and H. J. Ache, *Chem. Ber.* **95**, 505 (1962); L. Skattebol, *Chem. & Ind.* 2146 (1962).
[20] We thank Mr. F. Meyer and Dr. A. G. Harrison of this Department for this determination.

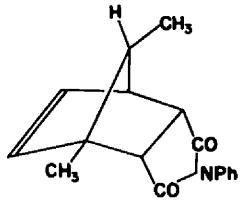
with material obtained from synthetic XXII;[21] the NMR spectrum of the adduct included a slightly broadened peak at 8·95τ (2 non-equivalent CH_3 groups at C-7) and a narrow multiplet at 3·81τ (2 vinyl protons).

1,5-Dimethylcyclopentadiene (XVI) and its 2,5-isomer (XIX) were always obtained together and they could not be isolated separately since they were unstable under the VPC conditions used. Their retention times[13] (3·46 and 3·00 respectively) were determined by chromatographing a sample of the mixture of isomers, recording the position of the peaks, and collecting the effluents. Rearrangement on the column caused the peaks to be badly broadened, but it was possible to show that, by the time it could be collected, material from the peak with retention time 3·46 produced a mixture of adducts XXIII, XXVII and XXVIII, demonstrating that the peak was associated with XVI. The other isomer (XIX) was identified by demonstrating that it rearranged to XX. The NMR spectrum of the mixture of XVI and XIX was interpreted using the information available concerning the composition of the mixture to help in the assignment of peaks to specific compounds. On this basis and by the application of experience gained with related compounds, the assignments were: for XVI, a doublet (J = 7·8 c/s) at 8·95τ (C-5 methyl) and a doublet (J = 1·5 c/s) at 8·10τ (C-1 methyl); for XIX, a doublet (J = 7·8 c/s) at 8·93τ (C-5 methyl) and a multiplet near 8·10τ (C-2 methyl); both isomers show their C-5 protons near 7·2τ (unresolved) and their vinyl protons between 3·6 and 4·1τ, but it was not possible to make complete individual assignments in these cases.

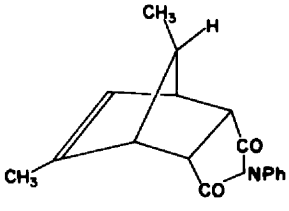
Reaction of the mixture of XVI and XIX with N-phenylmaleimide gave a mixture of adducts containing, presumably, XXVII, XXVIII, XXIX and XXX. The NMR



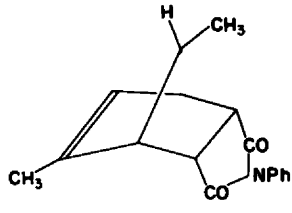
XXVII



XXVIII



XXIX



XXX

spectrum of the mixture of adducts showed methyl signals at 8·19τ (doublet; J = 1·8 c/s), 8·54τ (singlet), and 9·19τ (doublet; J = 6·3 c/s). Fractional crystallization

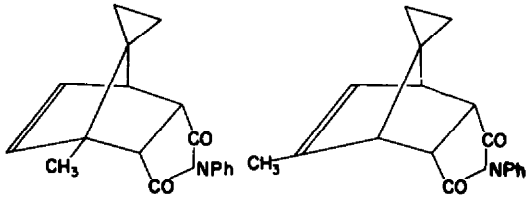
[21] C. F. Wilcox and M. Mesirov, *J. Org. Chem.* **25**, 1841 (1960). We thank Dr. Wilcox for a reference sample of the adduct.

of the mixture led to the isolation of an adduct, m.p. 173–174°, the NMR spectrum of which included a doublet (6·3 c/s) at 9·19τ (CH_3 at C-7) and a singlet at 8·54τ (bridgehead CH_3). This isomer was tentatively assigned structure XXVII on the basis of its NMR behaviour which resembled that of XIII (see above). It was not possible to isolate pure samples of the other adducts.

Reaction of sodium methylcyclopentadienide with dibromoethane

Early in our study we recognized that the reaction of sodium methylcyclopentadienide with dibromoethane offered several operational advantages. In the first stage of this reaction, the attack of —CH_2Br at the β or γ positions in III (R = Me) should be essentially identical with the methylation reaction; however, by analogy with the reaction of the unsubstituted case,[22] reaction of the second —CH_2Br at the same ring position should produce a methylspiroheptadiene (XXXI or XXXII); only two isomers are possible, and from their relative yields the positional selectivity for electrophilic attack by —CH_2Br on III (R $\neq$ Me) can be deduced. This reaction has in fact been described previously,[22b] but only one isomer (XXXI) was isolated.

XXXI XXXII



XXXIII XXXIV

When the reaction was carried out in liquid ammonia, 1-methylspiroheptadiene (XXXI) and its 2-methyl isomer (XXXII) in the ratio 2·8:1 were separated by VPC. The 1-methyl isomer (XXXI), $\lambda\lambda_{max}$ 263, 218 mμ, was isolated and converted to its N-phenylmaleimide adduct (XXXIII), m.p. 135–135·5°, the NMR spectrum of which established the structure of the adduct and consequently of the parent diene; it showed a single, slightly broadened peak at 9·52τ (four cyclopropyl protons), a singlet at 8·78τ (bridgehead CH_3), and the pattern for two non-equivalent vinyl protons, one of which was split by a third proton (cf. X) (3·77τ; an AB quartet, J = 6·0 c/s, with internal chemical shift 10·4 c/s: the low field half of the quartet was split further into a pair of doublets, J = 2·8 c/s).

[22a] R. Y. Levina, N. N. Mezentsova and O. V. Lebeda, *Zh. obschch. Khim.* **29**, 1097 (1955); B. F. Hallam and P. L. Pauson, *J. Chem. Soc.* 646 (1958); [b] K. Alder, H. J. Ache and F. H. Flock, *Chem. Ber.* **93**, 1888 (1960).

2-Methylspiroheptadiene (XXXII), $\lambda\lambda_{max}$ 259, 222 mμ, formed an N-phenylmaleimide adduct (XXXIV), m.p. 114–114·5°, that was characterized by its NMR spectrum: a doublet (J = 1·8 c/s) at 8·14τ (CH_3 at a double bond), an unresolved multiplet at 4·13τ (one vinyl proton) and a closely-spaced multiplet at 9·45τ (four cyclopropyl protons).

Unfortunately, yields were low (approximately 30%) in the reaction and it is not possible to give a complete account of the products of higher molecular weight. Consequently, the ratio of XXXI to XXXII in the isolated material may have been influenced by differences in the extent to which the monobromo precursors were involved in side reactions. However, the value obtained (2·8:1) is in general agreement with the results of simple methylation (3·5:1 is the comparable value), and indicates preferential reaction at the α position.

DISCUSSION

We have demonstrated that a cyclopentadienide anion can be subjected to electrophilic substitution by a weak electrophile; thus III (R = Me) may be formed from I. In the absence of an appropriate base, the reaction can be terminated at an intermediate stage (e.g. II). When a methyl substituent is already present on the ring (e.g. III; R = Me), it exerts a directing influence on the electrophile, and in this case, the order of positional selectivity is $\beta > \gamma > \alpha$, the attack at β being about 3·5 times more effective than attack at γ, while the α position appears to be the least susceptible to attack, probably being about five times less susceptible than γ, allowing for the statistical factor.

The selectivity follows the order of electron densities at the different sites than can be calculated using a simple Hückel molecular orbital treatment,[23] and it is natural to suspect that the differences in electron density lead to the positional selectivity. This would imply a transition state which retains much of the character of the reactants. It is of interest then to note that, in related systems where the substituent on the cyclopentadienide ring is electron-withdrawing, the positional selectivity follows the same order. At least as far as the β and γ positions are concerned, the order is opposite to that expected if steric effects were decisive, regardless of the nature of the substituent. Of particular interest is the discussion of substitution on diazocyclopentadiene by Cram and Partos[8b] who explain their results by postulating a transition state that resembles product, that is, the reaction intermediate corresponding to II (or XVI or XIX). It might have been expected that a similar argument could have been applied to substitution on the methylcyclopentadienide anion, invoking hyperconjugation by CH_3 as the deciding influence (i.e. to choose between XVI and XIX), but the evidence[10] we have available concerning the effect of a methyl substituent on the diene would then indicate that γ attack should be preferred (rather than the observed β attack) since 2-methylcyclopentadiene (VIII) predominates slightly in the equilibrium with its 1-methyl isomer (VII). It is instructive to note that Rosenblum and Howells[24] have carried out molecular orbital calculations of localization energies for reaction sites in

[23] Electron densities at the ring positions of III (R = Me) were calculated to be α1·01, β1·28, γ1·22; this calculation used the inductive parameter for CH_3 recommended by Streitwieser; cf. A. Streitwieser, Jr., *Molecular Orbital Theory for Organic Chemists* p. 135. J. Wiley, New York, N.Y. (1961).

[24] M. Rosenblum and W. G. Howells, *J. Amer. Chem. Soc.* **84**, 1167 (1962).

ferrocenes carrying electron-donating and electron-withdrawing substituents; they use the cyclopentadienyl radical as a model (and note that results for the anion are similar), and conclude that, regardless of the nature of the substituent, the 2-position is more reactive toward electrophilic substitution than the 3-position. It will be necessary to have available a greater body of data in order to test these generalizations and predictions; we hope to continue our studies of the reactions of cyclopentadienide anions with this end in view.

EXPERIMENTAL

An F and M Model 500 Gas Chromatograph was used for VPC work; NMR spectra were recorded on a Varian A-60 Spectrometer, and a Bausch and Lomb 505 Spectrometer was used to obtain UV spectra. M.ps. were normally determined on a micro hot stage.

Reagents and solvents. Cyclopentadiene and a mixture of methylcyclopentadienes were obtained by thermally cracking the appropriate dimer[25] (170° and 200°, respectively). Tetrahydrofuran and diglyme (diethylene glycol dimethyl ether) were distilled from LAH under a N_2 atm;[26] dimethoxyethane was similarly distilled from Na wire. These solvents were stored over Na-wire and finally dried with molecular sieves prior to use. Dimethylsulphoxide was dried with molecular sieves.

Analysis by vapour phase chromatography. Methylation products were analysed on an 8′ × ¼″ column of 30% dimethylsulpholane on firebrick at 27° with 55 ml/min He as carrier gas.[11] Components were recognized by their retention times and assignments were confirmed by peak enhancement with authentic material where possible, and by allowing the several fractions to accumulate in dry ice traps and then converting them to crystalline N-phenylmaleimide[27] adducts. Relative retention times (measured from the initial air peak) were: cyclopentadiene = 1·00 (by definition), methyl iodide 1·32, 5-methylcyclopentadiene (IX) 1·36, 2-methylcyclopentadiene (VIII) 2·42, 1-methylcyclopentadiene (VII) 2·71, 5,5-dimethylcyclopentadiene (XXII) 1·32, 2,5-dimethylcyclopentadiene (XIX) 3·00, 1,5-dimethylcyclopentadiene (XVI) 3·46, 1,3-dimethylcyclopentadiene (XX) 6·08, 1,2-dimethylcyclopentadiene (XVII) 6.59, 2,3-dimethylcyclopentadiene (XVIII) 7·27, tetrahydrofuran 3·9, and dimethoxyethane 9·0 (positions of solvent peaks varied because of column overloading); diglyme and dimethylsulphoxide had considerably longer retention times. Other compounds obtained in the experiments described here were shown to be mainly polymethylcyclopentadienes[16] and small amounts of cyclopentenes.

Spiroheptadienes (and polymethylcyclopentadienes[16]) were analysed using 9′ × ¼″ column of 20% MEEE ($(MeOCH_2CH_2OCH_2CH_2)_2O$) on Chromosorb P (60–80 mesh) at 50° with 80 ml/min He as carrier gas.

It was assumed that, for the sets of dienes investigated, relative yields were linearly related to areas of peaks. This was confirmed for the more abundant products by remixing and reinjection.

Reactions in liquid ammonia

Sodium cyclopentadienide. Solutions of $NaNH_2$ (0·7 molar) in liquid ammonia were prepared by treating Na in liquid ammonia with catalytic amounts of a ferric salt. The apparatus consisted of a 3-necked flask equipped with a stirrer, a reflux condenser, and a dropping funnel; the apparatus was cooled in dry ice and acetone and protected from the atmosphere by drying tubes. The calculated amount of freshly-prepared cyclopentadiene was slowly added to the stirred $NaNH_2$ solution and stirring was continued for one hour; a homogeneous solution of sodium cyclopentadienide was obtained.

Sodium methylcyclopentadienide (0·7 molar) in liquid ammonia was prepared in the same way from the mixture of methylcyclopentadienes.

Methylation of sodium cyclopentadienide

(a) In presence of excess $NaNH_2$: MeI (14·2 g; 0·1 mole) was added dropwise to a stirred solution of sodium cyclopentadienide (0·1 mole) and $NaNH_2$ (0·2 mole) in liquid NH_3; the reaction

[25] Methylcyclopentadiene dimer was kindly donated by the Enjay Chemical Company, New York, N.Y.

[26] H. R. Watson, *Chem. & Ind.* 665 (1964).

[27] Maleimide and N-phenylmaleimide were kindly donated by the United States Rubber Company, Wayne, New Jersey.

mixture formed a single phase system. After 45 min, excess sat. NH_4Cl aq was carefully added to the solution and an organic layer then appeared; this was separated and analysed by VPC. It consisted of cyclopentadiene (14%), 1- and 2-methylcyclopentadienes in the ratio VII:VIII = 0·85:1 (57%), and other products (mainly higher homologs). When injected separately, VII and VIII retained their characteristic retention times and gave no evidence of rearrangement on the column. 1-Methylcyclopentadiene[36a,b] (VII), λ_{max}^{MeOH} 249 mμ (ε 4,200), reacted with N-phenylmaleimide in benzene to form an adduct (X), m.p. 179–180° (recrystallized from hexane). (Found: C, 76·11; H, 5·93; N, 5·68. $C_{16}H_{13}O_2N$ requires: C, 75·87; H, 5·97; N, 5·53%.) In a similar manner VII formed a maleimide adduct, m.p. 130–131°, (Found: C, 67·70; H, 5·96; N, 8·16. $C_{10}H_{11}O_2N$ requires: C, 67·78; H, 6·26; N, 7·91%). 2-Methylcyclopentadiene[36a,b] (VIII), λ_{max}^{MeOH} 242 mμ (ε 3,700) formed an N-phenylmaleimide adduct (XI), m.p. 128–129·5° (prior sublimation) (recrystallized from hexane). (Found: C, 76·02; H, 5·72; N, 5·62. $C_{16}H_{15}O_2N$ requires: C, 75·87; H, 5·97; N, 5·53%), and a maleimide adduct, m.p. 160–161° (sealed tube), (Found: C, 67·77; H, 6·11; N, 8·10. $C_{10}H_{11}O_2N$ requires: C, 67·78; H, 6·26; N, 7·91%).

(b) In absence of excess $NaNH_2$: MeI (14·2 g; 0·1 mole) was added dropwise to a stirred solution of sodium cyclopentadienide (0·1 mole) in liquid NH_3. Two layers formed and after 15 min the organic layer was analysed by VPC. It consisted of cyclopentadiene (2·5%), 1- and 2-methylcyclopentadienes in the ratio VII:VIII = 0·83:1 (80%), and other products. When the amount of MeI was doubled, the product consisted of cyclopentadiene (trace), 1- and 2-methylcyclopentadienes in the ratio VII:VIII = 0·81:1 (50%) and other products (principally higher homologs). Substitution of Me_2SO_4 for MeI did not produce a significant change in reaction products under comparable conditions.

Methylation of sodium methylcyclopentadienide

Methyl iodide (21·3 g; 0·15 mole) was added dropwise to a stirred solution of sodium methylcyclopentadienide (0·1 mole) in liquid NH_3. Two layers formed and after 1 hr the organic layer was analysed by VPC. It consisted of methylcyclopentadienes, dimethylcyclopentadienes in the following relative amounts: 1,5-(XVI) 24·8%, 1,2-(XVII) 27·4%, 2,3-(XVIII) 24·8%, 2,5-(XIX) 7·3%, 1,3-(XX) 13·4%, 5,5-(XXII) 2·3%, and other products (probably mainly polymethylcyclopentadienes), but the limitations of the column did not allow an accurate measure of the yield of the latter. The precise distribution of dimethylcyclopentadiene isomers was very sensitive to the conditions employed. When excess $NaNH_2$ was present during the reaction, or the products, b.p. 94–106°, were distilled before analysis, the 1,5-(XVI) and 2,5-(XIX) isomers (*vide infra*) were absent and the dimethylcyclopentadiene fraction consisted of the 1,2-, 2,3-, and 1,3-isomers in the ratio XVII:XVIII:XX = 2·0:1·5:1·0, and a trace of 5,5-dimethylcyclopentadiene (*vide infra*). Regardless of the conditions however, the dimethylcyclopentadienes were always found in the ratio (XVI + XVII + XVIII: XIX + XX) = 3·5(±0·2):1.

1,2-Dimethylcyclopentadiene[36a] (XVII), λ_{max}^{MeOH} 250·5 mμ,[38] formed an N-phenylmaleimide adduct (XXIII), m.p. 122–123° (prior sublimation) (recrystallized from hexane). (Found: C, 76·27; H 6·50; N, 5·19. $C_{17}H_{17}O_2N$ requires: C, 76·40; H, 6·41; N, 5·24%.) 2,3-Dimethylcyclopentadiene (XVIII), λ_{max}^{MeOH} 241·5 mμ, formed an N-phenylmaleimide adduct (XXIV), m.p. 126–127·5° (prior sublimation) (recrystallized from hexane). (Found: C, 76·37; H, 6·22; N, 5·27. $C_{17}H_{17}O_2N$ requires: C, 76·40; H, 6·41; N, 5·24%.) 1,3-Dimethylcyclopentadiene (XX),[36a,c] λ_{max}^{MeOH} 247·5 mμ formed an N-phenylmaleimide adduct (XXV), m.p. 100–101° (sealed tube) (recrystallized from hexane). (Found: C, 76·64; H, 6·59; N, 5·21. $C_{17}H_{17}O_2N$ requires: C, 76·40; H, 6·41; N, 5·24%.)

Reaction of sodium methylcyclopentadienide with dibromoethane

1,2-Dibromoethane (94 g; 0·5 mole) was slowly added to a stirred solution of sodium methylcyclopentadienide (0·4 mole) in liquid NH_3. After 4 hr the organic layer (29 g) was separated and analysed by VPC (MEEE column). Products with retention times (relative to spiro[2·4]hepta-1,3-diene[22a] = 1·00) 1·82, 2·22, and 2·49 were observed; they were shown to be, respectively, 2-methylspiro[2.4]hepta-1,3-diene (XXXII), 1-methylspiro[2.4]hepta-1,3-diene[22b] (XXXI), and dibromoethane. The spiroheptadienes were in the ratio XXXI:XXXII = 2·8:1, and their combined yield was estimated to be about 30%.

[38] Many extinction coefficients are not reported because of the difficulty of weighing accurately the fraction collected from the column.

1-Methylspiro[2.4]hepta-1,3-diene (XXXI), $\lambda\lambda_{max}^{MeOH}$ 263, 218 mμ, mol. wt. 106 (mass spectrum[20]), reacted with N-phenylmaleimide in benzene to form an adduct (XXXIII), m.p. 135–135·5° (recrystallized from hexane). (Found: C, 77·40; H, 6·35; N, 4·85. $C_{18}H_{17}O_2N$ requires: C, 77·39; H, 6·13; N, 5·01%.) 2-Methyl[2.4]spirohepta-1,3-diene (XXXII), $\lambda\lambda_{max}^{MeOH}$ 259, 222 mμ, mol. wt. 106 (mass spectrum[20]), formed an N-phenylmaleimide adduct (XXXIV), m.p. 114–114·5° (recrystallized from hexane). (Found: C, 77·34; H, 6·11; N, 4·96. $C_{18}H_{17}O_2N$ requires: C, 77·39; H, 6·13; N, 5·01%.)

Reactions in other solvents

Sodium cyclopentadienide in ether solvents was prepared by Wilkinson's method.[20] Sodium was finely dispersed in toluene under an atmosphere of dry, O_2-free N_2. The toluene was replaced with tetrahydrofuran, dimethoxyethane, or diglyme and a calculated amount of cyclopentadiene was then added and the solution stirred for 1 hr. Sodium cyclopentadienide in dimethylsulphoxide was prepared by removing under red. press. the solvent from a solution of NaC_5H_5 in tertahydrofuran and replacing it with dimethylsulphoxide.

Sodium methylcyclopentadienide solutions were prepared by substituting the methylcyclopentadiene mixture for cyclopentadiene in the above method.

Methylation of sodium cyclopentadienide. Methyl iodide (14·2 g; 0·1 mole) was slowly added to a stirred solution of sodium cyclopentadienide (0·1 mole) in tetrahydrofuran at room temp under a N_2 atm. After 30 min the solution was analysed by VPC; it consisted of cyclopentadiene (16%), methylcyclopentadienes (66%) in the ratio VII:VIII = 0·82:1, and other products (mainly polymethylcyclopentadienes). When the amount of MeI was increased, the amount of cyclopentadiene recovered decreased and the yield of polymethylcyclopentadienes increased, but the ratio VII:VIII remained 0·83(±0·02):1.

When dimethoxyethane was the solvent the yields of cyclopentadiene, methylcyclopentadienes, and polymethylcyclopentadienes were similar to those obtained with tetrahydrofuran, but the ratio of VII:VIII varied from 1·77 (for $MeI:NaC_5H_5$ = 1:1) to 3·25 (for $MeI:NaC_5H_5$ = 4:1) and was also very dependent on the precise conditions (especially time) used. Addition of sodium cyclopentadienide in dimethoxyethane to an excess of methyl iodide at room temperature produced a ratio of VII:VIII = 5·8:1 in the products; small amounts of polymethylcyclopentadienes were also detected.

A reaction in dimethylsulphoxide gave rise to cyclopentadiene, methylcyclopentadienes in the ratio VII:VIII = 3·67:1, and other products.

Formation of 5-substituted cyclopentadienes

5-Methylcyclopentadiene (IX). Sodium cyclopentadienide was prepared from cyclopentadiene (16·5 g; 0·25 mole) and Na (5·75 g; 0·25 mole) in 200 ml diglyme. The mixture was refluxed 2 hr and then filtered through a sintered glass disc under a positive pressure of dry, O_2-free N_2, and collected in a dropping funnel. The funnel was attached to a three-necked flask equipped with a stirrer and flushed with N_2. Methyl sulphate (51 g; 0·4 mole) was placed in the flask, cooled to −10°, and kept well stirred. The sodium cyclopentadienide solution was slowly added to the Me_2SO_4; the reaction mixture maintained at −10° for a further 2 hr and then distilled under red. press. (<1 mm) at the same temp. The distillate consisted of 5-methylcyclopentadiene[9a,b] (IX), λ_{max}^{MeOH} 245 mμ (determined by adding IX to MeOH in the cell and recording the spectrum immediately) and a trace of diglyme. The distillate (2·1 g; 0·026 mole) was carefully added to a solution of N-phenylmaleimide in benzene cooled in an ice-bath. When the reaction was complete, the solvent was removed and a crystalline material (5·8 g), m.p. 110–119° (Found: C, 75·45; H, 5·91; N, 5·58. $C_{16}H_{15}O_2N$ requires: C, 75·87; H, 5·97; N, 5·53%), was recovered. This proved to be a mixture containing about equal amounts of the two stereoisomeric N-phenylmaleimide adducts (XII and XIII) of 5 methylcyclopentadiene (IX); one isomer (probably XIII), m.p. 130–132° (from hexane) (Found: C, 75·82; H, 6·10; N, 5·71. $C_{16}H_{15}O_2N$ requires: C, 75·87; H, 5·97; N, 5·53%), was isolated by fractional crystallization from CCl_4.

1,5-, 2,5-, and 5,5-Dimethylcyclopentadienes (XVI, XIX and XXII) were prepared from sodium methylcyclopentadienide and methyl sulphate by the above method but with the difference that the products were distilled under red. press. at 23°. The distillate consisted of dimethylcyclopentadienes

[20] G. Wilkinson, *Org. Synth.* **36**, 31 (1956).

with VPC retention times[18] of 1·32, 3·00, and 3·46 of relative areas 0·45:1·00:3·45, respectively and a small amount of diglyme. The component of retention time 1·32 formed an N-phenylmaleimide adduct, m.p. 171–172°, identical in every respect with a sample of the adduct (XXVI) of 5,5-dimethylcyclopentadiene (XXII).[21] The component of retention time 3·46 was shown to be 1,5-dimethylcyclopentadiene[9a] (XVI); it underwent partial rearrangement on the column and the material collected from this fraction (mol. wt. 94[20]) reacted with N-phenylmaleimide to form a mixture of the adducts (XXIII, XXVII, and XXVIII) of 1,2-dimethylcyclopentadiene (XVII) and 1,5-dimethylcyclopentadiene (XVI) (characterized by NMR). The component of retention time 3·00 was then 2,5-dimethylcyclopentadiene; this fraction had mol. wt. 94 (mass spectrum[20]). The original mixture of 5-substituted dimethylcyclopentadienes (1·6 g; 0·02 mole) was treated with N-phenylmaleimide (3·5 g; 0·02 mole) in benzene; a crystalline material (4·8 g) was isolated. Fractional crystallization of this from benzene led to an adduct (0·55 g), m.p. 173–174° (recrystallized from benzene–hexane). (Found: C, 76·27; H, 6·36; N, 5·50. $C_{17}H_{17}O_2N$ requires: C, 76·40; H, 6·41; N, 5·25%); it was an adduct of 1,5-dimethylcyclopentadiene and was tentatively assigned structure XXVII.

The original mixture of 5-substituted dimethylcyclopentadienes was allowed to rearrange[10] and the rearranged mixture was analyzed by VPC; it consisted of 5,5-, 1,3-, and 1,2-dimethylcyclopentadienes in the ratio XXII:XX:XVII = 0·45:1·00:3·30 (characterized by retention times and by their N-phenylmaleimide adducts) which allowed the products of rearrangement to be identified by relationship to their precursors.

Alternative syntheses of dimethylcyclopentadienes

1,3-*Dimethylcyclopentadiene*[18] (XX). 3-Methyl-2-cyclopentenone[20] (24 g; 0·25 mole) was added dropwise to a stirred solution of MeMgBr (0·5 mole) in 200 ml tetrahydrofuran contained under a N_2 atm. in an ice-cooled flask. After 1 hr saturated NH_4Cl aq was added and the product extracted and distilled; 1,3-dimethyl-2-cyclopentenol (19 g; 0·17 mole) was obtained as a colourless liquid b.p. 55°/11 mm, n_D^{25} 1·4613 (Found: C, 75·55; H, 10·81. $C_7H_{12}O$ requires: C, 74·95; H, 10·78%), with IR absorption (pure liquid) at 3370 (broad) and 1658 cm^{-1}. A few crystals of *p*-toluenesulphonic acid and hydroquinone were added to this alcohol (11·2 g; 0·10 mole), and the mixture distilled at atm. press. The organic layer was separated from the distillate boiling 75–90°, dried (Na_2SO_4), and redistilled. 1,3-Dimethylcyclopentadiene (XX; 7·9 g; 0·084 mole), b.p. 93–95°, λ_{max}^{MeOH} 248·5 mμ (ε 2750), n_D^{25} 1·4574, absorption at 1634 cm^{-1} in the IR, (Found: C, 89·42; H, 10·65. C_7H_{10} requires: C, 89·29; H, 10·71%) (analysis was presumably carried out on the dimer), was isolated.[21] It had a VPC retention time (6·08) identical, both separately and on admixture, with the material described previously (*vide supra*), and formed in 80% yield an N-phenylmaleimide adduct (XXV); m.p. 100–101°, identical in every respect with that described above. The maleic anhydride adduct of XX was an oil which was converted in refluxing dil. HCl to the lactone-acid, m.p. 152–153° (from benzene–hexane). (Found: C, 63·13; H, 6·64. Calc. for $C_{11}H_{14}O_4$: C, 62·84; H, 6·71%.) (The characteristics of XX and its derivatives are in accord with those reported by Mironov[9c] with the exception of the UV spectrum of XX for which he reports λ_{max} 254·5 mμ.)

1,2- *and* 2,3-*Dimethylcyclopentadiene* (XVII and XVIII). 2,3-Dimethyl-2-cyclopentenone[22] (1·1 g) was treated overnight with a large excess of $NaBH_4$ aq. The mixture was heated on the steam bath for 1 hr and then treated with excess NH_4Cl. The organic layer (0·65 g) was analysed by VPC (dimethylsulfolane column) and shown to consist of two components; 1,2-dimethylcyclopentadiene (XVII; 14%) retention time 6·59, and 1,3-dimethylcyclopentadiene (XVIII; 86%), retention time 7·27. These were also shown by peak enhancement to correspond with the appropriate diene obtained in the methylation reaction.

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[20] R. M. Acheson and R. Robinson, *J. Chem. Soc.* 1127 (1952).
[21] We thank Mr. J. J. Ryan for his assistance with this experiment.
[22] S. Dev and C. Rai, *J. Ind. Chem. Soc.* **34**, 266 (1957).