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SUBSTITUTION IN THE CYCLOPENTADIENIDE ANION SERIES

POLYMETHYLATION

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Abstract—The reaction of sodium cyclopentadienide with a large amount of methylating agent led to polymethylcyclopentadienes. The resulting product distribution supported our previous conclusions that the cyclopentadienide ring can undergo electrophilic substitution and that a substituent already present on the ring has a directing influence on the electrophile.

It has been demonstrated[2] that the cyclopentadienide anion (I) can undergo electrophilic substitution by, for example, methyl iodide in the presence of an appropriate base, and so produce the methylcyclopentadienide anion (II). Three methylcyclopentadienes (III, IV, V) can be formed by protonation of II; alternatively II can undergo further reaction with the electrophile, and our previous results[2] show that the methyl substituent of II has a directing influence on the electrophile, leading to positional selectivity in the order $\beta > \gamma > \alpha$. The latter reaction can lead eventually to the formation of dimethylcyclopentadienes; seven structures (VI–XII) are possible and all except XI have been identified in reaction mixtures (under specified conditions).

We have now allowed sodium cyclopentadienide to react with a large amount of a methylating agent (6 moles Me_2SO_4 per mole NaC_5H_5) in liquid ammonia containing an amount of sodium amide equivalent to that of the methylating agent. A comparable reaction, in which sodium methylcyclopentadienide was methylated with methyl iodide, was also carried out. The complex mixture of substituted cyclopentadienes obtained was deliberately allowed to establish prototropic equilibrium[2,3] among the sets of isomers; it was then analyzed by vapor phase chromatography, and the results are set out in the Table. The chromatogram for the methylcyclopentadienide reaction (the distribution of products among various mol. wts was better illustrated in this case) is reproduced in the Fig., in which the peaks corresponding to compounds of assigned constitution are labelled with the number used in the text to identify the appropriate structure, and unassigned peaks are labelled with letters (A to E). We do not wish to overrate the significance of the percentages shown in Table 1 (their accuracy depends on the accuracy with which the peak areas were measured and the degree to which it is true that the detector response was the same for all components) since many reaction variables were not taken into account in these experiments, but we quote them to illustrate the general features that become apparent when they are examined. We shall first justify our structural assignments, and then discuss the results of the methylation reactions in the light of our previous hypotheses and results.[2]

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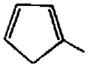
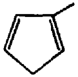
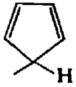
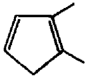
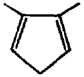
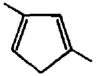
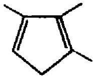
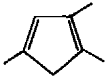
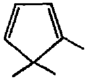
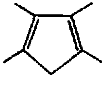
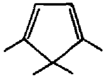
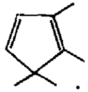
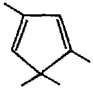
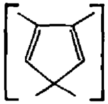
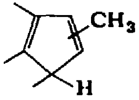
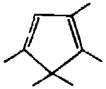
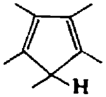
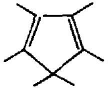
[1] Holder of National Research Council (Canada) Scholarship (1963–1964).

[2] S. McLean and P. Haynes, *Tetrahedron* (21, 2313 (1965)).

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

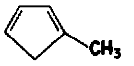
TABLE 1. PRODUCT DISTRIBUTION
YIELDS OF SUBSTITUTED CYCLOPENTADIENES FROM METHYLATION REACTIONS
(Percentages of the total diene product as determined by v.p.c.).

Cyclopentadiene derivative	Yield (%) from NaC_5H_5	Yield (%) from $NaMeC_5H_4$		Isomer distribution; % of total yield (i) from NaC_5H_5 (ii) from $NaMeC_5H_4$			
Methyl	v. small	5·9					
				III	VI	V	
			(i)	—	—	—	
			(ii)	2·7	3·2	v. small	
Dimethyl	3·2	5·4					
				VII	VIII	X	XII
			(i)	0·9	0·65	0·45	1·2
			(ii)	1·8	1·3	0·9	1·4

Trimethyl	52·4	19·1	 XIII  XIV  XV (i) 25·6 11·6 15·2 (ii) 4·0 1·8 13·3
Tetramethyl	27·7	36·7	 XVI  XVII  XVIII  XIX  XX  XXI (i) 6·1 14·9 5·2 + 1·5 — v. small (ii) 6·0 21·8 6·7 + 2·2 — v. small
Pentamethyl and Hexamethyl	16·7	32·9	 XXII  XXIII  XXIV  XVX (i) 13·4 3·3 (ii) 20·9 12·0

I

II



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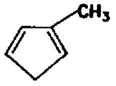

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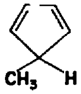

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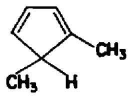
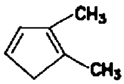
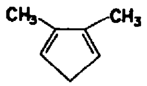


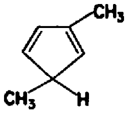
VI



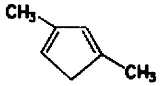
VII



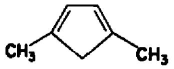
VIII



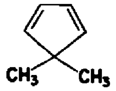
IX



X



XI



XII

The component from each peak of the chromatogram was collected and identified by its physical and chemical characteristics, the number of characteristics examined being governed by the size of the peak. In all cases the degree of substitution could be determined from the molecular weight (mass spectrum[4]), in most cases the UV λ_{max} could be measured, and in many cases a characteristic crystalline N-phenylmaleimide adduct could be obtained. Structural assignments depended principally on interpretation of the NMR spectra of these adducts. It was useful to find that the VPC retention times of the substituted cyclopentadienes depended on the degree of substitution on the double bond system rather than on the total number of substituents; thus 1- (III) and 2- (IV) methylcyclopentadienes had similar retention times, but the 5-methyl isomer (V) appeared close to cyclopentadiene and 5,5-dimethylcyclopentadiene (XII). This pattern appeared to hold true for more highly substituted cyclopentadienes of established structure, and it was used as a guide to possible assignments for some products of unknown structure.

The methyl- and dimethylcyclopentadienes were recognized by their characteristic retention times, and they have been described adequately elsewhere.[2]

1,2,3-Trimethylcyclopentadiene (XIII), λ_{max} 251 mμ,[5] formed an N-phenylmaleimide adduct (XXVI), m.p. 100·5–102°, showing in the NMR a singlet at 8·47 τ (bridgehead CH_3), broadened peaks at 8·38 τ and 8·30 τ (two non-equivalent CH_3

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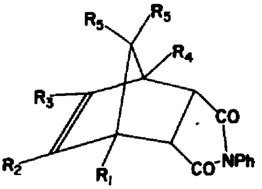
[4] We thank Mr. F. Meyer and Dr. A. G. Harrison of this Department for these determinations. It has also been noted that *gem*-dimethyl derivatives have mass spectra characteristically different from those of their isomers. (F. Meyer, P. Haynes, S. McLean and A. G. Harrison, to be published.)

[5] V. A. Mironov, E. V. Sobolev and A. N. Elizarova, *Tetrahedron* **19**, 1939 (1963).

groups at a double bond),[6] and no signal attributable to vinyl protons. 1,2,4-Trimethylcyclopentadiene[7] (XIV), λ_{max} 258 mμ, formed an N-phenylmaleimide adduct (XXVII), m.p. 106·5–107·5°, showing a sharp signal at 8·48 τ (two unresolved bridgehead CH_3 groups), a doublet (J = 1·7 c/s) at 8·27 τ (CH_3 at a double bond), and a broad (7 c/s total width) unresolved multiplet at 4·35 τ (one vinyl proton). 1,5,5-Trimethylcyclopentadiene (XV),[8] λ_{max} 254 mμ, formed an N-phenylmaleimide adduct (XXVIII), m.p. 114–115°, which showed a very slightly broadened peak at 9·07 τ (two unresolved CH_3 groups at C-7), a singlet at 8·64 τ (bridgehead CH_3) and the characteristic pattern for two non-equivalent vinyl protons, one of which was split by a third, at 3·94 τ (an AB quartet with J = 6·0 c/s and internal chemical shift of 12·6 c/s; the low field half of the signal was split further and appeared as a pair of doublets, J = 3·0 c/s; in addition, the two high field peaks of the AB pattern were very slightly broadened).

Five peaks associated with tetramethylcyclopentadienes have been identified, but at present we are able to make with confidence complete structural assignments to two only. 1,2,3,4-Tetramethylcyclopentadiene[5,9] (XVI), λ_{max} 260 mμ, formed an N-phenylmaleimide adduct (XXIX), m.p. 119–120°, which showed in the NMR a single sharp peak at 8·49 τ (two equivalent bridgehead CH_3 groups), a single sharp peak at 8·38 τ (two equivalent CH_3 groups at a double bond), and no signal attributable to a vinyl proton. 1,4,5,5-Tetramethylcyclopentadiene (XVII), λ_{max} 258 mμ, formed an N-phenylmaleimide adduct (XXX), m.p. 119–120° which showed a very slightly broadened peak at 9·21 τ (two unresolved CH_3 groups at C-7), a singlet at 8·65 τ (two equivalent bridgehead CH_3 groups), and a singlet at 3·11 τ (two equivalent vinyl protons). Two other peaks appeared in the region of the chromatogram associated with cyclopentadienes having two methyl groups at the double bonds; one component had λ_{max} 256 mμ and the other λ_{max} 257 mμ, and their mass spectra[4] confirmed that they were tetramethylcyclopentadienes having *gem*-dimethyl substitution. Insufficient material was available to characterize these compounds further, but only three possible structures (XVIII, XIX, XX) remain for them, and on the basis of the pattern that has emerged in the present study (*vide infra*), we feel that XX is an improbable product; thus the products should be 1,2,5,5-(XVIII) and 1,3,5,5-(XIX) tetramethylcyclopentadienes. A very small peak appearing in the region of the chromatogram associated with cyclopentadienes having three methyl groups on the diene system was shown by



	R_1	R_2	R_3	R_4	R_5
XXVI	Me	Me	Me	H	H
XXVII	Me	Me	H	Me	H
XXVIII	Me	H	H	H	Me
XXIX	Me	Me	Me	Me	H
XXX	Me	H	H	Me	Me
XXXI	Me	Me	H	Me	Me

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[6] It was noted that the broadening presumably resulted from coupling between the protons of the two CH_3 groups at the double bond, since the signals were sharp for compounds with pairs of identical CH_3 groups in the same environment (e.g. the adducts of 2,3-dimethyl-(VIII) and 1,2,3,4-tetramethyl-(XVI) cyclopentadiene.

[7] I. N. Nazarov and A. N. Elizarova, *Izv. Akad. Nauk SSSR. Otd. Khim. Nauk* 295 (1951).

[8] A. Damsky, *Ber. Dtsch. Chem. Ges.* **20**, 2966 (1887). K. Alder and E. Windemuth, *Liebigs Ann.* **543**, 28, 41, 56 (1940). P. Yates and L. Kilmurry, *Tetrahedron Letters* 1739 (1964).

[9] V. A. Mironov, T. M. Fadeeva, E. V. Sobolev and A. N. Elizarova, *J. Gen. Chem. U.S.S.R.* **33**, 77 (1963).

mass spectrometry[4] to have the characteristics of a non-geminally substituted tetramethylcyclopentadiene; it is then probably 1,2,3(or 4),5-tetramethylcyclopentadiene (XXI).[5,9,10]

Two other peaks in the chromatogram have been associated with penta- and hexamethylcyclopentadienes. The first is in the region associated with a diene having three methyl groups on the double bond system and the material, λ_{max} 258·5 mμ, isolated from it has been shown by mass spectrometry[4] to contain pentamethylcyclopentadienes having *gem*-dimethyl substitution. It is probably a mixture of 1,2,3,5,5- (XXII) and 1,2,4,5,5-(XXIII) pentamethylcyclopentadienes since with N-phenylmaleimide a non-crystalline product was formed, which on the basis of its NMR spectrum, appeared to consist mainly of the adduct (XXXI) of XXIII: the spectrum showed peaks at 9·25 and 9·20 τ (two non-equivalent CH_3 groups at C-7), peaks at 8·71 and 8·68 τ (two non-equivalent bridgehead CH_3 groups), a doublet ($J = 1·7$ c/s) at 8·30 τ (CH_3 at a double bond) and a broadened signal at 4·48 τ (vinyl proton) (the latter was surprisingly poorly resolved, but the signal had a total width of about 7 c/s).

The peak of longest retention time was shown to arise from the known 1,2,3,4,5-penta-(XXIV) and 1,2,3,4,5,5-hexa-(XXV) methylcyclopentadienes.[11] The mixture of dienes reacted with N-phenylmaleimide to form a material, m.p. 95–106°, which showed no vinyl protons in the NMR. A cut from the leading edge of the VPC peak was shown from its mass spectrum[4] to consist entirely of hexamethylcyclopentadiene (XXV), λ_{max} 252 mμ;[11] similarly, a cut from the tail of the peak consisted of pure 1,2,3,4,5-pentamethylcyclopentadiene (XXIV), λ_{max} 248, 264 (shoulder) mμ.[11]

In addition to the products already discussed, the mixture contained at least five incompletely characterized components which appeared as small peaks (A–E) in the chromatogram. The components isolated from peaks B and C had the molecular weight 110 (mass spectrum[4]) indicating that they were trimethylcyclopentenes. The other peaks were too small to allow characterization of their components; it is possible that some (particularly A) of these were also associated with traces of products of reduction.

DISCUSSION

It is clear that the complex mixture of products obtained arose from successive substitutions on the cyclopentadienide anion.[2] We make the reasonable assumption that the methylation process is irreversible, so that any non-geminally substituted cyclopentadiene formed would be converted to its related anion by the sodium amide present and be capable of continuing the substitution sequence, but once a *gem*-dimethyl product is formed, it constitutes a dead-end diversion from the main sequence. In the present study, the number of products was reduced to a minimum by allowing the sets of isomers to undergo prototropic equilibration resulting in the almost complete elimination of 5-monosubstituted products.[2,3,10] As a further simplification in considering the processes involved, only the relative positions of substituents need concern us, since double bond positions are governed by the equilibration reactions.

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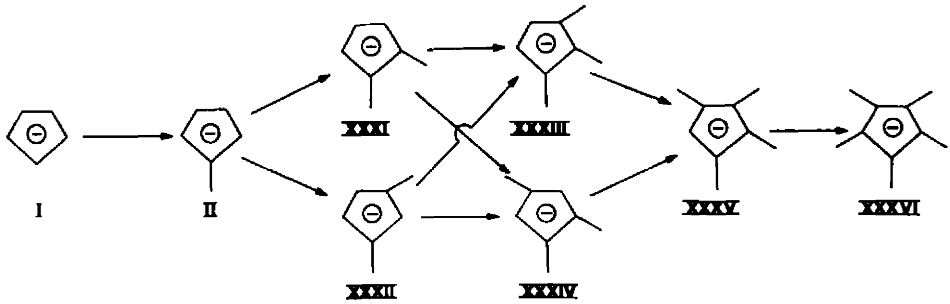
[10] Although it is well established[2,3] that cyclopentadienes having one C-5 methyl substituent undergo a facile hydrogen shift that places the methyl group on a double bond, and that, for the lower members of the series, the equilibrium mixture contains very little of the initial 5-methyl derivative, there is evidence that in the higher homologs these isomers become more important members of the equilibrium.[5]

[11] L. de Vries, *J. Org. Chem.* **25**, 1841 (1960).



The backbone of the system of substitution reactions can be recognized by considering only the anionic products (I, II, XXXI–XXXVI) resulting from each substitution step; each of these can lead to the next higher substituted anion (XXXVI cannot do this), a *gem*-dimethylcyclopentadiene having one more methyl group, or, after protonation and equilibration, to the cyclopentadiene having the same number and relative distribution of substituents as the parent anion. It can be seen that an investigation of the directing influences of substituents on the electrophile in these reactions is particularly concerned with a consideration of the origin and fate of the dimethyl-(XXXI, XXXII) and trimethyl-(XXXIII, XXXIV) cyclopentadienide anions. This system of consecutive and competitive reactions is still exceedingly complex for two principal reasons: firstly, there is a "crossover" between the dimethyl- and trimethylcyclopentadienide anions since both XXXIII and XXXIV can be produced from XXXI or XXXII, and secondly, the dead-end reactions leading to *gem*-dimethyl derivatives can remove isomeric anions from the main sequence at different rates. An attempt to make a detailed analysis of this situation on the basis of the product distributions we have obtained would be completely unjustified, but we feel that it is appropriate to note the main features of the substitution pattern as they appear to us.

To start with, we note that the extent to which substitution has taken place is different in the two reactions, one starting from the cyclopentadienide anion and the other from the methylcyclopentadienide anion. This was probably because the reactions were carried out under slightly different conditions, perhaps the most important difference being in the nature of the methylating agent used. However, we are not so much concerned at present with the extent of substitution as with the positional distribution of substituents. Our previous results would lead us to expect a methyl substituent already present to direct an incoming methyl group mainly to the adjacent ring position, and this is borne out by the observation that products derivable from 1,2-dimethyl-(XXXI) and 1,2,3-trimethyl-(XXXIII)cyclopentadienide anions predominate over those derivable from the anions (XXXII and XXXIV) having the 1,3 and 1,2,4 pattern of substituents. *gem*-Dimethyl derivatives are found in significant amounts only when they have at least one methyl group adjacent to the geminally-substituted position (XV, XVII, XVIII, XIX, etc.), and, in the tetramethylcyclopentadienes, the predominant geminally substituted isomer (i.e. XVII) has two methyl groups flanking the 5-position. It follows that the electrophile tends to attack a cyclopentadienide anion at a ring position already carrying a methyl substituent only when that position is activated by at least one adjacent methyl substituent, and, when the anion has the 1,2,3-trimethyl substitution pattern, the position activated by methyl substituents on both sides is the one most effectively attacked.

These results confirm the conclusions we have drawn previously:[2] a cyclopentadienide anion can undergo an electrophilic substitution reaction leading to a monosubstituted anionic product; the product itself may undergo further substitution, and the electrophile then shows a positional selectivity which is in the order $\beta > \gamma > \alpha$ when the substituent already present is methyl (e.g. II).

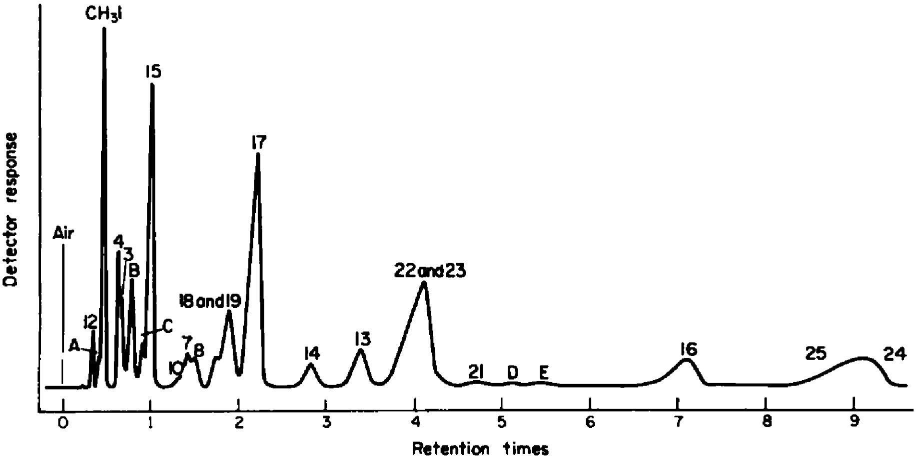


Fig. 1. Chromatogram of the products of methylation of sodium methylcyclopentadienide.

EXPERIMENTAL

Polymethylation of sodium cyclopentadienide. Methyl sulphate (126·1 g; 1·0 mole) was added to a stirred solution of sodium cyclopentadienide (0·17 mole) in liquid NH_3 containing about 1 mole $NaNH_2$. After 6 hr water was added and the organic layer (4·1 g) that formed was separated, washed with water, dried (Na_2SO_4), and analyzed by vapour phase chromatography using an MEEE column.[3] Once it was isolated, the mixture of products was kept over dry ice.

Polymethylation of sodium methylcyclopentadienide was carried out in the same way using sodium methylcyclopentadienide (0·2 mole) and MeI (142 g; 1·0 mole).[2]

The chromatogram of the products of the second reaction is reproduced in the Fig. Results from both reactions are documented in the Table. The scale of retention times (measured from the initial air peak) was conveniently established by setting the retention time of XV equal to 1·00.

Individual components were allowed to accumulate in dry ice traps. Physical data[12] reported are for these fractions; mol. wts were determined by mass spectrometry.[4] N-Phenylmaleimide adducts were prepared by allowing the diene to react with a slight excess of N-phenylmaleimide in benzene.

Methyl- and dimethylcyclopentadienes[2] were identified by their retention times: 1-methyl-(III) 0·65, 2-methyl-(IV) 0·62, 1,2-dimethyl-(VII) 1·40, 2,3-dimethyl-(VIII) 1·49, 1,3-dimethyl-(X) 1·30, 5,5-dimethyl-(XII) 0·33.

1,2,3-Trimethylcyclopentadiene (XIII), retention time 3·38, λ_{max}^{MeOH} 251 mμ (lit.[5] 253 mμ), mol. wt. 108, formed an N-phenylmaleimide adduct (XXVI), m.p. 100·5–102°, (Found: C, 76·79; H, 7·04; N, 5·11. $C_{18}H_{19}O_2N$ requires: C, 76·84; H, 6·81; N, 4·98%.)

1,2,4-Trimethylcyclopentadiene (XIV), retention time 2·81, λ_{max}^{MeOH} 258 mμ, mol. wt. 108, formed an N-phenylmaleimide adduct (XXVII), m.p. 106·5–107·5°, (Found: C, 77·07; H, 6·67; N, 5·29. $C_{18}H_{19}O_2N$ requires: C, 76·84; H, 6·81; N, 4·98%.)

1,5,5-Trimethylcyclopentadiene (XV), retention time 1·00, λ_{max}^{MeOH} 254 mμ, mol. wt. 108, formed an N-phenylmaleimide adduct (XXVIII), m.p. 114–115°, (Found: C, 76·55; H, 6·45; N, 4·86. $C_{18}H_{19}O_2$ requires: C,76·84; H, 6·81; N, 4·98%.)

1,2,3,4-Tetramethylcyclopentadiene (XVI), retention time 7·05, λ_{max}^{MeOH} 260 mμ, mol. wt. 122,

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[12] UV extinction coefficients are not usually reported because of the difficulty of weighing the sample accurately.

formed an N-phenylmaleimide adduct (XXIX), m.p. 119–120°. (Found: C, 77·37; H, 6·94; N, 4·72. $C_{19}H_{21}O_2N$ requires: C, 77·26; H, 7·17; N, 4·74%.)

1,4,5,5-Tetramethylcyclopentadiene (XVII), retention time 2·20, $\lambda_{\max}^{\mathrm{MeOH}}$ 258 mμ, mol. wt. 122, formed an N-phenylmaleimide adduct (XXX), m.p. 119–120°. (Found: C, 77·19; H, 6·99; N, 4·77. $C_{19}H_{21}O_2N$ requires: C, 77·26; H, 7·17; N, 4·74%.)

The components of the peaks of retention times 1·73 and 1·88 both had mol. wt. 122; their UV spectra showed $\lambda_{\max}^{\mathrm{MeOH}}$ 256 mμ and $\lambda_{\max}^{\mathrm{MeOH}}$ 257 mμ, respectively. One was probably XVIII and the other XIX. The component of the peak of retention time 4·68 had mol. wt. 122. It was probably XXI.

Material from the peak of retention time 4·08 contained components of mol. wt. 136 only. It showed $\lambda_{\max}^{\mathrm{MeOH}}$ 258·5 mμ and reacted with N-phenylmaleimide to form a non-crystalline material that was mainly the adduct XXXI of XXIII.

Compound XXIV, $\lambda\lambda_{\max}^{\text{iso-octane}}$ 248, 264 (shoulder) mμ (lit,[11] 248, 265 (sh), 232 (sh) mμ), mol. wt. 136, was isolated from the tail of the broad peak of retention time about 9. Compound XXV, $\lambda_{\max}^{\text{iso-octane}}$ 252 mμ (lit.[11] 252 mμ), mol. wt. 150, was isolated from the leading edge of this peak. The composite peak gave material, $\lambda_{\max}^{\mathrm{MeOH}}$ 257 mμ, which reacted with N-phenylmaleimide to form a product, m.p. 95–106°.

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