Tetrahedron, 1966, Vol. 22, pp. 1949 to 1976. Pergamon Press Ltd. Printed in Northern Ireland

# STUDIES IN SESQUITERPENES—XXIII

## METHYLCADALENES—SYNTHESIS AND CHARACTERIZATION

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**Abstract**—In connection with the characterization of methylcadalenes by modern spectroscopic methods, all five, theoretically possible, methylcadalenes have been prepared by new and simpler procedures. UV, IR and PMR spectra of these compounds are reported and discussed. TLC of isomeric naphthalenes over silica gel impregnated with trinitrobenzene is described.

METHYLCADALENES[1,2] constitute important reference compounds for the structure elucidation of cadalenic sesquiterpenoids. The sesquiterpenoid is labelled with an extra methyl group at the site of a functional group and the product after dehydrogenation gives a methylcadalene. The method has been used for locating the nuclear double bonds[1,3–13] as well as the secondary hydroxyl groups.[14] The scope and limitations of this method have been discussed[15] and a modified procedure for labelling the nuclear double bonds by isomerization of the epoxide with $BF_3$-etherate followed by the reaction of the resulting ketone with methyl–lithium, reported.[15]

### *Synthesis*

All five theoretically possible methylcadalenes have been synthesized.[1,2] and the products characterized by the preparation of complexes with polynitro compounds. In the structure determination[8] of α-cadinol (I) it was observed that whereas the picrate, styphnate and trinitrotoluene complex of 5-methylcadalene (II) obtained

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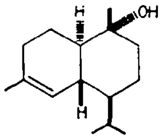
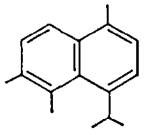
[1] W. P. Campbell and M. D. Soffer, *J. Amer. Chem. Soc.* **64**, 417 (1942).
[2] Sukh Dev and P. C. Guha, *J. Ind. Chem. Soc.* **25**, 13 (1948); Sukh Dev, *Ibid.* **25**, 69 (1948).
[3] M. D. Soffer, C. Steinhardt, G. Turner and M. E. Stebbins, *J. Amer. Chem. Soc.* **66**, 1520 (1944).
[4] L. H. Briggs and W. I. TAYLOR, *J. Chem. Soc.* 1338 (1947).
[5] Sukh Dev and P. C. Guha, *J. Indian Chem. Soc.* **26**, 263 (1949).
[6] B. B. Ghatgey, R. K. Razdan and S. C. Bhattacharyya, *Perfum. Essent. Oil Rec.* **47**, 157 (1956).
[7] O. Motl, V. Sykora, V. Herout and F. Sorm, *Coll. Czech. Chem. Comm.* **23**, 1297 (1958).
[8] M. D. Soffer, M. Brey and J. Fournier, *J. Amer. Chem. Soc.* **81**, 1678 (1959).
[9] S. C. Bhattacharyya, K. K. Chakravarti and K. L. Surve, *Chem. & Ind.* 1352 (1959).
[10] C. C. Kartha, P. S. Kalsi, A. M. Shaligram, K. K. Chakravarti and S. C. Bhattacharyya, *Tetrahedron* **19**, 241 (1963).
[11] O. Motl, V. G. Bucharov, V. Herout and F. Sorm, *Chem. & Ind.* 1759 (1963).
[12] R. R. Smolders, *Canad. J. Chem.* **42**, 2836 (1964).
[13] F. M. Couchman, A. R. Pinder and N. H. Bromham, *Tetrahedron* **20**, 2047 (1964).
[14] A. S. Rao, K. L. Surve, K. K. Chakravarti and S. C. Bhattacharyya, *Tetrahedron* **19**, 233 (1963).
[15] K. L. Murthy, Ph.D thesis, p. 1, Bombay University (1959).

from α-cadinol were identical with those from the synthetic product, the trinitrobenzene complex of the synthetic product was the complex of 1,2,5-trimethylnaphthalene. Apparently the isopropyl group had been eliminated during the last stage of the synthesis, *viz.* dehydrogenation. Examination of the records revealed that whereas the picrate, styphnate and the trinitrotoluene complex of 5-methylcadalene had been obtained from a preparation in which sulphur dehydrogenation was employed at the last stage, the trinitrobenzene complex had been obtained from a preparation in which selenium dehydrogenation had been used in the last step. The elimination of non-angular alkyl groups during dehydrogenations, though unsuspected are well established,[16–19] especially for selenium dehydrogenation. Since selenium dehydrogenation[2] has been employed during the synthesis of several methylcadalenes, in view of their importance as reference substances, it was decided to check their structures by modern methods of spectroscopy. All five methylcadalenes were synthesized, new and simpler methods being used for all except 5-methylcadalene which was prepared by the procedure already reported.[2]



I



II

2-*Methylcadalene.* The procedure followed for the synthesis of 2-methylcadalene is outlined in Fig. 1. The acylation of 2-methyl-*p*-cymene (IV) can take place at $C_5$ or $C_6$ or both depending on the relative importance of electronic or steric factors. If substitution occurs at $C_6$ (steric factors), the product would be VII which can be readily converted into 2-methylcadalene. However, the product from this reaction on oxidation furnished only pyromellitic acid (VIa), hence the keto acid must be V. This preference for substitution at $C_5$ was subsequently made use of for the synthesis of 2-methylcadalene as shown in Fig. 1. The compound was previously synthesized by Soffer *et al.*[1]

3-*Methylcadalene* (with Charanjit Rai). 3-Methylcadalene previously synthesized,[2] was prepared following the scheme outlined in Fig. 2. As anticipated from the syntheses of 2-methylcadalene, the acylation of 3-methyl-*p*-cymene with methylsuccinic anhydride yielded the required compound, the structure of which was proved by its oxidation to pyromellitic acid (VIa). A point of special interest in this work has been that the action of polyphosphoric acid on the acid (XIX) or the action of aluminium chloride on the acid chloride of XIX furnished only 2,5,7-trimethyltetralone-1 (XX), rather than the expected 2,5,7-trimethyl-8-isopropyltetralone-1 (XXIII). The

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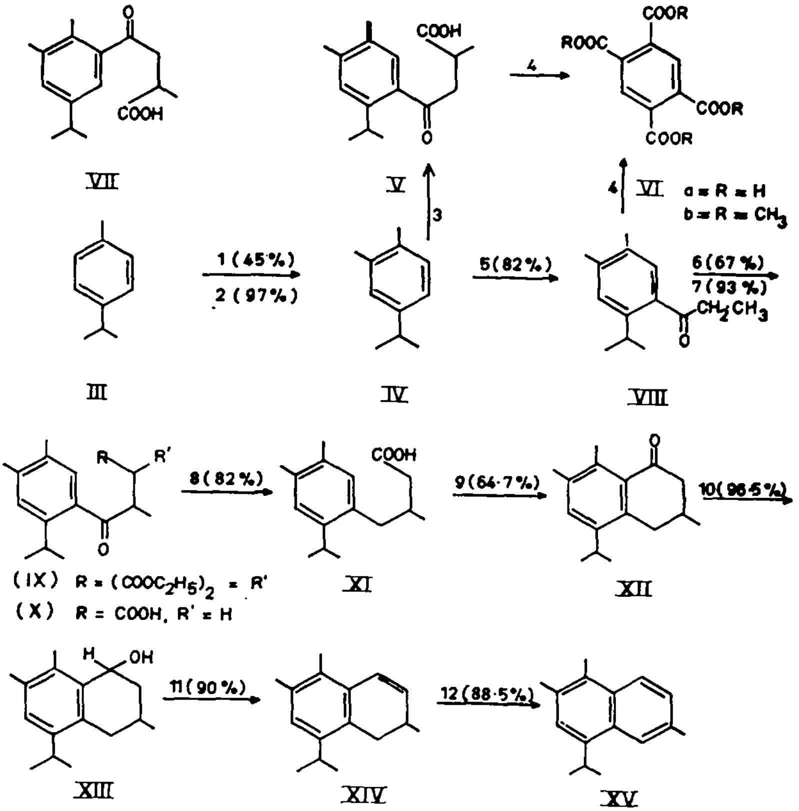
[16] W. Cocker, B. E. Cross, A. K. Fateen, C. Lipman, E. R. Stuart, W. H. Thompson and D. R. A. Whyte, *J. Chem. Soc.* 1781 (1950).

[17] W. S. Cocker, B. E. Cross and J. McCormick, *J. Chem. Soc.* 72 (1952).

[18] W. Cocker, B. E. Cross, J. T. Edward, D. S. Jenkinson and J. McCormick, *J. Chem. Soc.* 2355 (1953).

[19] W. Cocker and D. S. Jenkinson, *J. Chem. Soc.* 2420 (1954).



REAGENTS

1 HCHO. HCl
2 $H_2$.Pd–C
3 Methylsuccinic anhydride
4 $HNO_3$
5 $CH_3CH_2COCl$. $AlCl_3$
6 $Br_2$: diethylmalonate, Na
7 Hydrolysis
8 Zn–Hg, HCl
9 PPA
10 LAH
11 $I_2$
12 Sulphur

FIG. 1. Synthesis of 2-methylcadalene.

tetralone (XX) was duly characterized by its oxidation to mellophanic acid (XXI) and its conversion to 1,3,6-trimethylnaphthalene (XXII). Though dealkylations[20–22] and rearrangement of alkyl groups is a recognized feature in certain Friedel-Crafts reactions not many cases of dealkylations have been recorded for the intramolecular ringclosure reactions.[23]

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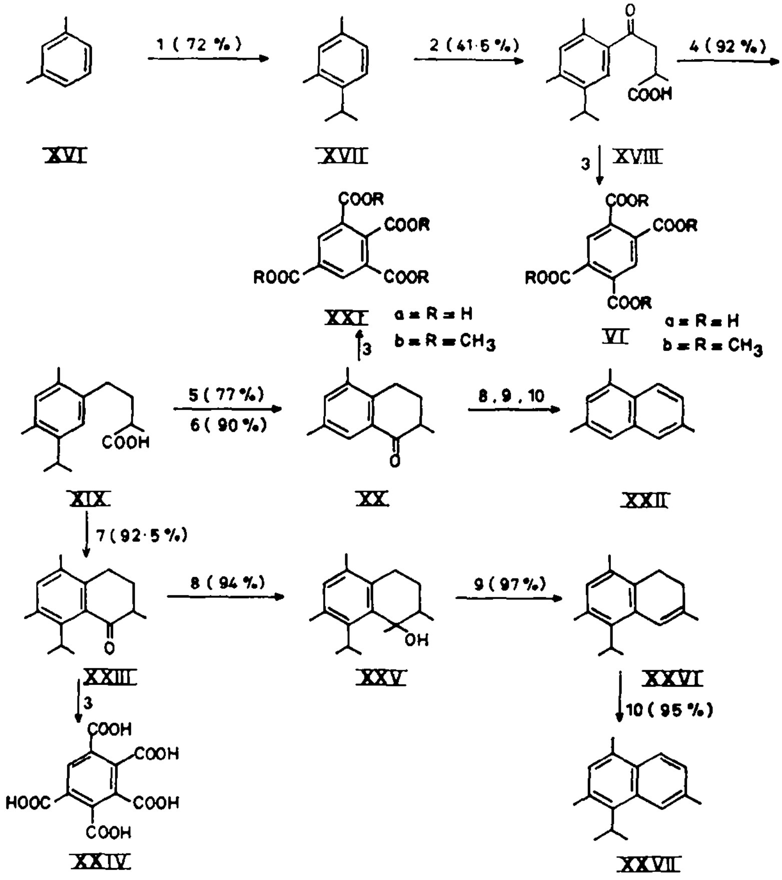
[20] R. Anschütz and H. Immendorff, *Ber. Dtsch. Chem. Ges* **18**, 657 (1885).

[21] C. Friedel and J. M. Crafts, *C.R. Acad. Sci., Paris* **100**, 692 (1885).

[22] O. Jacobsen, *Ber. Dtsch. Chem. Ges.* **18**, 338 (1885).

[23] For example, W. S. Johnson, in the Chapter, *The formation of cyclic ketones by intramolecular acylation* in *Organic Reactions* (Edited by Roger Adams) Vol. II; p. 114. Wiley, New York (1946) which covers the literature up to 1946 no such case has been reported.

The cleavage of a t-butyl group during intramolecular ring-closure of γ-(2-methyl-4-t-butylphenyl)butyric acid, has been reported: N. P. Buu-Hoi and P. Cagniant, *Bull. Soc. Chim. Fr.* **11**, 349 (1944).



REAGENTS—

1 $(CH_3)_2CHOH$. $H_2SO_4$
2 Methylsuccinic, anhydride, $AlCl_3$
3 $HNO_3$
4 Zn-Hg, HCl
5 $AlCl_3$
6 PPA
7 $SnCl_4$
8 LAH
9 $I_2$
10 Sulphur

FIG. 2. Synthesis of 3-methylcadalene.

5-*Methylcadalene*. This was prepared according to the method of Sukh Dev[2] with suitable modifications (Fig. 3).

7-*Methylcadalene* (with K. L. Murthy). 7-Methylcadalene was obtained by following the scheme outlined in Fig. 4. This method is far simpler than the route followed by previous workers.[1]

8-*Methylcadalene*. 8-Methylcadalene was synthesized following the procedure shown in Fig. 5. The first synthesis of 8-methylcadalene was reported by Sukh Dev.[2]

In connection with the reduction of the acid (XXXIX) and the lactone (XL) with hydriodic acid and red phosphorous, the formation of a tetralone during such reactions has been reported earlier.[24–26]

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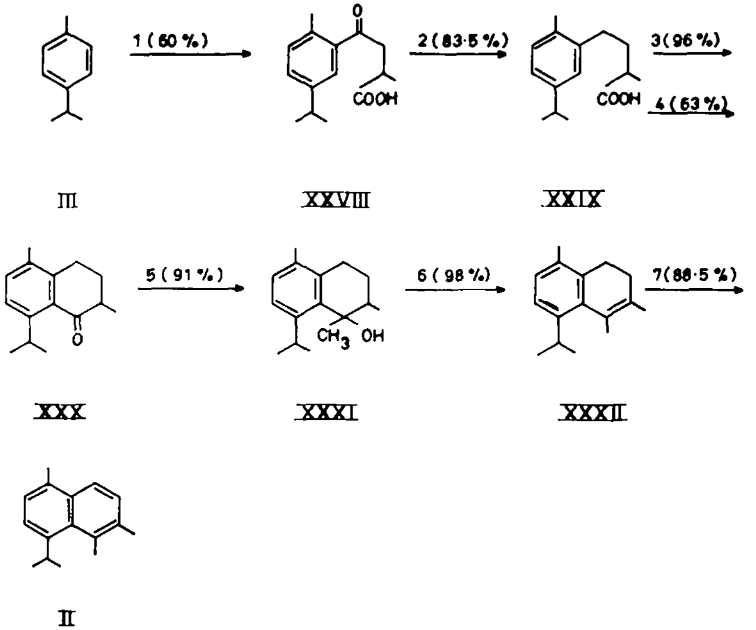
[24] Ullmann, *Liebigs Ann.* **291**, 19 (1896).

[25] K. Miescher and J. R. Billeter, *Helv. Chim. Acta* **22**, 605 (1939).

[26] Sukh Dev, *J. Ind. Chem. Soc.* **25**, 323 (1948).



REAGENTS—

1 Methylsuccinic anhydride. $AlCl_3$
2 Zn–Hg. HCl
3 $PCl_5$, $AlCl_3$
4 PPA
5 Methyl-lithium
6 $I_2$
7 Sulphur

FIG. 3. Synthesis of 5-methylcadalene.

*1,2,7-Trimethyl-4-isopropylnaphthalene.* The fact that the acylation of 2-methyl-*p*-cymene yielded V (Fig. 1) was utilized to prepare (Fig. 6) 1,2,7-trimethyl-4-isopropylnaphthalene, which was of interest in connection with NMR studies[27] of alkylnaphthalenes.

*Some general remarks.* In all these syntheses, the final step of dehydrogenation was carried out with sulphur in order to avoid the loss of alkyl groups during dehydrogenation. In order to make this reaction easier, the tetralones were converted to the corresponding alcohols, which were dehydrated with iodine[28] to give the corresponding dialins in excellent yields, which in turn could be smoothly dehydrogenated to the required naphthalenes.

The UV and IR data of the various tetralones are summarized in Table 1. Whereas the UV data fall within the expected range,[29,30] in the IR, tetralones (XII and XLVII) display their carbonyl stretching bands at frequencies lower than the expected range[31] (1680 $cm^{-1}$), although no explanation for this is apparent. It may further be noted

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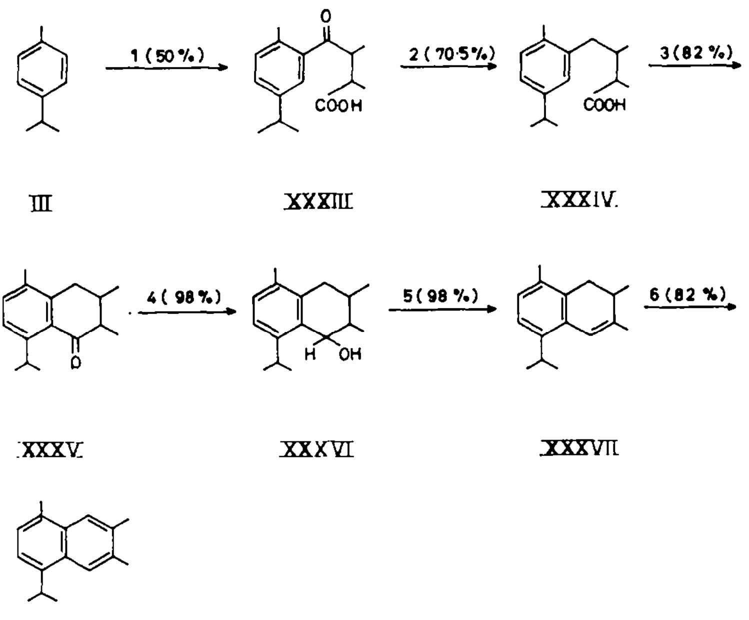
[27] B. A. Nagasampagi, R. C. Pandey, V. S. Pansare, J. R. Prahlad and Sukh Dev, *Tetrahedron Letters* No. 8, 411 (1964).

[28] W. L. Mosby, *J. Amer. Chem. Soc.* **74**, 2564 (1952).

[29] G. D. Hedden and W. G. Brown, *J. Amer. Chem. Soc.* **75**, 3744 (1953).

[30] J. W. Huffman, *J. Org. Chem.* **24**, 1759 (1959).

[31] P. H. Christol, R. Jacquier and M. Mousseron, *Bull. Soc. Chim. Fr.* 248 (1958).



REAGENTS—

| | |
|---|---|
| 1 Dimethylsuccinic anhydride, $AlCl_3$ | 4 LAH |
| 2 Zn–Hg, HCl | 5 $I_2$ |
| 3 PPA | 6 Sulphur |

FIG. 4. Synthesis of 7-methylcadalene.

that tetralone (XXIII) displays a carbonyl doublet which may be assigned to Fermi resonance of the carbonyl fundamental with the first harmonic of the 885 $cm^{-1}$ band, due to the out-of-plane CH deformation of the aromatic proton.[32]

The UV absorption data of the various dialins obtained have been summarized in Table 2 and are in accord with the expectations.[33]

## *Characterization*

The physical properties of the various naphthalenes synthesized are summarized in Table 3. The m.ps of their complexes with polynitro compounds have been collected in Table 4.

The methylcadalenes obtained yielded derivatives (Table 4) identical with those described previously[1,2,34] with the exception of the trinitrobenzene complex of 5-methylcadalene.

*UV absorption.* The UV absorption characteristics of the various methylcadalenes as well as those of cadalene graphically represented in Fig. 7. As was anticipated

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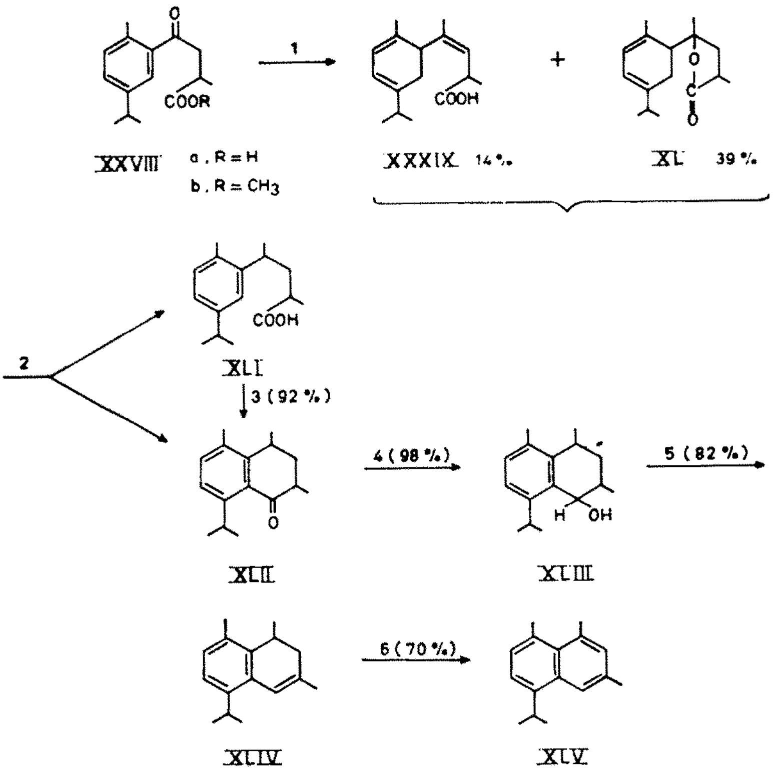
[32] e.g. see: K. Noack, *Spectrochim. Acta* **18**, 697 (1962).

[33] W. M. Schubert and W. A. Sweeney, *J. Amer. Chem. Soc.* **77**, 4172 (1955).

[34] W. T. G. Johnston, J. C. Smith and C. M. Staveley, *Chem. & Ind.* 607 (1954).



REAGENTS—

| | |
|---|---|
| 1 MeMgI | 4 LAH |
| 2 HI, red P | 5 $I_2$ |
| 3 PPA | 6 Sulphur |

Fig. 5. Synthesis of 8-methylcadalene.

there is no significant difference in the UV absorption of the various isomeric methylcadalenes and all show the expected bathochromic shift[35–37] due to four alkyl groups, the expected red shift being of the order of 10–15 mμ with respect to naphthalene.[37]

*IR absorption.* The IR spectra of the various methylcadalenes and cadalene are shown in Figs. 8–13. The differentiating features in the IR spectra of isomeric aromatic compounds are the out-of-plane deformation of nuclear hydrogens in the regions 650–1000 $cm^{-1}$ and the absorption patterns in the 1660–2000 $cm^{-1}$ region.

*650–1000 $cm^{-1}$ region.* The 650–1000 $cm^{-1}$ region has been used extensively[38] in determining the substitution pattern in benzene derivatives. The applications of these correlations to variously substituted naphthalenes has been considered by Cencelz and Hadzi[39] who concluded that the original benzene substitution rules are applicable in the case of naphthalenes, but the number of bands considerably exceeds those

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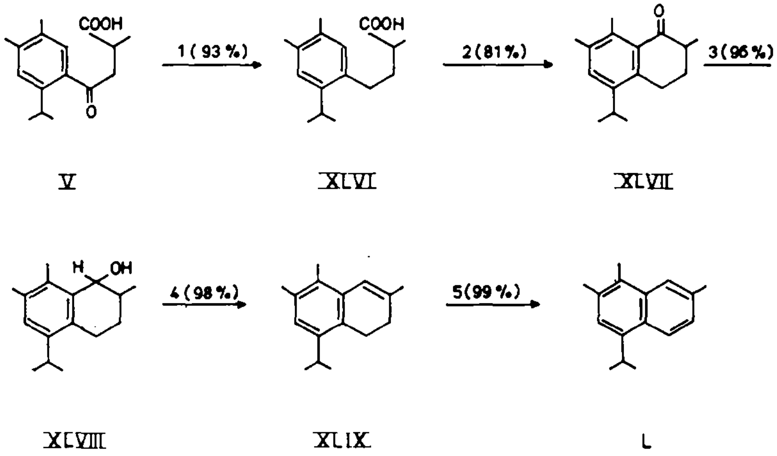
[35] W. L. Mosby, *J. Amer. Chem. Soc.* **75**, 3348 (1953).

[36] A. S. Bailey, K. C. Bryant, R. A. Hancock, S. H. Morrell and J. C. Smith, *J. Inst. Pet.* **33**, 203 (1947).

[37] H. H. Jaffe and M. Orchin, *Theory and applications of Ultraviolet spectroscopy* p. 287. Wiley, New York (1962).

[38] L. J. Bellamy, *The Infrared spectra of complex Molecules* p. 64. Methuen, London (1958).

[39] L. Cencelz and D. Hadzi, *Spectrochim. Acta* **7**, 274 (1955).



REAGENTS—

| | |
|---|---|
| 1 Zn–Hg, HCl | 4 $I_2$ |
| 2 PPA | 5 Sulphur |
| 3 LAH | |

Fig. 6. Synthesis of 1,2,7-trimethyl-4-isopropylnaphthalene.

Table 1. UV and IR spectral data of various tetralones

| Tetralone | UV | | IR* |
|---|---|---|---|
| | $\lambda_{max}^{EtOH}$ (m$\mu$) | $\varepsilon_{max}$ | $\nu^{C=O}$ cm$^{-1}$ |
| 3,7,8-Trimethyl-5-isopropyl- | 305 | 2274 | |
| (XII) | 257·7 | 10160 | 1667 |
| | 214 | 26050 | |
| 2,5,7-Trimethyl-8-isopropyl- | 304 | 2050 | 1689 |
| (XXIII)$^+$ | 257 | 8213 | |
| | 220 | 24090 | 1678 |
| 2,5-Dimethyl-8-isopropyl- | 302 | 2134 | |
| (XXX) | 253 | 9475 | 1681 |
| | 217 | 21440 | |
| 2,3,5-Trimethyl-8-isopropyl- | 300 | 1643 | |
| (XXXV)$^+$ | 251·6 | 7645 | 1681 |
| | 217 | 19770 | |
| 2,4,5-Trimethyl-8-isopropyl- | 301 | 2428 | |
| (XLII) | 254 | 9055 | 1678 |
| | 218·5 | 21090 | |
| 2,7,8-Trimethyl-5-isopropyl- | 308 | 2420 | |
| (XLVII) | 256 | 9774 | 1667 |
| | 214·5 | 30430 | |
| 2,5,7-Trimethyl- | 328 | 1914 | 1678 |
| (XX) | 253 | 10480 | |

* In Nujol mull, except for those marked + which were taken as liquid smear.

TABLE 2. UV ABSORPTION OF DIALINS

| Dialin | $\lambda_{max}^{EtOH}$ (mμ) | $\varepsilon_{max}$ |
|---|---|---|
| XIV | 267 | 11530 |
| | 231 (s)* | 41260 |
| | 225 | 36370 |
| | 219 | 28480 |
| XXVI | 263 | 15150 |
| | 223 | 50190 |
| XXXII | 262 | 9707 |
| | 224 | 29180 |
| | 219 | 29660 |
| XXXVII | 271 | 12350 |
| | 233 (s)* | 24710 |
| | 225 | 36530 |
| | 219 | 35180 |
| XLIV | 271 | 12630 |
| | 233 | 25260 |
| | 225·5 | 36110 |
| | 218 | 31760 |
| XLIX | 269 | 12900 |
| | 234 (s)* | 20140 |
| | 226 | 34150 |
| | 221 | 33360 |

* s = shoulder.

TABLE 3. PHYSICAL PROPERTIES OF CADALENE, METHYLCADALENES AND SOME OTHER NAPHTHALENIC HYDROCARBONS

| Compound | m.p. | b.p./mm | $d_4^{30}$ | $n_D^{30}$ | $M_D$ | $EM_D$ | $E\Sigma_D$ |
|---|---|---|---|---|---|---|---|
| Cadalene | — | 117–119°/1 | 0·9690 | 1·5810 | 70·52 | 1·167 | 0·5893 |
| 2-Methylcadalene | — | 128–130°/1·5 | 0·9707 | 1·5838 | 72·98 | 3·6270 | 1·7070 |
| 3-Methylcadalene | — | 129–131°/1·5 | 0·9721 | 1·5840 | 72·97 | 3·6170 | 1·7060 |
| 5-Methylcadalene | — | 144–145°/1·5 | 0·9847 | 1·5926 | 72·86 | 3·5070 | 1·6550 |
| 7-Methylcadalene | 39–40° | 139–140°/1·5 | — | — | — | — | — |
| 8-Methylcadalene | — | 135–136°/1·5 | 0·9800 | 1·5876 | 72·79 | 3·3870 | 1·5980 |
| 1,2,7-Trimethyl-4-isopropylnaphthalene | 59–60° | 139–140/1·5 | — | — | — | — | — |
| 1,3,6-Trimethylnaphthalene | — | 119–120°/1·5 | 0·9956 | 1·5976 | 58·19 | 2·6910 | 1·5830 |

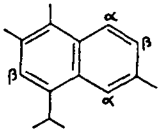
Table 4. Derivatives of methylcadalenes and their M.ps

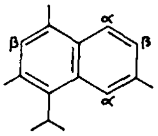
| Methylcadalene | TNB complex | | TNT complex | |
|---|---|---|---|---|
| | Present sample | Reported | Present sample | Reported |
| 2-Methylcadalene | 169–170° | 168·5–169°[1] | 118–120 | — |
| 3-Methylcadalene | 162–163° | 165°[2] | 97–98·5° | — |
| 5-Methylcadalene | 112–113·5° | 160–161°[2] | 86–87·5° | 87–88°[3] |
| 7-Methylcadalene | 126–127° | — | 72–73° | — |
| 8-Methylcadalene | 116–117° | 118–118·5°[3]<br>117·5°[34] | 45–64°* | 56–61°[34] |

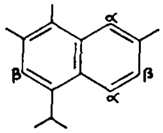
* The complex is unstable.

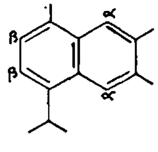
expected on the basis of these rules; and it was suggested that the absence of a particular band is more diagnostic than its presence. Work on these lines has also been reported by Whiffen *et al*,[40] Werner *et al.*[41] and Luther and Gunzler.[42]

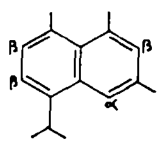
For the purpose of the present discussion, the 2-, 3-, 7-, and 8-methylcadalenes (two adjacent hydrogens and two lone hydrogen atoms) should display strong peaks in the 800–860 cm$^{-1}$ and 860–900 cm$^{-1}$, while 5-methylcadalene (two sets of two adjacent hydrogens) is expected to display only in the 800–860 cm$^{-1}$ region. Further differentiation of the compounds containing two lone hydrogens and a pair of adjacent hydrogens can be made on the basis of whether the hydrogens involved are α or β on the naphthalene nucleus. Thus we have the following subdivision:











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[40] J. G. Hawkins, E. R. Ward and D. H. Whiffen, *Spectrochim. Acta* **10**, 105 (1957).

[41] R. L. Werner, W. Kennard and D. Rayson, *Aust. Naturf. J. Chem.* **8**, 346 (1955).

[42] H. Luther and H. Günzler, *Z. Naturf.* **10b**, 445 (1955).

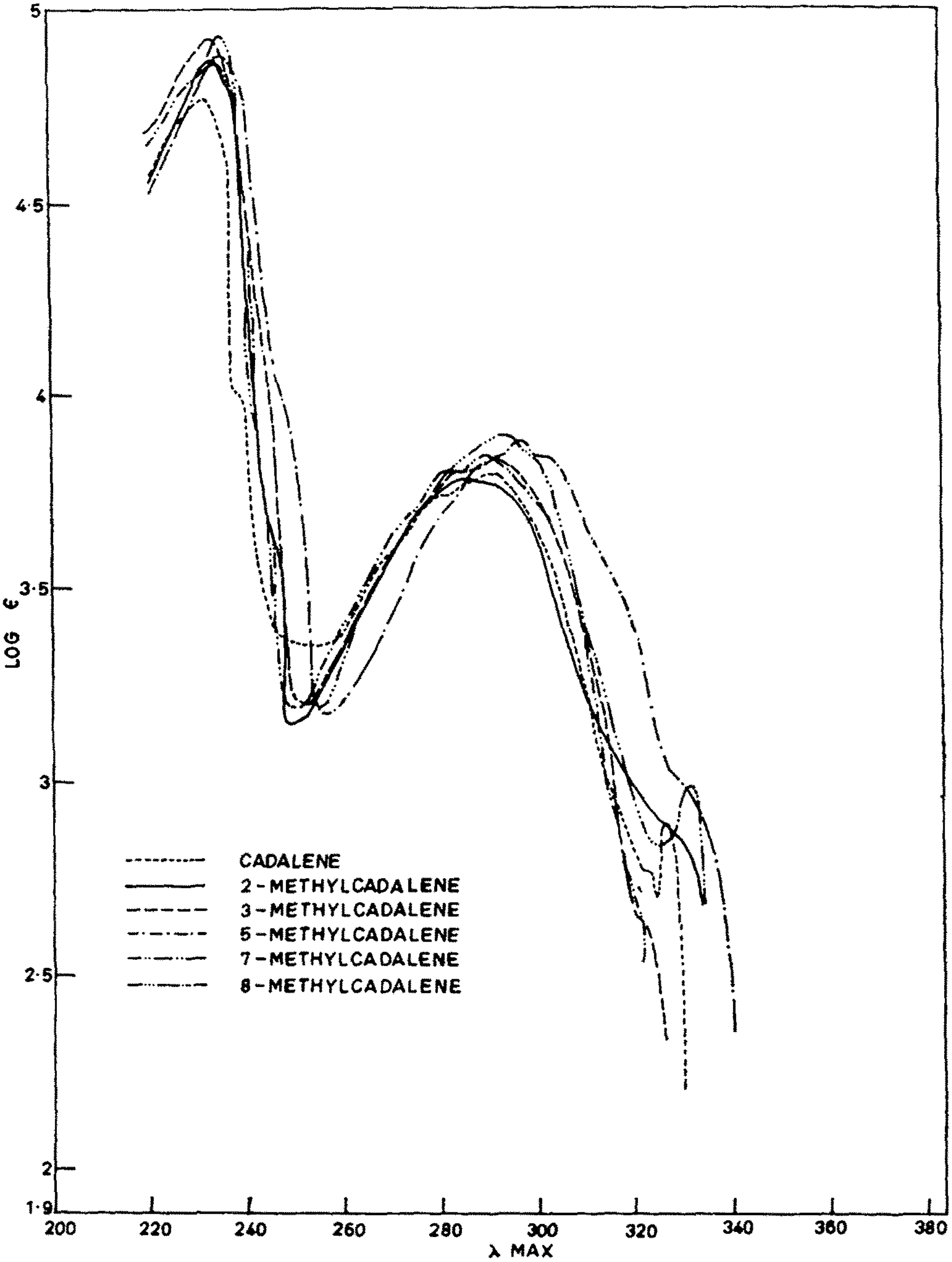

FIG. 7. UV spectra of cadalene and methylcadalenes.

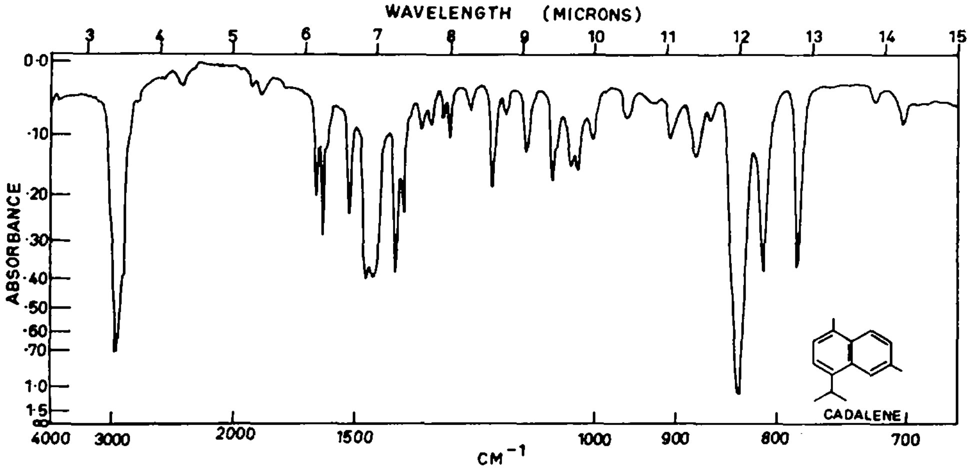

Fig. 8. IR spectrum of cadalene.

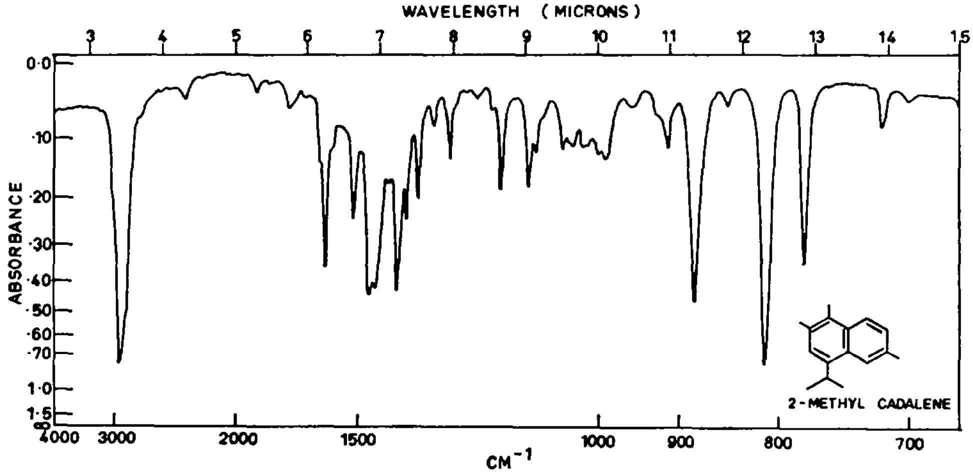

Fig. 9. IR spectrum of 2-methylcadalene.

As can be seen from Fig. 14, the patterns for 2- and 3- methylcadalenes as well as 1,2,7-trimethyl-4-isopropylnaphthalene, which also has a similar disposition of hydrogens, are essentially the same. 7-Methyl- and 8-methylcadalenes which differ slightly in the disposition of the hydrogens have different patterns of absorption in this region. Thus by making use of this fact it is possible to differentiate the methylcadalenes with the exception of 2-methyl and 3-methylcadalenes which, though differing from the others cannot be distinguished from each other.

The trinitrobenzene complexes of the methylcadalenes can be utilized to differentiate all the methylcadalenes by a study of the IR absorption patterns in the 750–950 $cm^{-1}$ region (Fig. 15). In this region trinitrobenzene has only one strong band at 928 $cm^{-1}$ and this is slightly modified by interaction with the naphthalene in the complex; the remaining bands are all due to the C—H out-of-plane deformation of

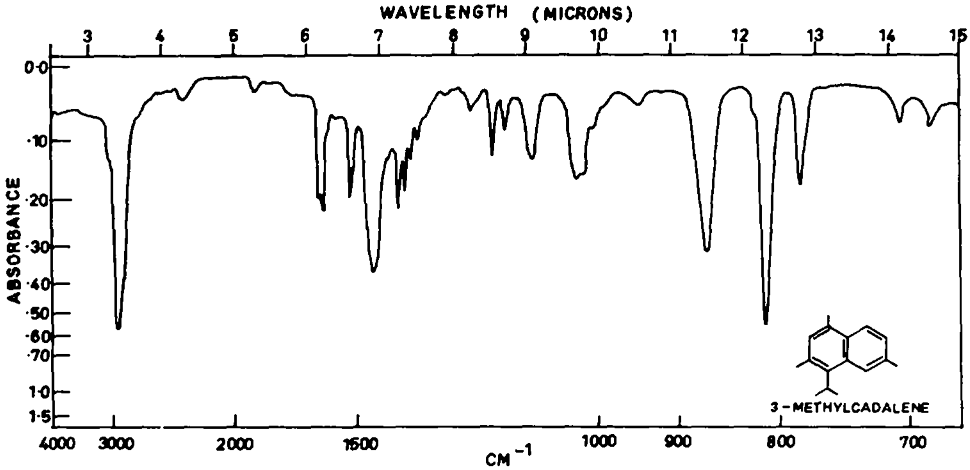

FIG. 10. IR spectrum of 3-methylcadalene.

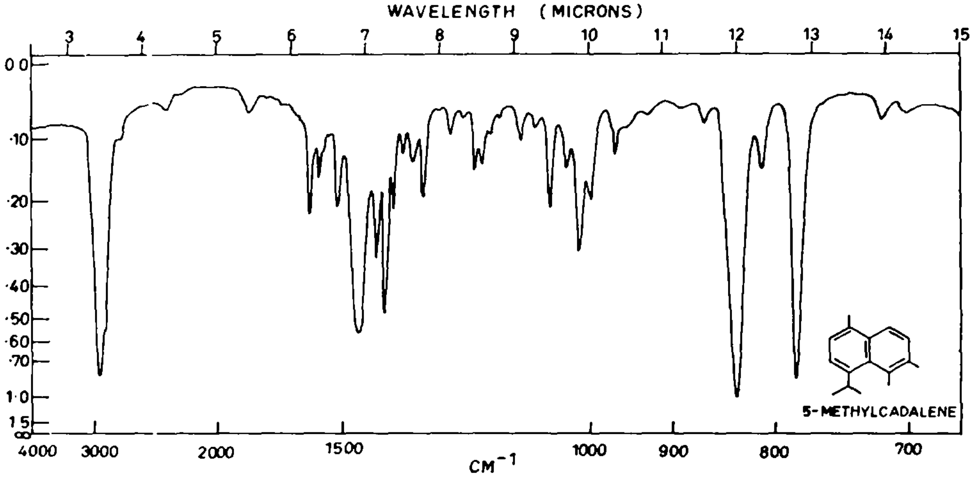

FIG. 11. IR spectrum of 5-methylcadalene.

the protons on the naphthalene and the overall pattern of the absorption, though remaining the same, the bands suffer a shift (14 cm$^{-1}$) to the higher frequencies.

*1660–2000 cm$^{-1}$ region.* Young *et al.*[43] showed that the absorption patterns produced by substituted benzenes in the region 1650–2000 cm$^{-1}$ are typical, within limits, of the types of substitutions and are independent of the nature of substituents. Therefore, this region may be used to determine the orientation on the benzene ring.[38] It has been shown by Whiffen[44] that these bands are summation bands (overtone and combination bands of the C—H out-of-plane fundamentals which occur between 700–1000 cm$^{-1}$).

[43] C. W. Young, R. B. DuVall and N. Wright, *Analyt. Chem.* **23**, 709 (1951).

[44] G. H. Whiffen, *Spectrochimica Acta* **7**, 253 (1955).

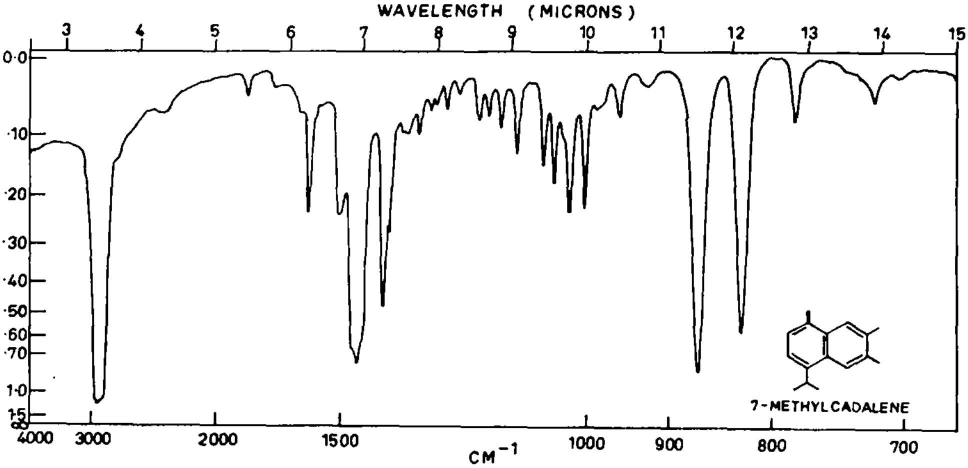

Fig. 12. IR spectrum of 7-methylcadalene.

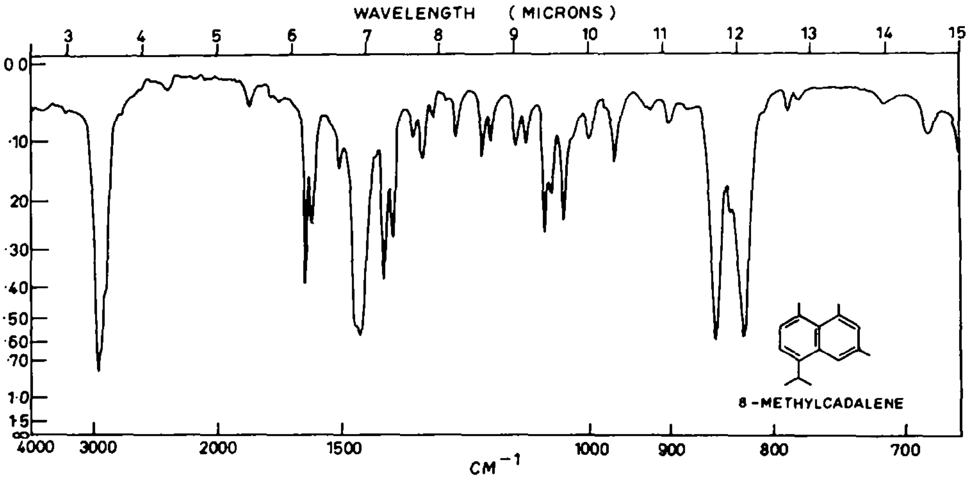

Fig. 13. IR spectrum of 8-methylcadalene.

Little data are available on the applicability of these absorptions to naphthalenes and Bellamy[38] has suggested that though the patterns in this region may not be helpful in determining the orientation in naphthalenic and polycyclic hydrocarbons, the patterns appear to be quite distinct.[45]

Fig. 16 shows the absorptions in the region 1660–2000 $cm^{-1}$ for the various methylcadalenes, cadalene and 1,2,7-trimethyl-4-isopropylnaphthalene. The distinct pattern of each compound can be used with advantage for its identification. However, some regularities regarding substitution may also be noticed. For example, 5-methyl-, 7-methyl- and 8-methylcadalenes which have the similar type of substitution (i.e. $\beta,\beta$-hydrogens free) in ring A, show a band around ~1850 $cm^{-1}$; likewise 2-methyl

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[45] N. Fuson and M. L. Josien [*J. Amer. Chem. Soc.* **78**, 3049 (1956)] have arrived at a similar conclusion with regard to substituted benzanthracenes.

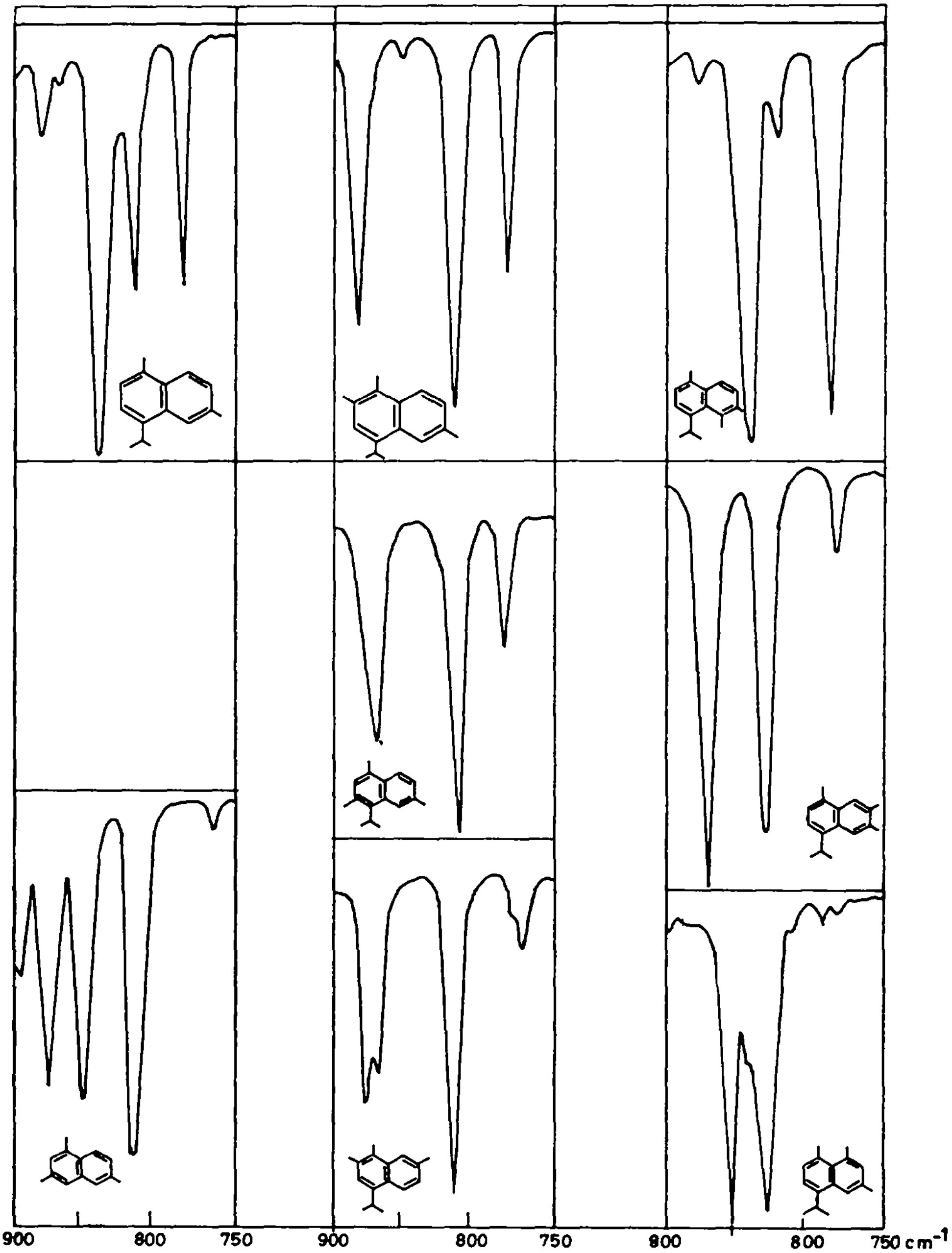

FIG. 14. Aromatic substitution patterns in the 750–900 cm$^{-1}$ region.

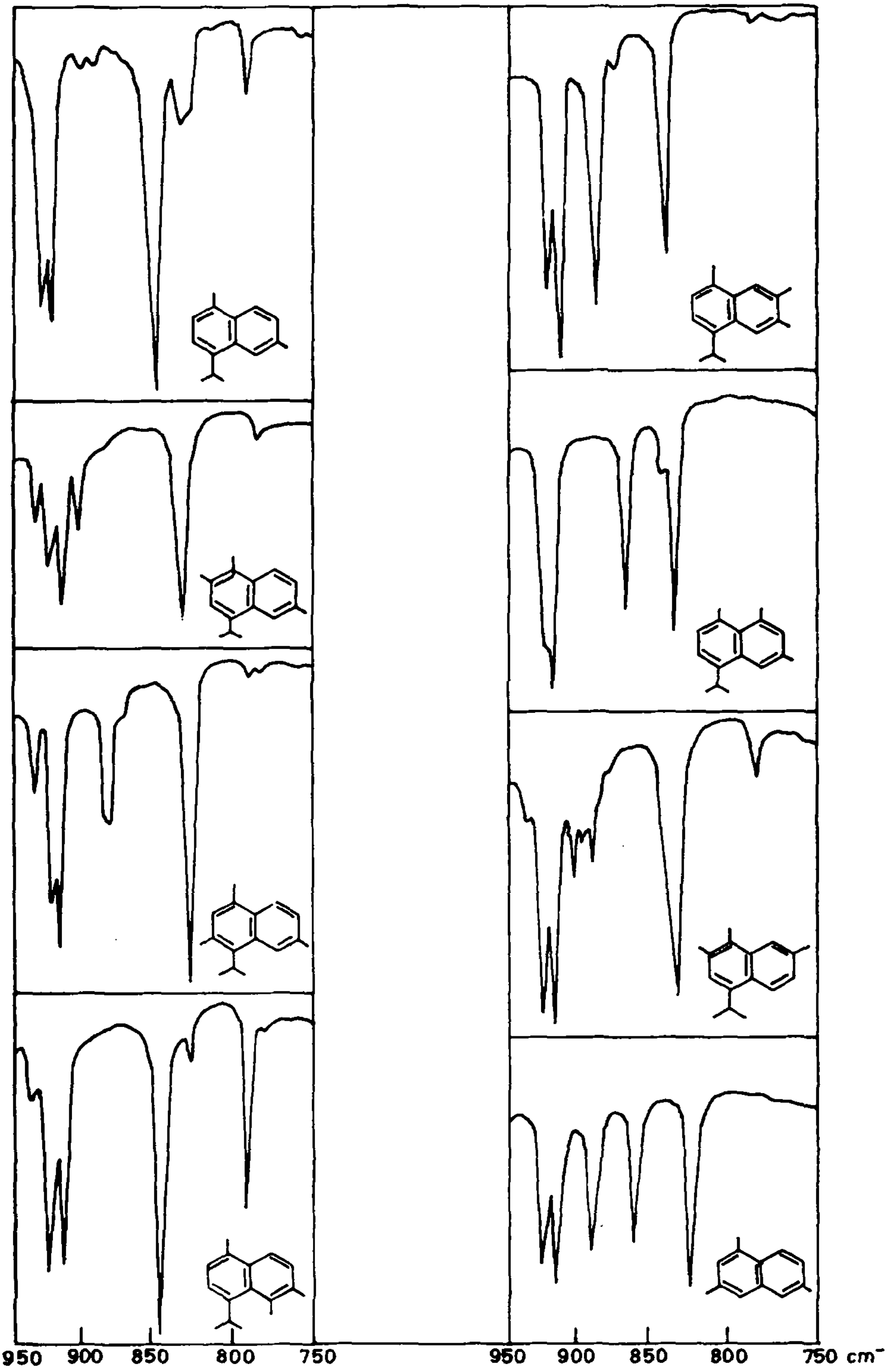

Fig. 15. Subsitution patterns of TNB complexes in the 750–950 cm$^{-1}$ region.

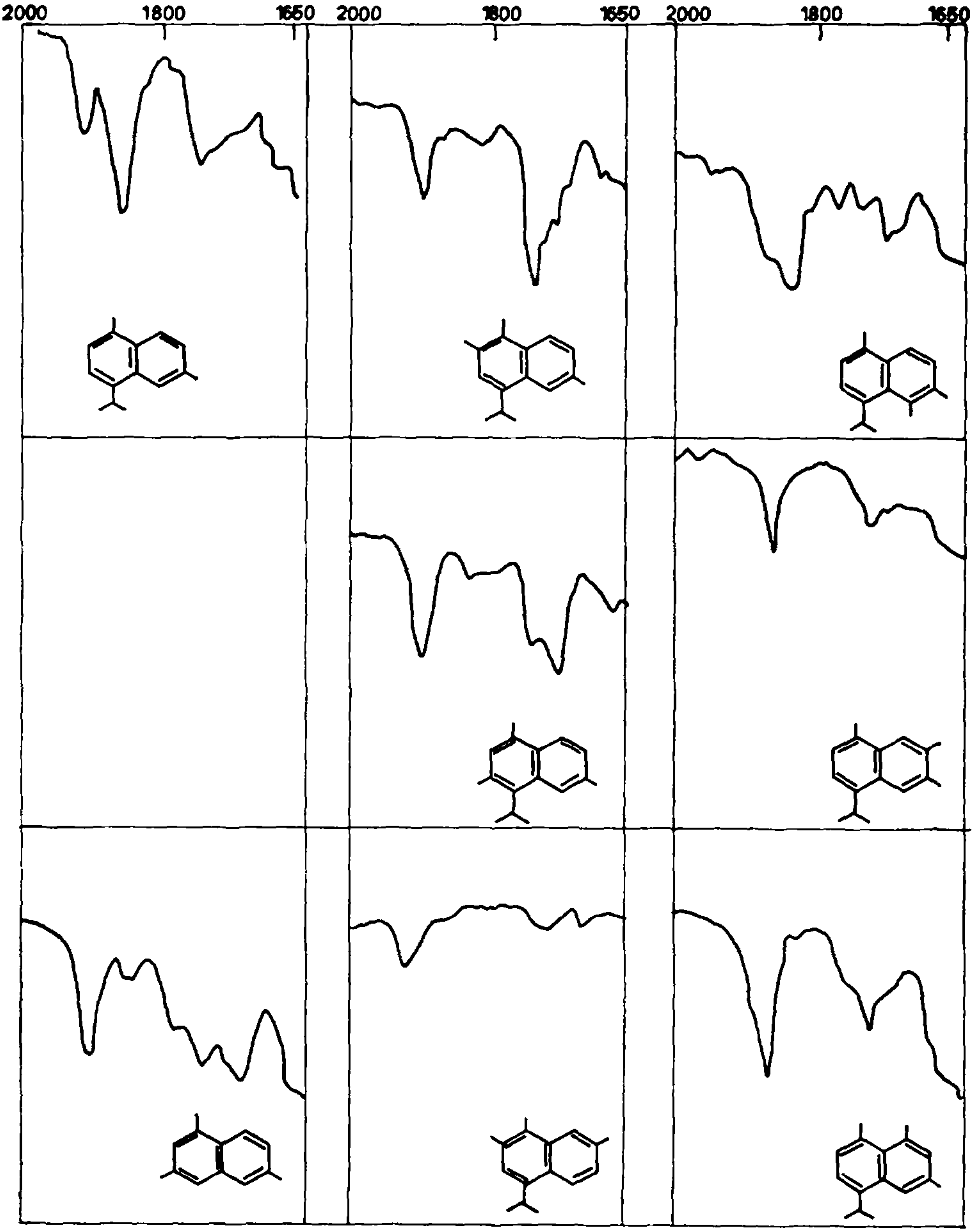

FIG. 16. Substitution patterns in the 1650–2000 cm$^{-1}$ region.

and 3-methylcadalenes and 1,2,7-trimethyl-4-isopropylnaphthalene with a similar type of substitution (αβ, α hydrogens free) in ring B, there is an absorption peak around ~1735 $cm^{-1}$. In accordance with expectation, both these bands are present in cadalene. Similarly, 1,3,6-trimethylnaphthalene in which ring B has a disposition similar to ring B in cadalene also shows a band at ~1900 $cm^{-1}$. It would, thus, appear that this region may, in fact, prove useful for subdividing substituted naphthalenes into different classes.

*Nuclear magnetic resonance.* Table 5 shows the methyl signals of the various methylcadalenes, cadalene and 1,2,7-trimethyl-4-isopropylnaphthalene. The chemical shift of methyls directly attached to the naphthalene nucleus is dependent on environment and useful rules which help in locating the position of methyls have been suggested.[46,27] The signal due to the isopropyl group in the various cadalenes occurs as a symmetrical doublet (J = 7 c/s) centred at ~80 c/s, with the exception of the isopropyl signal in 3-methylcadalene which is centred at 91 c/s. This unexpected shift to lower field strength in 3-methylcadalene could be due to steric factors originating from vicinal substitution.

TABLE 5. METHYL SIGNALS OF THE METHYLCADALENES AND SOME OTHER NAPHTHALENIC HYDROCARBONS*

| Compound | Methyl signals | |
|---|---|---|
| | Aromatic (singlet) in c/s | Isopropyl, 6H doublet centred at c/s (J = c/s) |
| 2-Methylcadalene | 144, 149, 149 | 81; (7·5) |
| 3-Methylcadalene | 146, 150, 152 | 91; (7·5) |
| 5-Methylcadalene | 144, 154, 158·5 | 78·5; (7) |
| 7-Methylcadalene | 144·5, 144·5, 154 | 80·5; (7) |
| 8-Methylcadalene | 145, 168, 168 | 79·5; (7) |
| 1,2,7-Trimethyl-4-isopropylnaphthalene | 145, 149, 149 | — |

* Spectra were run at 60 Mc/s.

The aromatic protons of cadalenes form the lowest fieldstrength (415–480 c/s) portion of the spectra. As may be anticipated, the compounds can be divided into two groups depending on identical orientation in ring A (5-, 7-, 8-methylcadalene) or in ring B (2-, and 3-methylcadalene). The spectra (Fig. 17) of the first group are characterized by the presence of a two proton signal (sharp or a slightly split singlet) at 423–432 c/s and assignable to the two β-protons of ring A.[47] The remaining aromatic protons in 7-methylcadalene are both α-proton and occur as one-proton signals in the farthest part of the spectrum i.e. 457–465 c/s, practically uncoupled, as the protons concerned are *para* to each other. In the spectrum of 8-methylcadalene the two protons in ring B are *meta* to each other and have α,β-orientation; in accord with this

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[46] F. F. H. YEW, R. Kurland and B. J. Mair, *Analyt. Chem.* **36**, 843 (1964).

[47] J. A. Popple, W. G. Schneider and H. J. Bernstein, *High-resolution Nuclear Magnetic Resonance* p. 147. McGraw-Hill, New York (1959) have shown that in naphthalene the β-protons absorb upfield relative to the α-protons and furthermore $J_{\beta\beta}$ is smaller than $J_{\alpha\beta}$.

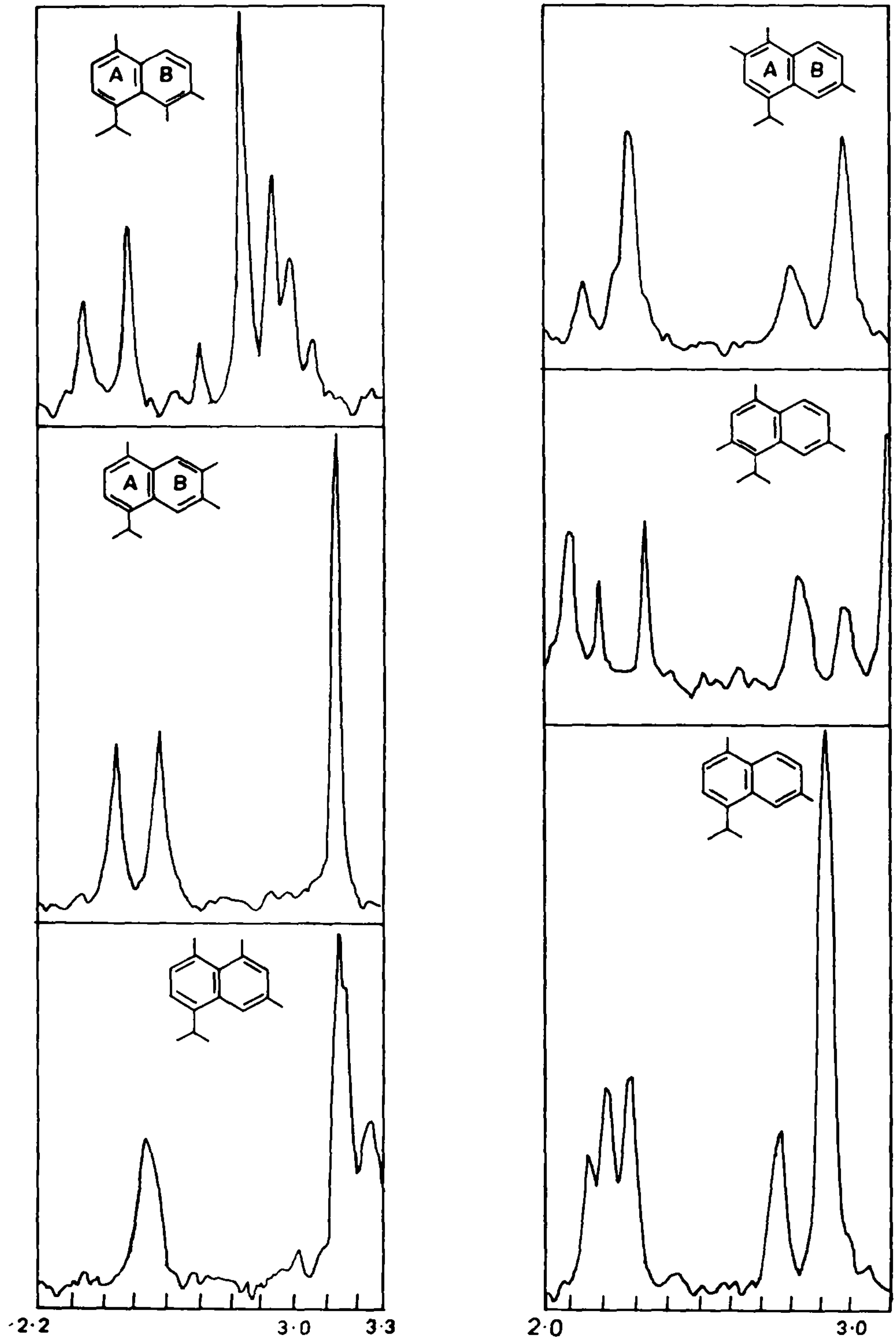

FIG. 17. Aromatic-proton signals of methylcadalenes.

the $\beta$-proton occurs as a similar singlet at 460 c/s; the broadening of these signals is expected, as the two protons have a *meta* relationship [$J_{HH(meta)}$ = 2–3 c/s]. The signals due to the protons ($\alpha,\beta$) in ring B of 5-methylcadalene should show an AB-type quartet and though this can be recognized in the spectrum the pattern is complicated possibly due to coupling.

TABLE 6. RETENTION TIME OF METHYLCADALENES IN GAS-LIQUID CHROMATOGRAPHY*

| Compound | Retention time cadalene† |
|---|---|
| Cadalene | 1 |
| 2-Methylcadalene | 1·428 |
| 3-Methylcadalene | 1·286 |
| 5-Methylcadalene | 1·771 |
| 7-Methylcadalene | 1·486 |
| 8-Methylcadalene | 1·828 |

* *Column*: $6' \times \frac{1}{4}''$, 20% diethylene glycol polysuccinate on Chromosorb W; Temp: 200°; *pressure*: 25 lbs/sq. in.; *carrier gas*: $H_2$

$$\dagger\ \text{Retention time}_{\text{Cadalene}} = \frac{\text{Retention time of the compound}}{\text{Retention time of cadalene.}}$$

In the second group the characteristic two-$\beta$-proton signal ($\beta,\beta$) of group A is absent and an AB quartet due to $\alpha,\beta$ protons in ring B is clearly seen in the spectra of both 2- and 3-methylcadalenes. The $\alpha$-proton of ring B in 3-methylcadalene occurs at 475 c/s while the $\beta$-proton of ring A occurs at 415 c/s. In 2-methylcadalene the $\alpha$-proton of ring B overlaps (at 464 c/s) one of the components of the AB quartet while the $\beta$-proton of ring A overlaps the signal at 424 c/s.

TABLE 7. $^{R}$DYE VALUES OF METHYLCADALENES IN TLC

| Compound | $^{R}$dye[44] |
|---|---|
| Azobenzene | 1 |
| 2-Methylcadalene | 0·7968 |
| 3-Methylcadalene | 1·1875 |
| 5-Methylcadalene | 1·25 |
| 7-Methylcadalene | 0·8437 |
| 8-Methylcadalene | 1·0937 |

The spectrum of cadalene has the characteristics expected of both of the above groups.

As can be seen from the above discussion the signals for the various aromatic protons of cadalenes are characteristic of each compound and serve as excellent identifying features.

*Gas-liquid chromatography* (*GLC*). The retention times of various cadalenes (Table 6) differ widely and this should help in the identification and detection of methylcadalenes and their mixtures.

*Thin-layer chromatography.* TLC of various cadalenes failed to show any difference in the $R_f$ values on silica gel using pet. ether. In view of our success[48] in the separation of olefins by taking advantage of their complexing with $Ag^+$ it was thought worthwhile to see if complexing of an aromatic hydrocarbon with a polynitro compound could be used to effect separation of isomeric aromatic hydrocarbons. For this purpose some preliminary work was carried out with α- and β-methylnaphthalenes using both 2,4,7-trinitrofluorenone and trinitrobenzene in varying concentrations in silica gel, as components of the π-complex. The results were better[49] with TNB and a concentration of 10% was found adequate. With this procedure some of the cadalenes show distinct differences (Table 7) in the R dye values.

## EXPERIMENTAL

All m.ps and b.ps are uncorrected. Pet. ether refers to the fraction b.p. 40–60°. All solvent extracts were finally washed with brine before drying ($Na_2SO_4$).

UV spectra were taken on a Beckman DK-2 Ratio Recording spectrophotometer. IR spectra were taken on Perkin–Elmer spectrophotometer, model 221 or Perkin–Elmer infracord model 137-E, either as smears (liquids) or in nujol (solids).

Alumina used for chromatography was made neutral by $HNO_3$ method[50] and standardized according to Brockmann.[51]

*NMR spectra.* All NMR spectra were taken in 20% $CCl_4$ solution with tetramethylsilane as the internal standard on a Varian A-60 spectrometer; peaks are reported in c/s.

*Gas-liquid chromatography.* Gas-liquid chromatography was carried out on a Perkin–Elmer vapour fractometer model 154-D.

*Thin-layer chromatoraphy.* Silica gel impregnated with TNB (10%), for use in TLC, was prepared as follows:

A hot solution of TNB (2·0 g) in 95% EtOH (20 ml) was thoroughly mixed with silica gel G (20 g). The solvent was evaporated and the impregnated silica gel dried at 60°. The dry mixture was finely powdered, mixed with a proper quantity of water and the plates were prepared in the usual way using a spreader. On drying, the plates were activated by heating at ~90° for 1½ hr and were thus made ready for use. Azobenzene (3%) was used as a standard dye-solution. After spotting the samples the plate was kept for saturation in the usual manner for 20 min. It was developed with pet. ether (40–60°) up to 15 cms; no spraying with any reagent was necessary as the spots were visible as such.

### *2-Methylcadalene*

*2-Methyl-*p*-cymene* (IV). A mixture of *p*-cymene (purified by $H_2SO_4$ method and distilled over Na, 92 g), paraformaldehyde (40 g), glacial AcOH (90 ml), syrupy $H_3PO_4$ (60 ml) and conc HCl (135 ml) in a 3-necked flask was stirred vigorously at 100 ± 2° for 7 hr. The reaction mixture was cooled, diluted with ice-cold water (120 ml) and the upper hydrocarbon layer separated. The aqueous part was extracted with ether (50 ml × 4), the combined hydrocarbon layer and ether extracts washed with water and dried. The solvent was flashed off and the residue fractionated to give the required 2-chloromethyl-*p*-cymene, contaminated with some 3-isomer, b.p. 138–140°/15 mm, $n_D^{26.5}$ 1·5220, yield 56·420 g (45%). (Lit.[52]: b.p. 123–124°/20 mm).

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[48] A. S. Gupta and Sukh Dev, *J. Chromat.* **12**, 189 (1963).

[49] After the completion of this work two sets of authors [M. Frank-Neumann and P. Jössang, *J. Chromat.* **14**, 280 (1964); A. Berg and J. Lam, *Ibid.* **16**, 157 (1964)] reported the separation of polycyclic aromatic hydrocarbons on similar lines. However, these authors did not study the chromatography of isomeric naphthalenes or other isomeric compounds. We find our procedure useful for the separation of various other polycyclic aromatic compounds, but further projected work on the subject was discontinued in view of the publications mentioned above. We find preparative TLC on impregnated layers useful for separating products of dehydrogenation.

[50] E. Lederer and M. Lederer, *Chromatography* p. 24, Elsevier, New York (1957).

[51] H. Brockmann and H. Schodder, *Ber. Dtsch. Chem. Ges.* **74**, 73 (1941).

[52] W. G. Whittleston, *J. Amer. Chem. Soc.* **59**, 826 (1937).

The above product (55 g) in 95% EtOH (200 ml) was shaken in presence of 10% Pd–C (3·0 g) for 8 hr in an atmosphere of $H_2$ ($H_2$ consumed at 28°/720 mm, 8·774 l.) and worked up to yield 2-methyl-*p*-cymene (~90% purity; see below), b.p. 111–112°/40 mm, $n_D^{23}$ 1·5000, yield 43·3 g (97%) (Lit.[53]: b.p. 86·87·5°/16 mm, $n_D^{21.1}$ 1·4991).

*α-Methyl-β-(3,4-dimethyl-6-isopropylbenzoyl)propionic acid* (V). To an intimate mixture of IV (19·6 g, 1·1 moles), methylsuccinic anhydride (12·6 g, 1 mole) and nitrobenzene (freshly distilled, 75 ml), chilled to −5°, anhydrous $AlCl_3$ (35·2 g, 2·2 moles) was added in 4 lots during 2 hr with vigorous stirring. The stirring was continued for 3 hr and the reaction mixture left overnight (23°). The syrupy complex was chilled, treated with crushed ice (100 g) and conc HClaq (30 ml). The product was allowed to stand for 1 hr and then extracted with ether (50 ml × 5). The combined ether extracts were washed with HClaq (25 ml), water (50 ml × 3) and extracted with 5% NaOHaq (50 ml × 4). The alkaline extract was charcoaled for 2 hr, filtered hot, the filtrate cooled and acidified with dil HCl (congo red). The liberated acid was initially gummy in nature but solidified on standing (4 days), m.p. 55–60°, yield 27 g (77·8%); recrystallization from pet. ether gave a material (20 g) of m.p. 68–72°. An analytical sample had m.p. 72·5–73·5°. (Found: C, 77·67; H, 8·54. $C_{16}H_{22}O_3$ requires: C, 77·25; H, 8·95%.)

From the mother liquors an acid (2·5 g, 10%) m.p. 131–133° was obtained. Mixed m.p. with XVIII remained undepressed and hence this by-product must have originated from 3-methyl-*p*-cymene, present in the above 2-methyl-cymene preparation.

Compound V (0·2 g) was mixed with water (2 ml) and conc $HNO_3$ (1 ml) and heated in a sealed Carius tube at 190–200° for 15 hr.[54] The product was evaporated to dryness and freed from $HNO_3$ by repeated evaporations with water. The residue (0·115 g) was treated with a slight excess of diazomethane and the resulting methyl ester crystallized from MeOH, m.p. 141–142·5° (Lit.[1] gives the m.p. 142–143·5° for VIb, yield 0·06 g. (Found: C, 54·82; H, 4·89. $C_{14}H_{14}O_8$ requires: C, 54·20 H, 4·55%.)

3,4-*Dimethyl-6-isopropylpropiophenone* (VIII). Anhydrous $AlCl_3$ (35 g, 2 moles) was added in two lots to nitrobenzene (freshly distilled, 45 ml), placed in a 3-necked flask and mechanically stirred. When all the $AlCl_3$ had dissolved the flask was chilled to 0° with separation of the $AlCl_3$-nitrobenzene complex. A mixture of IV (19·1 g; 1 mole) and propionyl chloride (12 g, 1 mole) was then introduced dropwise (45 min) while maintaining the temp at 5–10°. The reaction mixture was left overnight (20°) and then treated with crushed ice (100 g) and conc HCl (30 ml). The oil was extracted with ether (50 ml × 4), the combined ether extracts washed with conc HCl (25 ml), water and dried. The solvent was flashed off and the residue fractionated to give the required VIII, b.p. 144–145°/12 mm, $n_D^{25}$ 1·5180, yield 20·1 g (80·5%). (Found: C, 82·90 H, 10·20. $C_{14}H_{20}O$ requires: C, 82·35 H, 9·8%.) IR spectrum: C=O 1678 $cm^{-1}$.

The 2,4-*dinitrophenylhydrazone* prepared from the ketone (0·2 g) by diglyme method[55] crystallized from EtOH in 70% yield, m.p. 131–132·5°.

Compound VIII (0·44 g) was oxidized with dil $HNO_3$, and the pyromellitic acid isolated as the methyl ester, m.p. 136–140°, yield 0·21 g. Mixed m.p. with an authentic sample (m.p. 141–142·5°) of VIb was 140–142°.

*β-Methyl-(3,4-dimethyl-6-isopropylbenzoyl)propionic acid* (X). Compound VIII (10 g, 1 mole) in dry ether (10 ml) was chilled to 0° and to it was added a trace of $AlCl_3$ and then $Br_2$ (2·9 ml, 1 mole) in 1 ml portions. Decolourization was quite rapid and when the reaction was complete, ether and HBr were removed immediately under suction in a current of dry air. The syrupy liquid residue was used as such in the next step.

Sodium (2·42 g) was powdered under dry xylene (50 ml) which was then replaced with dry toluene (50 ml). To this diethylmalonate (17 g, 1 mole) was added dropwise (40 min) at room temp (~25°) and finally refluxed at 130–140° for 2 hr. The product was cooled, and the above bromoketone added dropwise and the mixture refluxed for 10 hr. The mixture was then cooled, made just acidic with dil HCl and steam-distilled to remove the unreacted malonic ester. The residue was taken up in ether (50 ml × 3), washed with water and the solvent flashed off to give crude IX (11·8 g; 67·6%) which was hydrolysed with 15% alcoholic NaOH (100 ml; 5 hr). The usual work up gave a brown solid,

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[53] A. Klages, *Ber. Dtsch. Chem. Ges.* **39**, 2306 (1906).

[54] W. P. Campbell and M. D. Soffer, *J. Amer. Chem. Soc.* **64**, 425 (1942).

[55] H. J. Shine, *J. Org. Chem.* **24**, 252 (1959).

m.p. 112–124°, yield 8·1 g, which was the required X contaminated with some diacid. A small portion (1 g) on repeated crystallizations from 90% AcOH gave a pure compound (0·65 g), m.p. 142–143·5° and analysed for X. (Found: C, 73·13 H, 8·65; $C_{16}H_{22}O_3$ requires: C, 73·25; H, 8·45%.)

*β-Methyl-γ-*(3,4-*dimethyl-6-isopropylphenyl*)*butyric acid* (XI). The above keto acid (m.p. 112–124° 10 g) was reduced with Zn–Hg (from 20 g Zn wool, 2 g $HgCl_2$, 3 ml conc, HCl and 40 ml $H_2O$) and dil HCl (56 ml conc HCl, 27 ml $H_2O$) with the addition of toluene (35 ml) and glacial AcOH (4 ml) by refluxing the mixture at 130–140° for 36 hr. After every 6 hr, conc HCl (15 ml) was added. The reaction mixture was cooled, the toluene layer separated, washed with water and dried. The solvent was removed and the residue distilled to yield XI as a colourless, viscous liquid, b.p. 152–155°/0·5 mm, $n_D^{25}$ 1·5786, yield 7·8 g (82·4%). (Found: C, 77·10; H, 9·61 $C_{16}H_{24}O_2$ requires: C, 77·37; H, 9·74%.)

3,7,8-*Trimethyl-5-isopropyltetralone*-1 (XII). The above acid (4 g) was added, all at once, with mixing to polyphosphoric acid (from 20 g $P_2O_5$ and 12 ml syrupy $H_3PO_4$) kept at 95–100° and the mixture maintained at this temp for ½ hr, with occasional stirring. The reaction product was poured onto ice (50 g) and extracted with a mixture of pet. ether (1:1; 25 ml × 4). The combined extracts were washed with water (20 ml × 2), 5% $Na_2CO_3$aq (10 ml × 2) and finally with water (20 ml × 3) and then dried. The solvent was removed and the residue fractionated to yield XII as a pale yellow oil which solidified immediately, b.p. 142–155°/1·5 mm, m.p. 44–60°, yield 3·0 g. By repeating the above experiments a total of 12·5 g (m.p. 44·60°) of the tetralone was collected. As the purification of the tetralone by crystallization was wasteful, it was best achieved by chromatography (10·6 g of the tetralone) over $Al_2O_3$/I (185 g; 24 cm × 3 cm):

| | | |
|---|---|---|
| Frac. 1: | Pet. ether (15 × 200 ml) | 7·115 g m.p. 62–70° |
| Frac. 2: | Benzene (1 × 200 ml) | 1·101 g m.p. 49–54° |
| Frac. 3: | Benzene (2 × 200 ml) | 0·9991 g m.p. 79–85° |
| Frac. 4: | Benzene (4 × 200 ml) | 0·20 g m.p. 50–82° |

Fraction 1 was crystallized from pet. ether to constant m.p. 69·5–70·5°, yield 6·0 g, and analysed for $C_{16}H_{22}O$. (Found: C, 83·79; H, 9·71. $C_{16}H_{22}O$ requires: C, 83·43; H, 9·63%). IR spectrum: C=O 1667 cm$^{-1}$.

Fraction 3 on recrystallization from benzene gave a solid, m.p. 95·96°. (Found: C, 83·01, 83·2; H, 8·6, 8·35. $C_{13}H_{16}O$ requires: C, 82·97; H, 8·5%.) This indicated that, in all possibility, the isopropyl group had been cleaved during the PPA cyclization (cf: PPA cyclization of XIX). This was not studied further.

1,2,6-*Trimethyl-4-isopropyl*-5,6-*dihydronaphthalene*. The above tetralone (2·0 g) was reduced with LAH (0·495 g) in ether (80 ml) at 0°, during 12 hr and then worked up with ice-water (80 ml) followed by 40% sodium potassium tartrateaq (75 ml) to yield, ultimately, 1·92 g crude carbinol, which was used as such in the next step.

The above product (2·92 g) was mixed with $I_2$ (50 mg) and heated on a waterbath at 95° for 1 hr. The product was taken up in pet. ether (50 ml), washed with water (15 ml × 2), 10% $NaHSO_3$aq (25 ml × 2), water (15 ml × 2) and dried. The solvent was flashed off and the residue distilled over Na, to furnish XIV as a colourless liquid, b.p. 122–124°/2 mm, $n_D^{24}$ 1·5545, yield 2·42 g (89·9%). (Found: C, 89·40; H, 9·90. $C_{16}H_{22}$ requires: C, 89·65; H, 10·35%.)

2-*Methylcadalene* (XV). The dialin (2·38 g) was mixed with S (0·36 g) and heated at 205–210°/200 mm for 3 hr. The product was distilled over a little freshly prepared Cu powder: b.p. 131–133°/2 mm, $n_D^{24}$ 1·5792, yield 2·09 g.

Trinitrobenzene (TNB; 1·6 g), 90% EtOH (12 ml) and the above product (2·092 g) were mixed and warmed to a clear solution. On cooling, crystals separated which were filtered off, washed with EtOH and dried, m.p. 166–167°, yield 2·70 g. Two recrystallizations from 80% AcOH furnished an analytical sample of the TNB complex, soft yellow needles, m.p. 169–170·5°. (Found: C, 62·10; H, 5·10; N, 9·87. $C_{22}H_{23}O_6N_3$ requires: C, 62·16; H, 5·45; N, 9·88%.)

The above complex of 2-methylcadalene (m.p. 169–170·5°, 2·92 g) was passed through a column of $Al_2O_3$/I (120 g, 17 cm × 3 cm) using pet. ether as the eluent. The regenerated hydrocarbon, obtained after solvent removal, was distilled over Na: b.p. 128–130°/1·5 mm.

*Trinitrotoluene complex* was prepared from 0·2 g TNT and 0·2 g pure 2-methylcadalene, in EtOH (3 ml) and, recrystallized twice from 95% EtOH, yellow needles, m.p. 119–120°. (Found: C, 63·20; H, 5·80. $C_{23}H_{25}O_6N_3$ requires: C, 62·86; H, 5·73%.)

### 3-*Methylcadalene*

*α-Methyl-β(2,4-dimethyl-5-isopropylbenzoyl)propionic acid* (XVIII). A mixture of XVII[56] (45 g, 1·1 moles) methylsuccinic anhydride (29·0 g, 1 mole) and freshly distilled nitrobenzene (175 ml) in a 3-necked flask was chilled to ~5°, and anhydrous $AlCl_3$ (80 g, 2 moles) added in 4 lots during 1½ hr with stirring. The reaction was worked up as described for V and yielded the crude acid (58 g, 72·8% m.p. 120–130°) which was crystallized from benzene–pet. ether (1:2), m.p. 131·5–133·5°, yield 33 g (41·4%). (Found: C, 73·41; H, 8·39. $C_{16}H_{22}O_3$ requires: C, 73·28; H, 8·39%.)

The acid (0·2 g) was oxidized with dil $HNO_3$ (1 ml $HNO_3$ and 2 ml $H_2O$) as described earlier and the product isolated as its methyl ester, m.p. 140–142·5°, yield 0·40 g. Mixed m.p. with an authentic sample of VIb (m.p. 141–142·5°) was 141·5–142·5°.

*α-Methyl-γ-(2,4-dimethyl-5-isopropylphenyl)butyric acid* (XIX). Pure XVIII (28 g) was reduced by refluxing with Zn–Hg (from 65 g Zn wool, 6·5 g $HgCl_2$, 6·5 ml conc HCl and 108 ml $H_2O$), dil HCl (16 ml conc HCl and 55 ml $H_2O$), toluene (81 ml) and glacial AcOH (8 ml) for 36 hr. The usual work up gave the required acid which was purified by distillation, b.p. 163–167°/0·5 mm, $n_D^{28}$ 1·5110, yield 24·6 g (92·7%). The acid solidified on standing and was crystallized from pet. ether, m.p. 64–65°. (Found: C, 77·38; H, 9·50. $C_{16}H_{24}O_2$ requires: C, 77·40; H, 9·60%.)

Oxidation of XIX (0·2 g) with dil $HNO_3$ (1 ml conc. $HNO_3$ and 2 ml $H_2O$) in the above manner gave pyromellitic acid identified as its methyl ester, m.p. 140–142°.

2,5,7-*Trimethyl-tetralone*-1 (XX). (i) *PPA method.* The XIX (15 g) was treated with PPA (from 75 g $P_2O_5$ and 45 ml syrupy $H_3PO_4$) at 97° for ½ hr. The usual work up furnished XX which was purified by distillation, b.p. 126–128°/1 mm, yield 10·2 g (89·9%). The ketone solidified immediately, and was crystallized from pet. ether m.p. 59–60° (Lit.[57]: b.p. 163–164°/12 mm). (Found: C, 82·7; H, 8·37. $C_{13}H_{16}O$ requires: C, 82·93; H, 8·57%.)

Nitric acid oxidation of XX (0·2 g) followed by esterification of the resulting acid (0·19 g) with diazomethane furnished the tetramethyl ester of XXIb which was crystallized from MeOH, m.p. 105–107° (Lit.[58]: m.p. 107–109°), yield 0·15 g.

(ii) $AlCl_3$ *method.* $PCl_5$ (0·97 g) was placed in a distillation flask (100 ml, side tube plugged) and covered with dry benzene (15 ml). The acid (1 g) dissolved in dry benzene (5 ml) was added in two lots to the $PCl_5$. Benzene and $POCl_3$ were removed by distillation under vacuum at <90°. Anhydrous $AlCl_3$ (0·69 g, 1·1 moles) was placed on a flask carrying a guard tube and immediately covered with dry benzene (thiophene free) and chilled to −10°. The acid chloride, as prepared above, was taken up in benzene, chilled to −5° and added at once to the $AlCl_3$–benzene mixture. On warming to room temp the reaction started with the evolution of HCl gas. After the vigour of the reaction had subsided, the reaction product was warmed to 50° till all the $AlCl_3$ dissolved. The reaction mixture was then worked up to furnish a product, b.p. 122–123°/0·8 mm, m.p. 58–60°, yield 0·59 g (77%). Mixed m.p. with PPA cyclized product (m.p. 59–60°) remained undepressed.

1,3,6-*Trimethylnaphthalene* (XXII). Compound XX (2·0 g, 1 mole) in ether (20 ml) was reduced with LAH (0·404 g, 1 mole) in dry ether (60 ml) and the carbinol (1·89 g), obtained heated with $I_2$ (50 mg) to furnish the dialin which was distilled over Na, b.p. 115–117°/2 mm, $n_D^{30}$ 1·5646, yield 1·45 g (85%). (Found: C, 90·80; H, 9·08. $C_{13}H_{16}$ requires: C, 90·64; H, 9·36%.)

The above dialin (1·42 g) and S (0·22 g) were heated together at 210–220°/200 mm for 3 hr. The product was distilled over a little Cu powder: b.p. 126–129°/0·9 mm, $n_D^{29}$ 1·5874, yield 1·34 g. Its *trinitrobenzene complex* was prepared in the usual manner, m.p. 148–149°. (Found: C, 59·70; H, 4·20; N, 11·1. $C_{19}H_{17}O_6N_3$ requires: C, 59·53; H, 4·47; N, 10·96%.)

The above TNB complex (m.p. 148–149°, 4·53 g) was passed through a column of basic $Al_2O_3$/I (160 g; 22 cm × 3 cm) using pet. ether for elution. After solvent removal, the regenerated hydrocarbon was distilled over Na: b.p. 119–120°/1·5 mm, $n_D^{20}$ 1·5976. (Lit.[56,59,60]: b.p. 140–144°/10 mm, 115–120°/3 mm, 104–108°/1 mm resp.).

2,5,7-*Trimethyl*-8-*isopropyltetralone*-1 (XXIII). $PCl_5$ (9·2 g) placed in a flask carrying a $CaCl_2$ guard tube, was covered with thiophene-free benzene (60 ml) and to this, XIX (10 g) was added and

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[56] D. V. Nightingale and B. Carton, *J. Amer. Chem. Soc.* **62**, 280 (1940).

[57] L. Ruzicka, L. Ehmann and E. Mörgeli, *Helv. Chim. Acta* **16**, 323 (1933).

[58] L. I. Smith and G. D. Byrkit, *J. Amer. Chem. Soc.* **55**, 4305 (1933).

[59] L. Ruzicka, L. Ehmann, H. Arni and Ed. Bernasconi, *Helv. Chim. Acta* **15**, 154 (1932).

[60] R. C. Gupta and M. S. Muthana, *J. Ind. Inst. Sci.* **35A**, 310 (1953).

the mixture swirled well till all $PCl_5$ disappeared. The crude product was chilled to ~ −5° and to it anhydrous $SnCl_4$ (10 ml) in thiophene-free benzene (10 ml) was added in one lot and the mixture swirled for 5 min. The mixture, which was deep red in colour, was left as such for ½ hr when the colour had changed to dirty brown. The reaction product was poured onto crushed ice (250 g), conc HCl (80 ml) and ether (50 ml) and worked up to give the required tetralone, b.p. 146–147°/3 mm, $n_D^{28}$ 1·5442, yield 8·75 g (92·5%). (Found: C, 83·40; H, 10·0. $C_{16}H_{22}O$ requires: C, 83·43; H, 9·60%.)

Nitric acid oxidation of XXIII (0·22 g) followed by esterification of the acid (0·24 g) with diazomethane, furnished an ester which crystallized from MeOH m.p. 148–150°, identical with the pentamethyl ester of XXIV (Lit.[54]: m.p. 149–150°); yield 0·19 g. Mixed m.p. with VIb (140–142°) was 115–130°.

1,3,6-*Trimethyl-4-isopropyl-7,8-dihydronaphthalene* (XXVI). Compound XXIII (3·0 g) in ether (30 ml) was reduced with a slurry of LAH (0·54 g) in dry ether (100 ml) at ~ −5° and the usual work up gave XXV (2·86 g) which was dehydrated by heating with $I_2$ (0·1 g). The dialin, thus obtained, was distilled over Na: b.p. 126–127°/2 mm, $n_D^{28}$ 1·5602, yield 2·56 (97%). (Found: C, 89·90; H, 10·20. $C_{16}H_{22}$ requires: C, 89·65; H, 10·35%.)

3-*Methylcadalene* (XXVII). The above dialin (2·54 g) was dehydrogenated with S (0·39 g) at 205–210°/200 mm for 3 hr, and the crude 3-methylcadalene directly distilled off over Cu powder: b.p. 132–134°/2·5 mm, $n_D^{28.5}$ 1·5834, yield 2·38.

*The trinitrobenzene complex* was prepared and recrystallized from 90% AcOH to give orange yellow needles, m.p. 162–163°. (Found: C, 61·90; H, 5·60; N, 10·10. $C_{22}H_{23}O_6N_3$ requires: C, 62·16; H, 5·45; N, 9·88%.)

The TNB complex (5·49 g, m.p. 162–163°) was passed through a column of basic $Al_2O_3$/I (200 g, 25 cm × 3·5 cm) using pet. ether as the eluent. The regenerated hydrocarbon, so obtained, was finally distilled over Na: b.p. 129–131°/1·5 mm.

*The trinitrotoluene complex* was prepared from pure 3-methylcadalene (0·2 g) and recrystallized from EtOH to yield yellow needles, m.p. 97–98·5°. (Found: C, 63·22; H, 5·98. $C_{23}H_{25}O_6N_3$ requires: C, 62·86; H, 5·93%.)

### 5-*Methylcadalene*

2,5-*Dimethyl-8-isopropyltetralone*-1 (XXX). Compound XXIX (4 g) was treated with PPA (20 g, $P_2O_5$ and 12 ml syrupy $H_3PO_4$) at 97° for ½ hr with occasional stirring and then worked up to give the required tetralone, b.p. 120°/1 mm $n_D^{30}$ 1·5351, yield 2·34 g (63·3%). The above tetralone solidified after a day and crystallized from pet. ether, m.p. 50–51°; mixed m.p. with a sample obtained by the $AlCl_3$ method[2] remained undepressed.

1,5,6-*Trimethyl-4-isopropyl-7,8-dihydronaphthalene* (XXXII). To a solution of methyl-lithium in ether (from 1·7 g Li, 16·8 g MeI and 90 + 35 ml ether), the above tetralone (3·4 g in 15 ml ether) was introduced with stirring ($N_2$) at ~0°. The reaction mixture was finally refluxed for 15 hr and worked up with $NH_4Cl$ (20%, 30 ml) in the usual manner to give 3·3 g crude carbinol.

The above carbinol (3·26 g) and $I_2$ (0·1 g) were heated together for 1 hr at 98–100° on a waterbath and worked up to give XXXII which was distilled over Na b.p. 117–119°/1·5 mm, $n_D^{28}$ 1·5475, yield 2·95 g (98%). (Found: C, 89·16; H, 10·50. $C_{16}H_{22}$ requires: C, 89·65; H, 10·35%.)

5-*Methylcadalene* (II). The above dialin (1·71 g) was dehydrogenated with S at 205–210° for 3 hr as described to give II as a liquid: b.p. 122–128°/1·3 mm, $n_D^{28}$ 1·5863, yield 1·5 g (88·5%). The *TNB complex* was recrystallized from 80% AcOH to give orange needles, m.p. 110–111°, yield 2·02 g. One recrystallization from 80% AcOH gave an analytical sample, m.p. 112–113·5°. (Found: C, 62·40; H, 5·50; N, 10·10. $C_{22}H_{23}O_6N_3$ requires: C, 62·16; H, 5·45; N, 9·88%.)

The TNB derivative (5·27 g) was passed through a column of basic $Al_2O_3$/I (180 g, 25 cm × 3 cm) and eluted with pet. ether when pure 5-methylcadalene (2·53 g) was obtained, b.p. 144–145°/1·5 mm.

The *trinitrotoluene complex* was prepared from pure 5-methylcadalene (0·2 g) and the TNT reagent (0·2 g) and crystallized twice from EtOH to give orange needles, m.p. 86–87·5°. (Found: C, 62·40; H, 5·50. $C_{23}H_{25}O_6N_3$ requires: C, 62·86; H, 5·73%.)

*7-Methylcadalene*

*β-(p-Cymoyl-2)-α,β-dimethylpropionic acid* (XXXIII).[61] Dimethylsuccinic anhydride (10 g, 1 mole) was condensed with *p*-cymene (21·50 g, 1·1 moles) using nitrobenzene (50 ml) and anhydrous $AlCl_3$ (28 g, 3 moles), as detailed. The required acid (9·8 g) was a gum which was purified *via* its methyl ester.

The crude acid (9·8 g) was mixed with benzene (10 ml), anhydrous MeOH (10 ml) and conc $H_2SO_4$ (1 ml) and refluxed for 10 hr. Working up of the product gave the required ester, b.p. 134–139°/1 mm, yield 5·6 g. (Found: C, 73·92; H, 8·73. $C_{17}H_{24}O_3$ requires: C, 73·91; H, 8·70%.)

The above ester (9·8 g) was hydrolysed by refluxing with 10% alcoholic KOH (65 ml) for 15 hr. The acid obtained was a brown gummy product and was used as such in the next step.

*γ-(p-Cymyl-2-)-α,β-dimethylbutyric acid* (XXXIV). Compound XXXIII (8·7 g) was reduced with Zn–Hg (from 20 g Zn wool, 2 g $HgCl_2$, 2 ml conc HCl, 20 ml $H_2O$) and dil HCl (conc HCl 32 ml 13 ml $H_2O$) and toluene (21 ml) by refluxing for 48 hr. The product was worked up as detailed and the acid was purified by distillation, b.p. 150–153°/0·8 mm, yield 5·8 g (70·44%). (Found: C, 77·49; H, 9·73. $C_{16}H_{24}O_2$ requires: C, 77·37; H, 9·74%.)

2,3,5-*Trimethyl*-8-*isopropyltetralone*-1 (XXXV). To PPA (from 25 g $P_2O_5$ and 15 ml syrupy $H_3PO_4$) maintained at 97°, the above acid (4·7 g) was added and the mixture maintained at 97° for ½ hr with occasional stirring. The product was purified by fractionation: b.p. 125–127°/0·8 mm, yield 3·6 g (81·9%). (Found: C, 83·41; H, 9·84. $C_{16}H_{22}O$ requires: C, 83·49; H, 9·56%.)

1,6,7-*Trimethyl*-4-*isopropyl*-7,8-*dihydronaphthalene* (XXXVII). Compound XXXV (4 g) in ether (40 ml) was reduced with LAH (0·66 g, 120 ml ether) yielding crude XXXVI (3·9 g; 97·7%), which was mixed with $I_2$ (0·1 g), heated for 1 hr at ~95° and worked up to give 3·5 g of XXXVII. A small sample (0·95 g) was distilled over Na: b.p. 117–119°/1 mm, $n_D^{28.5}$ 1·5425, yield 0·79 g. (Found: C, 89·17; H, 10·40. $C_{16}H_{22}$ requires: C, 89·65; H, 10·35%.)

7-*Methylcadalene* (XXXVIII). The above dialin (3·2 g) was dehydrogenated with S (0·55 g) at 210–215°/200 mm for 3 hr and worked up as before: b.p. 128–130°/1 mm, $n_D^{29}$ 1·5782, yield 2·6 g.

*The trinitrobenzene complex* was prepared (from 2·6 g of the hydrocarbon) in the usual manner, m.p. 122–124°, yield 4·03 g. An analytical sample crystallized from 80% AcOH to give orange needles, m.p. 126–127°. (Found: C, 62·61; H, 5·40; N, 9·64. $C_{22}H_{23}O_6N_3$ requires: C, 62·16; H, 5·45; N, 9·88%.)

The TNB complex (2·80 g) was passed through a column of basic $Al_2O_3$/I (80 g, 18 cm × 2·5 cm) using pet. ether as the eluent and the regenerated hydrocarbon was distilled over Na, b.p. 139–140°/1·5 mm, m.p. 39–40°, yield 1·33 g (Lit.[1]: m.p. 39·5–40°).

*The trinitrotoluene derivative* was crystallized twice from EtOH, yellow needles, m.p. 72–73°. (Found: C, 62·84; H, 5·70. $C_{23}H_{25}O_6N_3$ requires: C, 62·86; H, 5·73%.)

*8-Methylcadalene*

*Methyl β-(p-cymoyl-2)α-methylpropionate* (XXVIIIb).[62] β-(*p*-Cymoyl-2)α-methylpropionic acid[9] (45·5 g) was mixed with benzene (90 ml), anhydrous MeOH (90 ml) and conc $H_2SO_4$ (8 ml) and refluxed for 12 hr. Usual work up furnished the required product: b.p. 152–154°/1·5 mm, yield 43·7 (91%). (Lit.[62]: b.p. 145°/0·5 mm yield 75%.)

*γ-(p-Cymyl-2-)α,γ-dimethylvinylacetic acid* (XXXIX) *and lactone* (XL). In a 3-necked flask carrying a dropping funnel, a stirrer and a condenser, the above keto ester (11 g) in dry ether (70 ml) was chilled in an ice-salt bath. The apparatus was flushed with $N_2$ and a solution of MeMgI (prepared from 1·35 g Mg, 7·7 g MeI and 15 ml dry ether) introduced dropwise with stirring (½ hr). The reaction mixture was allowed to stand for 2 hr until it attained room temp and then refluxed on a waterbath for 3 hr and finally left as such overnight (12 hr). The reaction product was chilled and cautiously treated with dil HCl (1:1; 60 ml). The reddish ether layer was separated and the aqueous part extracted with ether (50 ml × 4). The combined extracts were washed with water and then with 5% $Na_2CO_3$aq (25 ml × 4). The alkaline extract was charcoaled, cooled and acidified with dil HCl (congo red) and the liberated oil extracted with ether (25 ml × 4). The combined ether extracts

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[61] R. C. Gupta and M. S. Muthana, *J. Ind. Inst. Sci.* 35A, 259 (1953).

[62] R. C. Gupta and M. C. Muthana, *J. Ind. Inst. Sci.* 35A, 131 (1953).

were washed with water and dried. On removing the solvent the residual viscous liquid (XXXIX) weighted 1·48 g.

The ether extract after removing the acidic part was washed with water and dried. The residue (9·8 g) obtained after solvent removal was hydrolysed with 10% alcoholic KOH (50 ml) by refluxing on a waterbath for 6 hr. The alcohol was distilled off, the product diluted with water and extracted with ether to remove any unhydrolysed neutral fraction (1·4 g). The alkaline solution was charcoaled, cooled and acidified with HCl (congo red). The liberated oil (8·2 g) was collected and digested with HClaq (1:1; 10 ml) on a waterbath for 2 hr. This treatment converted the hydroxy acid/unsaturated acid into XL whereas the keto acid (XXVIII) remained unaffected. The product was taken up in ether and separated into acid (3·0 g) and neutral fractions (4·0 g).

The crude acid XXXIX and the lactone XL were used as such in the next step.

*γ-(p-Cymyl-2)α,γ-dimethylbutyric acid* (XLI).[62] The above lactone/acid (8·4 g), red P (5·3 g) and HI (45 g) were refluxed at 130–140° for 36 hr. The reaction mixture was cooled, diluted with water, extracted with ether (50 ml × 5) and separated into acidic and neutral fractions. The usual work up furnished XLI (7·2 g) and XLII (1·0 g). Compound XLI (15·2 g) was further purified by distillation, b.p. 156–158°/1 mm, yield 11·76 g (Lit.[62]: b.p. 145–155°/0·5 mm). (Found: C, 77·20; H, 9·41. $C_{16}H_{24}O_2$ requires: C, 77·40; H, 9·60%.)

2,4,5-*Trimethyl-8-isopropyltetralone*-1 (XLII). To PPA (from 43 g $P_2O_5$ and 26 ml syrupy $H_3PO_4$) maintained at 97°, compound XLI (8·5 g) was added all at once with stirring. Heating was continued for ½ hr with occasional stirring. The reaction product (XLII) was isolated as a colourless liquid, b.p. 117–118°/1 mm, yield 7·2 g (91·6%). The ketone solidified on standing and was crystallized from pet. ether, m.p. 43–44°. (Found: C, 83·43; H, 9·51. $C_{16}H_{22}O$ requires: C, 83·47; H, 9·56%.)

2,4,5-*Trimethyl-8-isopropyl-*7,8-*dihydronaphthalene* (XLIV). Compound XLII (2 g) in ether (20 ml) was reduced with LAH (0·33 g, ether 60 ml) yielding crude XLIII (2·0 g) which was heated with $I_2$ (0·1 g) for 1 hr at 98–100° on a waterbath and worked up to give XLIV, which was purified by distillation over Na: b.p. 112–114°/2·5 mm, $n_D^{29}$ 1·5491, yield 1·5 g (82%). (Found: C, 89·35; H, 10·26. $C_{16}H_{22}$ requires: C, 89·65; H, 10·35%.)

8-*Methylcadalene* (XLV). A mixture of the above dialin (1·5 g) and S (0·26 g) were heated together at 205–210° for 3 hr and worked up: b.p. 120–122°/1·2 mm, $n_D^{29}$ 1·5714, yield 1·05 g (70·3%).

The *trinitrobenzene adduct* prepared in the usual manner crystallized from 80% AcOH as orange needles, m.p. 116–117°. (Found: C, 62·20; H, 5·40; N, 9·94. $C_{22}H_{23}O_6N_3$ requires: C, 62·16; H, 5·45; N, 9·88%.) The TNB derivative on decomposition over $Al_2O_3$/I gave pure 8-methylcadalene b.p. 135–136°/1·5 mm.

The *trinitrotoluene complex* was prepared in the usual manner but was found to be unstable, m.p. 46–64°.

### 1,2,7-*Trimethyl-4-isopropylnaphthalene*

*α-Methyl-γ-*(3,4-*dimethyl-6-isopropylphenyl*)*butyric acid* (XLVI). Compound V (10 g) was reduced with Zn–Hg (from 24 g Zn wool, 2·4 g $HgCl_2$, 50 ml $H_2O$ and 4 ml conc HCl) and HCl (70 ml conc HCl and 24 ml $H_2O$) with the addition of toluene (40 ml) and glacial AcOH (4 ml) by refluxing the mixture at 130–140° for 36 hr. The required XLVII was obtained as a thick, colourless liquid, b.p. 169–170°/1 mm, $n_D^{27}$ 1·5080, yield 8·8 g (93·5%). (Found: C, 77·60; H, 9·80. $C_{16}H_{24}O_2$ requires: C, 77·39; H, 9·74%.)

2,7,8-*Trimethyl-5-isopropyltetralone*-1 (XLVII). To PPA (15 g $P_2O_5$ and 9 ml syrupy $H_3PO_4$) maintained at 97° in a 3-necked flask, 3·0 g of the above acid was added in one lot with stirring. The above temp was maintained for ½ hr with occasional stirring of the reaction product, which was then worked up, as detailed earlier, to give the required tetralone, b.p. 134–137°/0·8 mm, m.p. 60–64°, yield 2·25 g (81%). An analytical sample had m.p. 64–65°. (Found: C, 83·20; H, 9·65. $C_{16}H_{22}O$ requires: C, 83·43; H, 9·63%.)

1,2,7-*Trimethyl-4-isopropyl-*5,6-*dihydronaphthalene* (XLIX). The tetralone (4·5 g in 60 ml ether) was reduced with a slurry of LAH (0·90 g) in dry ether (140 ml) at ∼ −5° and the resulting crude XLVIII (4·36 g) was treated with $I_2$ (0·1 g) at 95–100° for 1 hr and worked up to give XLIX which was purified by distillation over Na: b.p. 123–125°/1 mm $n_D^{27}$ 1·5595, yield 3·96 g (98·5%). (Found: C, 89·45; H, 10·47. $C_{16}H_{22}$ requires: C, 89·65; H, 10·35%.)

1,2,7-*Trimethyl-4-isopropylnaphthalene* (L). The above dialin (2·5 g) was mixed with S (0·39 g) and heated at 205–210°/200 mm for 3 hr and worked up to give crude L: b.p. 120°/1 mm, yield 2·4 g (99%).

The above product (1·9 g), which had solidified, was converted into its *TNB complex* in the usual manner and recrystallized from 80% AcOH to give orange needles, m.p. 134–135·5°. (Found: C, 62·47; H, 5·30; N, 10·10. $C_{22}H_{23}O_6N_3$ requires: C, 62·16; H, 5·45; N, 9·88%.)

The above complex (2·44 g) was passed through a column of basic $Al_2O_3$/I (100 g; 21 cm × 2·5 cm) using pet. ether for elution. The regenerated hydrocarbon was distilled over Na: b.p. 139–140°/1·5 mm, m.p. 59–60°.

The *trinitrotoluene complex* was prepared from the pure regenerated hydrocarbon and TNT. It recrystallized from EtOH as yellow needles, m.p. 73–74°. (Found: C· 62·82; H, 6·0. $C_{23}H_{25}O_6N_3$ requires: C, 62·86; H, 5·73%.)