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IDENTIFICATION OF METHYLNAPHTHALENES BY PMR: SOME USEFUL RULES

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A variety of methylalkylnaphthalenes have been isolated as products of dehydrogenation of various types of terpenoids. Though the formation of a naphthalene is easily revealed by its ultraviolet absorption characteristics[1], the exact identification of an unknown naphthalene calls for considerable more effort, sometimes involving the synthesis of various possible alternatives. We now wish to report a procedure by which it is possible to considerably restrict the number of possible alternatives.

It is evident that proton magnetic resonance (PMR) spectrum of a methylalkylnaphthalene can reveal the number of methyl, isopropyl or ethyl groups, due to the chemical shift between the methyl groups directly attached to the aromatic ring and those attached through other alkyl carbon

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[1] R.A.Friedel and M. Orchin, Ultraviolet Spectra of Aromatic compounds, John Wiley and Sons, New York (1951).

links.[2] In connection with some other investigations in progress in this Laboratory, a number of methylnaphthalenes had become available. A critical study of their PMR spectra yielded the valuable information that the position of the methyl signal (aromatic) is governed not only by its position (α or β) on the nucleus, but also by the disposition of the neighbouring alkyl group(s). The following generalisations can be made[3]:

1. A methyl group attached to the α-position is always deshielded (~ 7 cps) in comparison to when situated on the β-position[4].
2. A methyl or alkyl group ortho to a methyl group mutually shield (~ 4 cps) each other; when located meta to each other the extent of diamagnetic shielding becomes less (~ 2 cps) and is absent for para orientation. When a methyl group has alkyl/methyl groups at both the ortho and the meta positions only the ortho is considered (for calculations).

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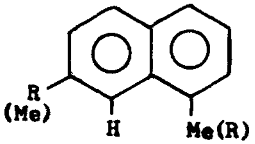
[2] L.M. Jackman, Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry, Pergamon Press, London (1959).

[3] The data, discussed herein, have been obtained on a Varian A-60 High Resolution NMR Spectrometer, on ~ 10% solutions in CCl_4 with tetramethylsilane as an internal reference. The values are reported in cycles/sec. from tetramethylsilane as zero.

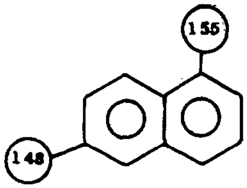
[4] Also see: S. Fujiwara and T.Wainai, Analyt.Chem. 33, 1085 (1961).

3. A methyl in the *peri*-position to another methyl results in a considerable paramagnetic shift (~ 12 cps)[5].
4. When an alkyl (other than methyl) and methyl group on two different rings have the following disposition



there is again a paramagnetic shielding, though to a lesser (~ 3 cps) extent.

The validity of these rules is best illustrated by a comparison of the actual and calculated values for an assortment of methyl (alkyl) naphthalenes. By taking the methyl signals in 1,6-dimethylnaphthalene (I) as standard



I

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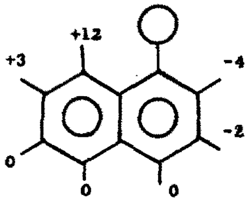
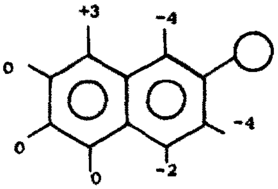
[5] cf. C.MacLean and E.L.Mackor, Mol.Phys.**3**,223 (1960).

for the α- and β-positions, and applying the above generalisations (summarised in II, III), the positions of the methyl signals for several methylnaphthalenes have been approximated (values in paranthesis) and compared with the experimental data (Chart 1). It is clear from these that the agreement is quite good.



II



III

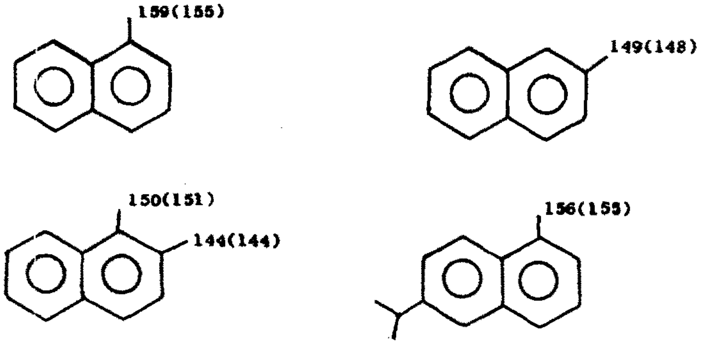


CHART 1

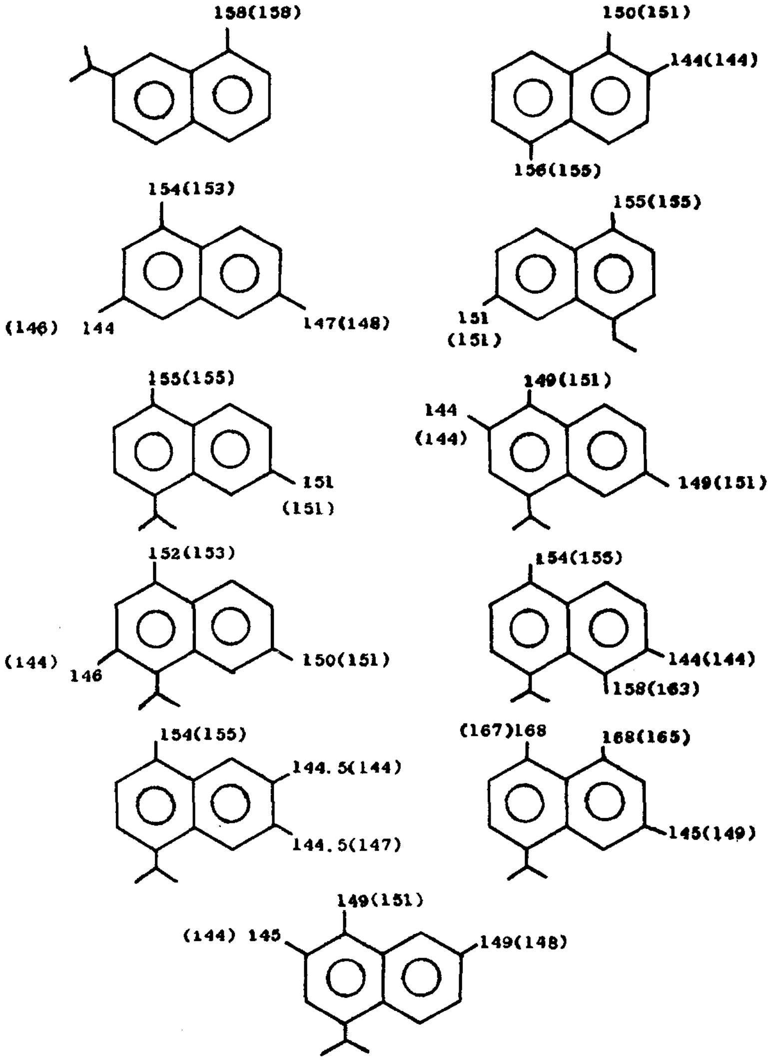


CHART 1 (Contd.)

These empirical rules have been used with great advantage in assigning structures to various methylnaphthalenes obtained during certain dehydrogenation studies designed to determine the extent of non-angular methyl group eliminations under different experimental conditions; these results will be reported elsewhere. In connection with this work it has also been found that the trinitrobenzene complexes of these naphthalenes could be directly used for the PMR studies. This is useful when only a small quantity of the naphthalene is available as its trinitrobenzene complex. The spectra are taken on a more or less saturated solution ($\sim$ 1%) in CS_2; the three protons of the trinitrobenzene moiety (sharp singlet at $\sim$ 550 cps) serve as a useful measure of the methyl count of the naphthalene; sometimes the signals are shifted to the higher field strength to the extent of 2-4 cps as compared to those in the spectrum of the pure naphthalene.