

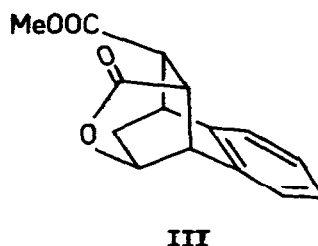
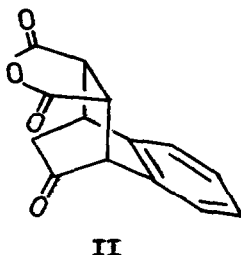
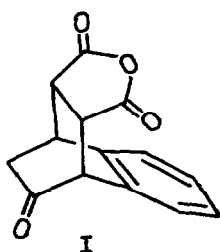
A NOVEL FMR TECHNIQUE FOR THE DETERMINATION OF THE CONFIGURATION OF DIELS-ALDER ADDUCTS OF MALEIC ANHYDRIDE: MODEL COMPOUNDS WITH NAPHTHALENE DERIVATIVES

S.M. Verma, O. Subba Rao and C. Koteswara Rao

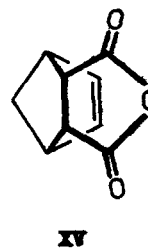
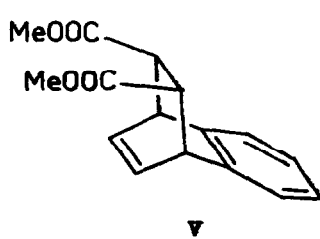
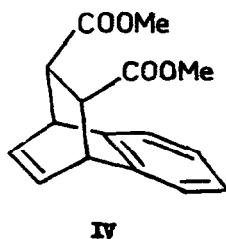
Department of Chemistry, Banaras Hindu University, Varanasi (221005), India

(Received in UK 18 January 1973; accepted for publication 28 March 1973)

The configurations of the β -naphthol-maleic anhydride adducts have earlier been proposed on the basis of their dipole moments; the one with smaller moment (2.86D) was assigned to the endo-configuration (I) and the other with larger moment (6.54D) to the exo-configuration (II).^{1,2} A rigorous chemical proof has also been provided by transforming the exo-adduct II into a lactone III.^{2,3} The



endo- and exo-configurations of the naphthalene-maleic anhydride adducts were established by their steric relationship with the corresponding β -naphthol adduct.⁴ However, none of these approaches is applicable to a variety of DA* adducts. The configurations of the naphthalene-maleic anhydride adducts have also been determined spectroscopically, by converting the adduct-anhydrides into the



*DA will be used for Diels-Alder.

corresponding methyl esters IV and V; the studies were based on the difference of the chemical shifts of the ester methyl protons in the endo- and exo-configurations (IV- δ 3.47 & V - δ 3.65) and the long range couplings.⁵ The scope of the applicability of this method for a variety of DA adducts of maleic anhydride is limited since the chemical shift of the ester protons in the endo-product is not much different from that in the exo-product. The configuration of either the endo- or exo-compound can be established using this method only when the PMR spectrum of the corresponding isomer is available, the limitation being that the isomer may not always be formed.

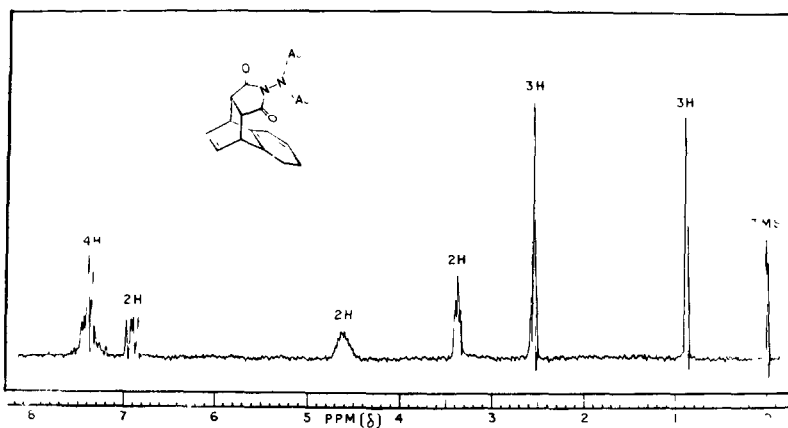


Fig.1: 60 MHz PMR spectrum of compound IX in CDCl_3 at 45° .

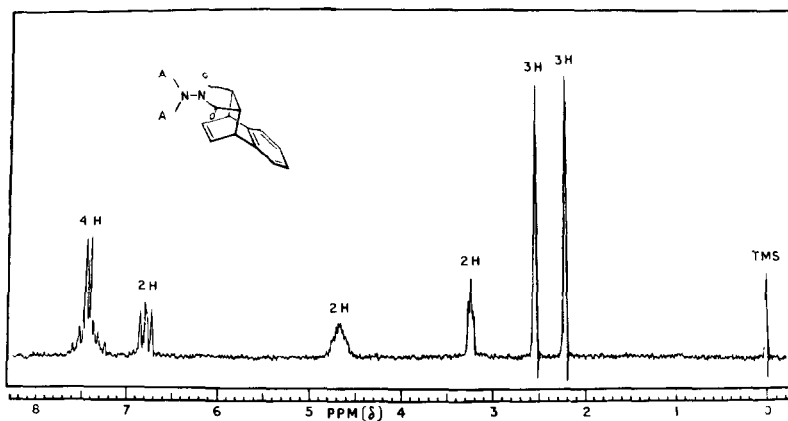
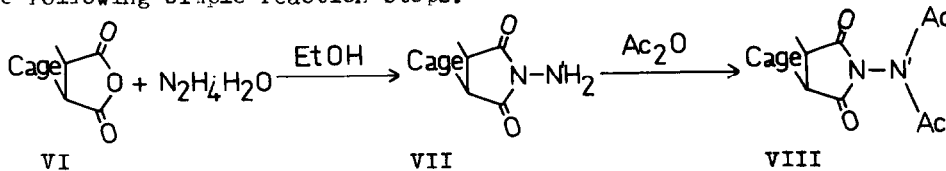
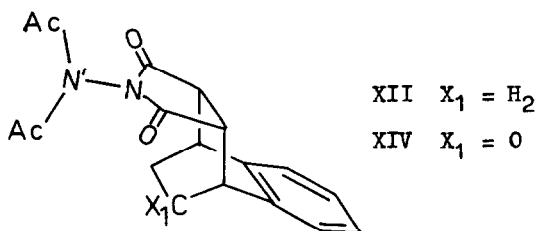
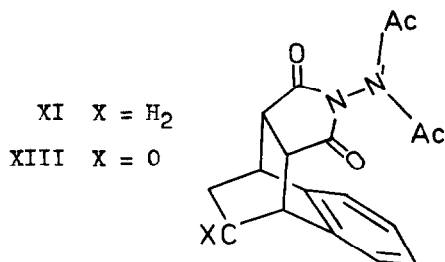


Fig.2: 60 MHz PMR spectrum of compound X in CDCl_3 at 45° .

We now report a new and a more convenient method for the determination of the configurations of a variety of DA adducts of maleic anhydride. The N,N'-diacetyl-N-amino imide derivatives (IX - XIV) of the model compounds are obtained by the following simple reaction steps:



The N-amino imide structures (VII) are established by the formation of benzal derivatives, which are characterised by a one-proton singlet at about δ 9 in the PMR spectra. Conformation of the acetyl groups about the N-N' bond in N-(diacetyl amino) imide derivative of the anthracene-maleic anhydride adduct was reported by Korsch and Riggs⁶ on the basis of the strong shielding effect (ca 1.5 ppm) of the cage-benzo-ring on one of the N'-acetyl groups in the PMR spectrum. In such systems (VIII) the two N'-acetyl groups, one lying above and the other below the plane of the succinimidyl ring, give rise to two different PMR signals and the free energies of the N-N' bond rotations have been reported to be in excess of 20 kcal/mole.^{6,7,8} In the spectrum of the compound IX (Fig.1) the acetyl group, anti to the benzo-ring, appears at the normal position (δ 2.55) while the other, syn to the benzo-ring, is strongly shielded and appears at δ 0.90. This large shielding effect on one of the N'-acetyls confirms the endo-structure of the compound IX. In the spectrum of the other isomeric product X (Fig.2) the N'-acetyl group, anti to the cage-moiety olefinic bond, appears at the normal



position (δ 2.53) while the other, syn to the olefinic bond, is slightly shielded (δ 2.20); the exo-structure is thus confirmed. This pattern is also observed for the other compounds XI - XIV (Table 1).

TABLE 1
Chemical shifts of the N'-acetyl signals of the compounds IX - XIV*

Compound	Acetyl <u>anti</u> to the cage (δ)	Acetyl <u>syn</u> to the cage (δ)	Internal chemical shift of the <u>anti</u> - and <u>syn</u> - acetyls (Hz)
IX	2.55	0.90	99.0
X	2.53	2.20	20.0
XI	2.52	0.79	104.0
XII	2.60	2.26	20.5
XIII	2.54	0.90	98.0
XIV	2.54	2.30	14.5

*Spectra are recorded on a 60 MHz PMR spectrometer in CDCl₃ at 45°.

By placing the testing probe, i.e. the N'-acetyl group, in the effective magnetic zone of the cage-moiety, a clear picture of the cage-moiety environments could be recorded, providing thereby evidence for the wide applicability of the method. It is evident that the present method enables the assignment of correct configuration to either the endo- or exo-adduct without the necessity of comparison with the pattern of the corresponding isomer, and therefore, this method offers a distinct advantage over the earlier methods especially when one of the isomers is not formed. One such example is provided by the assignment of the correct endo-configuration (XV) for the cyclopentadiene-maleic anhydride adduct,⁸ where the other isomer (exo-adduct) was not obtained.

REFERENCES

1. K. Takeda, S. Nagakura and K. Kitahonoki, Pharm. Bull. (Japan), **1**, 135 (1953).
2. K. Takeda, S. Hagishita, M. Sugiura, K. Kitahonoki, I. Ban, S. Miyazaki and K. Kuriyama, Tetrahedron, **26**, 1435 (1970).
3. N.S. Wariyar, Proc. Indian Acad. Sci., **43A**, 231 (1956);
R.C. Cookson and N.S. Wariyar, J. Chem. Soc., 2302 (1956).
4. K. Takeda, K. Kitahonoki, M. Sugiura and Y. Takano, Ber., **95**, 2344 (1963).
5. K. Tori, Y. Takano and K. Kitahonoki, Ber., **97**, 2798 (1964).
6. B.H. Korsch and N.V. Riggs, Tetrahedron Letters, 5897 (1966).
7. G.S.D. King, J. Chem. Soc. (B), 1224 (1966);
N.V. Riggs and S.M. Verma, Aust. J. Chem., **23**, 1913 (1970);
S.M. Verma and Rajendra Prasad, J. Org. Chem. (in Press).
8. S.M. Verma and C. Koteswara Rao, Tetrahedron, **28**, 5029 (1972).