32. **Ken'ichi Takeda*, Saburo Nagakura**, and Keizo Kitahonoki***: Diels-Alder Reaction. II. Reaction of β-Naphthol and Maleic Anhydride; Isolation of Another Isomeric Adduct[1].

(Research Laboratory, Shionogi & Co., Ltd., and Institute of Science and Technology, University of Tokyo**)*

In the first paper of this series[2], Takeda and Kitahonoki reported the reaction of β-naphthol and maleic anhydride by heating a mixture of these substances at 220~240° and the addition product (A), m.p. 194~195°, thereby obtained was clarified as the 1,4-addition of maleic anhydride on β-naphthol. Later, another substance (B), m.p. 193~194°, was separated from this reaction product, besides the above (A). The analytical values of (B) were the same as those of (A), corresponding to the formula $C_{14}H_{10}O_4$, and (B) also possessed a carbonyl group, similar to (A), and gave a dimethyl ester, m.p. 112~113.5°, and a *p*-nitrophenylhydrazone, m.p. 185~186°, of the ester. It was also found that the ultraviolet absorption spectrum of (B) showed similar absorption curve as that of (A) (Fig. 1).

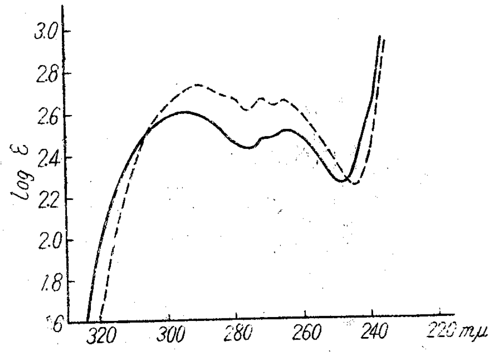

Fig. 1 Ultraviolet Absorbtion Spectra of β-Naphthol-Maleic Anhydride Adducts (in Alcohol) (Beckman Model DU Spectrophotometer)

—— m.p. 194~195° (A)

--- m.p. 193~194° (B)

From these results, (A) and (B) were assumed to be steric isomers and, therefore, (B) was submitted to Clemmensen reduction, as in the case of (A)[2], and derived to a desoxy compound of m.p. 207~208°. This substance was found to be identical with the reduction product, m.p. 207~208°, of an adduct of naphthalene and maleic anhydride obtained by Kloetzel and others[3]. This confirmed the fact that (B) is also a 1,4-adduct of β-naphthol and maleic anhydride, same as (A).

Since (A), (B), and the two kinds of naphthalene-maleic anhydride adducts were assumed to be exo and endo isomers, the dipole moments of these four kinds of adducts were determined and results as shown in Table I were obtained. As the moment of (A) is extremely smaller than that of (B), (A) is assumed to take a steric configuration by which the moments of the carbonyl group and the acid anhydride group cancel each other, and these moments act additively in (B) configuration. It is deduced, therefore, that (A) takes the exo form (I) and (B), the endo form (II). It is also possible to quantitatively explain to some extent the results of dipole moment determinations by the assumption of such configurations in (A) and (B) compounds.

The dipole moment of the acid anhydride group would probably be 4.32~4.05 D, from the results of the determination of the moments of naphthalene-maleic anhydride adducts. On the other hand, the moment of the carbonyl group is 2.5 D so that when the two moments are completely in the same direction and calculated as the sum, the total moment would be 6.8~6.6 D. It follows, therefore, that the observed moment of 6.54 D for (B) could be explained by assuming that the (B) configuration is in an endo form, with the moments

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* Imafuku, Amagasaki, Hyogo-ken (武田健一, 北朴木馨三).

** Komaba, Meguro-ku, Tokyo (長倉三郎).

[1] Cf. Communication to the Editor: J. Pharm. Soc. Japan, 73, 206 (1953).

[2] Part I: *Ibid.*, 73, 280 (1953).

[3] Kloetzel, Herzog: J. Am. Chem. Soc., 72, 1991 (1950).

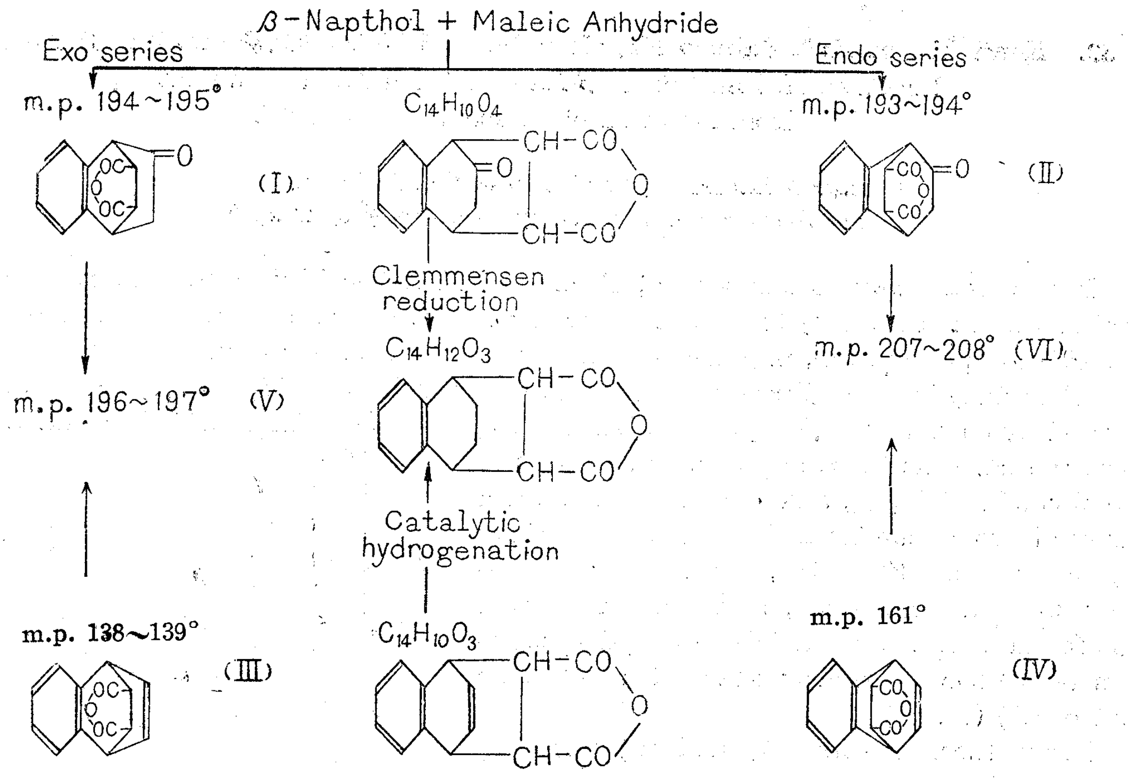

Fig. 2.

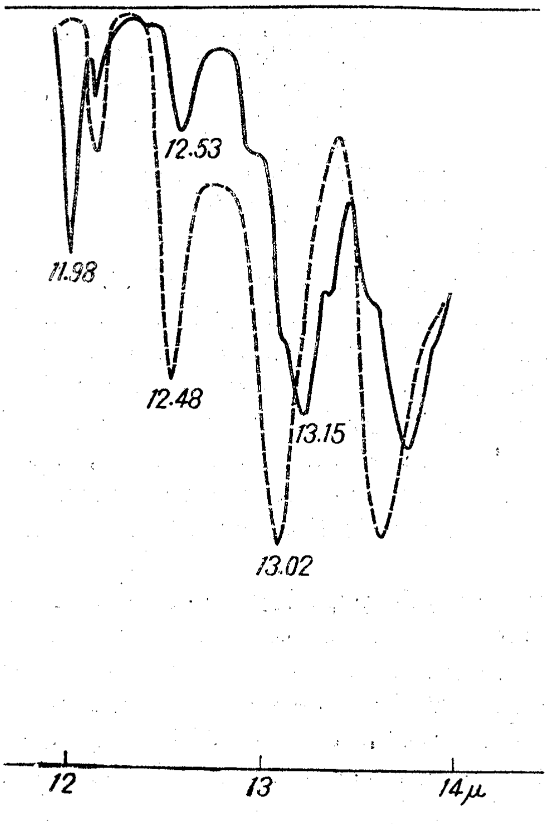

Fig. 3 Infrared Absorption Spectra of Naphthalene-Maleic Anhydride Adducts (in Nujol).
—— m.p. 138~139°
---- m.p. 161°

of the acid anhydride and carbonyl groups facing in almost the same direction. The observed value of 2.86 D for (A) could also be explained by assuming that (A) takes the exo form in which these two moments are at an angle of 136~141°.

The comparison of the dipole moments of the two kinds of naphthalene-maleic anhydride adduct, of m.p. 139° and of m.p. 161°, shows that the moment of the former is slightly larger than that of the latter. This is assumed to be due to the fact that the adduct of m.p. 139° takes such a steric configuration that the effect of the benzene nucleus is inductively increased by the moment of the acid anhydride group, from which it may be induced that the acid anhydride group in the adduct of m.p. 139° is in a position nearer to the benzene nucleus than that in the adduct of m.p. 161°. Therefore, exo form (III) could be assumed for the former, and the endo form (IV) for the latter.

These conclusions are in good agreement with the chemical relationships of these compounds shown in Fig. 2.

As described in the previous report[2], the purity of the naphthalene-maleic anhydride adduct of m.p. 139° was slightly doubtful and, therefore, its infrared spectrum was examined. The results showed that this compound showed absorptions at 11.98 μ, 12.53 μ, and 13.15 μ, whereas the substance of m.p. 161° showed absorptions at 12.48 μ and 13.02 μ, from which it might be considered that this compound is approximately pure. The absorption at 3~11 μ is about the same in the two compounds (Fig. 3).

TABLE I Dipole Moment

(A)	(I)	2.86 Debye Unit
(B)	(II)	6.54
m.p. 138~139°	(III)	4.32
m.p. 161°	(IV)	4.05

Chemical confirmation of these two isomers will be made at a later date.

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Experimental[4]

Isolation of β-naphthol-maleic anhydride adduct of m.p. 193~194° (B)—An equimolar mixture of β-naphthol and maleic anhydride was heated at 220~240° for about 30 minutes. Addition of ethyl acetate to the reaction mixture, when cool, yielded some crystals of m.p. 155~187°. Recrystallization from ethyl acetate first gave colorless prisms (A), m.p. 194~195°, and the mother liquor obtained by their separation, after careful condensation and cooling, yielded some square plates. Recrystallization of the latter yielded the pure product (B) of m.p. 193~194°, whose yield was extremely small compared to that of (A). The mixed melting point of (A) and (B) was 154~162°. *Anal.* (of (B), m.p. 193~194°) Calcd. for $C_{14}H_{10}O_4$: C, 69.40; H, 4.16. Found: C, 69.62; H, 4.21.

Dimethyl ester of the adduct (B)—The adduct of m.p. 193~194° was dissolved in cold 5% NaOH solution, acidified with hydrochloric acid, and extracted with ether. To this was added an ether solution of diazomethane by which the methylation was effected. Recrystallization from methanol yielded colorless prisms, m.p. 112~113.5°. *Anal.* Calcd. for $C_{16}H_{16}O_5$: C, 66.66; H, 5.59. Found: C, 66.23; H, 5.94.

***p*-Nitrophenylhydrazone of the (B) dimethyl ester**—The above dimethyl ester and *p*-nitrophenylhydrazine were reacted in methanol, and the precipitate obtained by the condensation of methanol was recrystallized from the same solvent as yellow prisms, m.p. 185~186°. *Anal.* Calcd. for $C_{22}H_{21}O_6N_3$: C, 62.40; H, 5.00; N, 9.93. Found: C, 62.43; H, 5.10; N, 10.11.

Clemmensen reduction of the adduct (B)—To 1.4 g. of the adduct (B) and 6 g. of zinc amalgam, 6 cc. of conc. HCl, 4.5 cc. of water, and 9 cc. of alcohol were added and the mixture was boiled for 15 hours, during which 11 cc. of conc. HCl was added in four lots. The reaction mixture was extracted with ether, and the pale yellow, oily residue from ether was stirred with 25 cc. of 5% NaOH, insoluble matter removed by extraction with ether, and the alkaline solution was extracted with ether after acidification. The ether residue, when allowed to stand with the addition of a small amount of ether, yielded some crystals of m.p. 190~201°. The crystals were dehydrated by boiling with acetic anhydride, and the residue obtained by the removal of acetic anhydride was sublimed under a reduced pressure (bath temp. 140~160°). Two recrystallizations from ethyl acetate gave colorless prisms of m.p. 207~208° which showed no depression of the melting point on admixture with the reduction product, m.p. 208°, obtained from the adduct (IV) of m.p. 161°. *Anal.* Calcd. for $C_{14}H_{12}O_3$: C, 73.67; H, 5.30. Found: C, 73.30; H, 5.45.

Dipole moment measurement—The dipole moment was determined with a benzene solution of the compounds at 25°. In order to obtain the value of molecular polarization, P_M, at infinite dilution from the values of dielectric constant and specific volume at various concentrations, the following formula of Halverstadt and Kumler was used.

$$P_M = M\left\{ \frac{3\alpha v_0}{(\varepsilon_0+2)^2} + \frac{\varepsilon_0-1}{\varepsilon_0+2}(v_0+\beta) \right\}$$

where M denotes the molecular weight of the solute, α and β, the slope of the straight lines $\varepsilon-\omega$ and $v-\omega$, and ε_0 and v_0, the respective points at which the straight line cuts the ordinate.

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[4] All m.p.s are uncorrected.

(I) m.p. 194∼195°

Weight Fraction ω	Dielectric Constant ε	Specific Volume v
0	2.274	1.14733
0.00155	2.279	1.14652
0.00229	2.284	1.14636
0.00345	2.287	1.14584

$\alpha=3.80$
$\beta=-0.38$
$\varepsilon_0=2.274$
$v_0=1.15$
$P_M=229$
$\mu=2.86$ D

(II) m.p. 193∼194°

ω	ε	v
0	2.273	1.14762
0.00072	2.289	1.14681
0.00143	2.300	1.14621
0.00164	2.306	1.14634

$\alpha=20.0$
$\beta=-0.73$
$\varepsilon_0=2.273$
$v_0=1.15$
$P_M=944$
$\mu=6.54$ D

(III) m.p. 138∼139°

ω	ε	v
0	2.273	1.14743
0.00276	2.299	1.14610
0.00424	2.313	1.14579
0.00616	2.326	1.14532

$\alpha=9.20$
$\beta=-0.37$
$\varepsilon_0=2.273$
$v_0=1.15$
$P_M=440$
$\mu=4.32$ D

(IV) m.p. 161°

ω	ε	v
0	2.274	1.14733
0.00307	2.299	1.14618
0.00588	2.323	1.14524
0.00812	2.344	1.14401

$\alpha=8.12$
$\beta=-0.38$
$\varepsilon_0=2.274$
$v_0=1.15$
$P_M=398$
$\mu=4.05$ D

Summary

The reaction product of β-naphthol and maleic anhydride yielded, besides the adduct of m.p. 194∼195° reported in the previous paper, a new substance of m.p. 193∼194° which was clarified as having the same structure as the adduct of m.p. 194∼195°. The steric configurations of these two adducts and the two kinds of naphthalene-maleic anhydride adduct of m.p. 138∼139° and of m.p. 161° were proposed from their dipole moment measurements.

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