SHORT COMMUNICATIONS

Stereochemistry Related to the Diels-Alder Adducts of 4-Methyl-1, 3-pentadienes[1]

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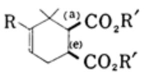
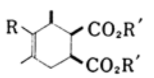
It has been obscure why the conclusions reported by several authors about the behaviour of 3, 4-dimethyl-1, 3-pentadiene (I)[2-4] and 4-methyl-1, 3-pentadiene (II)[5-8] in the Diels-Alder reaction did not agree with each other. We can, however, now reasonably surmise that, during the course of the Diels-Alder reaction with less reactive dienophiles, these dienes are mostly isomerized to more stable ones,[3] while with more reactive dienophiles the reaction smoothly proceeds to give the normal adducts.[8] A recent publication[9] discussing the formation of the normal adducts in the reaction of the dienes I and II with maleic anhydride has prompted us to report our independent studies of the formation and structure of the same adducts and some derivatives.

The diene I reacted easily with maleic anhydride in benzene at a temperature range of 70~120°C in a nitrogen atmosphere to afford an inhomogeneous adduct which gave, on hydrolysis with boiling water, a high yield of the diacid (IIIa) as colorless needles (m.p. 153~153.5°C (lit. m.p. 150~151°C[9])); dimethyl ester (IIIb), b.p. 106~107°C/0.4 mmHg, n_D^{15} 1.4781 (lit. b.p. 90~92°C/0.05 mmHg, n_D^{25} 1.4742[9]), ν_{max}^{film} 1735 cm^{-1}, NMR (in CCl_4): 8.98, 8.86 (gem-Me_2), 8.34 (Me at $C_{(4)}$), 6.45, 6.37 (ester Me) and 4.66 τ (olefinic H)), and the diacid (Va) (m.p. 173~174°C (lit. m.p. 167°C[2])); dimethyl ester (Vb), b.p. 149°C/0.7 mmHg, n_D^{15} 1.4816, ν_{max}^{film} 1735 cm^{-1}). It should be emphasized here that the formation of the adduct corresponding to Va tends to be promoted when air remains in the reaction vessel.

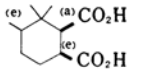
The diacid IIIa was hydrogenated over an Adams catalyst in ethanol or ethyl acetate to afford the saturated diacid (VIIa) (89%), (m.p. 191~192°C, ν_{max}^{KBr} 1706 cm^{-1}). When heated at 220~230°C with concentrated hydrochloric acid, the diacid gave the epimer (VIIb) (80%) (m.p. 202~202.5°C, ν_{max}^{KBr} 1706 cm^{-1}), which returned, after refluxing with acetic anhydride and succeeding hydrolysis, to the starting diacid VIIa. The diacid IIIa was readily lactonized, in the presence of a catalytic amount of hydrochloric acid, to a γ-lactonic acid (VIIIa) (90%) (m.p. 196~197°C, ν_{max}^{KBr} 1772, 1704 cm^{-1}; methyl ester (VIIIb), m.p. 112°C, ν_{max}^{KBr} 1775, 1741 cm^{-1}, NMR (in $CDCl_3$): 8.89 (gem-Me_2), 8.71 ($\mathrm{Me{-}\overset{|}{\underset{|}{C}}{-}O}$) and 6.27 τ (ester Me)). Considering the facile formation of VIIIa in addition to the non-bonded 1, 3-diaxial interaction, the present authors confirmed the conformation for the normal product as IIIa.



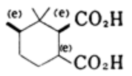
(IIIa) R=Me, R′=H
(IIIb) R=R′=Me
(IVa) R=R′=H



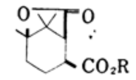
(Va) R=Me, R′=H
(Vb) R=R′=Me
(VIa) R=R′=H



(VIIa)



(VIIb)



(VIIIa) R=H
(VIIIb) R=Me

The infrared spectrum of IIIa in a KBr pellet or Nujol mull indicated bands at 1734 and 1709 cm^{-1} which can be ascribed to two

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[1] Presented before at the 16th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1963.

[2] I. N. Nazarov and M. V. Mavrov, *Zhur. Obshchei Khim.*, **29**, 1158 (1959).

[3] A. Arai and I. Ichikizaki, This Bulletin, **35**, 45 (1962).

[4] T. Nishida, A. Arai and I. Ichikizaki, ibid., **35**, 572 (1962).

[5] G. B. Bachman and C. G. Goebel, *J. Am. Chem. Soc.*, **64**, 787 (1942).

[6] I. N. Nazarov and M. V. Mavrov, *Zhur. Obshchei Khim.*, **28**, 3061 (1958).

[7] Y. M. Slobodin, V. I. Grigoreva and Y. E. Schmulyakovskii, ibid., **23**, 1873 (1953).

[8] C. A. Stewart, Jr., *J. Am. Chem. Soc.*, **84**, 117 (1963).

[9] N. L. Goldman, *Chem. & Ind.*, **1963**, 1036.

different $\nu_{C=O}$ bands and a considerably intense band at 1625 cm^{-1} assignable to $\nu_{C=O}$, while that in a solution ($CHCl_3$) showed only a single absorption, due to $\nu_{C=O}$, at 1709 cm^{-1}. Such spectral characteristics were also observed in a diacid (IVa) described below, but not in several other Δ^4-cyclohexene-1, 2-diacids, including 3, 3, 5-trimethyl-4-cyclohexene-1, *cis*-2-dicarboxylic acid (IX). The lactonization of IX gave δ-lactonic acid, 1, 8, 8-trimethyl-3-oxo-2-oxabicyclo [2, 2, 2]octane-exo-5-carboxylic acid (m.p. 166°C, $\nu_{\max}^{KBr}$ 1741, 1706 cm^{-1}; methyl ester, (b.p. 131∼132°C/0.8 mmHg, n_D^{20} 1.4755, $\nu_{\max}^{film}$ ∼1750 cm^{-1} (broad)).

The diene II produced the diacid IVa as colorless needles (m. p. 172∼173°C (lit. m. p. 172∼173°C[9]), $\nu_{\max}^{KBr}$ 1730, 1709 (sh), 1624, 705 cm^{-1}), along with the diacid (VIa) (m. p. 154°C (lit. m. p. 154°C[5])) and *cis*-3, 5-dimethyl-5(a)-hydroxycyclohexane-1, *cis*-2-dicarboxylic acid (m. p. 208∼209°C, $\nu_{\max}^{KBr}$ 3400, 1707, 1698 (sh), 1112 cm^{-1}); the latter two were converted into 1, 8-dimethyl-3-oxo-2-oxabicyclo [2, 2, 2] octane-exo-5-carboxylic acid (m. p. 147∼148°C, $\nu_{\max}^{KBr}$ 1748, 1709 cm^{-1}; methyl ester, b.p. 147∼148°C/1.8 mmHg, $n_D^{18.5}$ 1.4752, $\nu_{\max}^{film}$ ∼1743 cm^{-1} (broad)).

Satisfactory analyses were obtained for all compounds.

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