Diels–Alder Reactions of Methyl Coumalate with 1,3-Dienes

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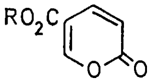
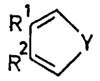
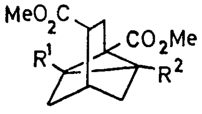
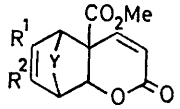
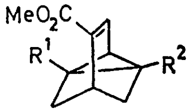
Summary Diels–Alder reaction of methyl coumalate (Ib) with 1,3-dienes afforded the tetrahydrocoumarin (IV) and/or the tricyclo[3,2,1,$0^{2,7}$]oct-3-ene (V) in which the reaction giving (IV) is the first example of the reaction of a 2-pyrone as a dienophile.

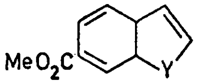

(I) a; R=H
b; R=Me

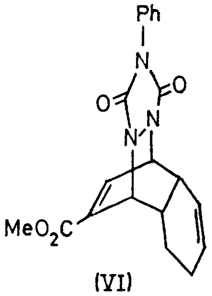

(II) a; $R^1=R^2=Me$, Y=H,H
b; $R^1=Me$, $R^2=H$, Y=H,H
c; $R^1=R^2=H$, Y=H,H
d; $R^1=R^2=H$, $Y=-[CH_2]_2-$
e; $R^1=R^2=H$, $Y=-CH_2-$

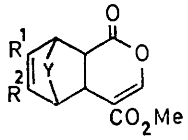

(III)


(IV) a; $R^1=R^2=Me$, Y=H,H
b; $R^1=Me$, $R^2=H$, Y=H,H
c; $R^1=R^2=H$, Y=H,H
e; $R^1=R^2=H$, $Y=-CH_2-$


(V) a; $R^1=R^2=Me$
b; $R^1=Me$, $R^2=H$
c; $R^1=R^2=H$


(V′) c; Y=H,H
d; $Y=-[CH_2]_2-$


(VI)


(VII)

Recently, we reported[1] the thermal addition reactions of coumalic acid (Ia) with buta-1,3-dienes (II) to afford the tricyclo[3,2,1,$0^{2,7}$]oct-3-ene derivatives (III). In contrast, we have now found that the thermal reaction of methyl coumalate (Ib) with several 1,3-dienes (II) gives the 4a,5,8,-8a-tetrahydrocoumarins (IV) together with the decarboxylative double Diels–Alder adducts (V); the reaction to give (IV) is the first example of the Diels–Alder reaction in which a 2-pyrone derivative functions as a dienophile.[2]

Heating the solution of (Ib) and (IIa) in benzene in a pressure bottle at 100° for 17 h gave two 1:1 adducts in a ratio of 10:1 (from the peak areas of the gas chromatogram). After a column chromatographic separation, the predominant adduct (lower R_F value), m.p. 112·5—114°, was shown to be (IVa) from spectroscopic data,† and the minor adduct, b.p. 80—83°/3 mm,‡ was found to be (Va) by comparison of n.m.r. spectra with those of (III).

The similar reaction of (Ib) and (IIb) gave (IVb) and (Vb) in a ratio of 4:3 (the position of the methyl group is tentatively assigned).

The reaction of (Ib) and (IIc) gave a mixture of (IVc) and (Vc) in a ratio of 3:4, but (IVc) is thermally unstable. When heated above 150°, (IVc) was transformed into a mixture of (V′c) and (Vc), and the same treatment of (V′c) gave only (Vc). Under these conditions (Vc) was recovered unchanged. On the other hand, (IVa) and (IVb) showed no change under the same conditions, but (IVb) changed slowly into (Vb) at 200°.

The reaction of (Ib) and (IId) gave exclusively (V′d) which was characterized by Pd–C dehydrogenation giving methyl naphthalene-2-carboxylate,[2] m.p. 76—77°, as well as by the Diels–Alder reaction with 4-phenyl-1,2,4-triazoline-3,5-dione[3] to give an adduct (VI),[4] m.p. 204—205°. An attempt to cyclize (V′d) into the tetracyclic compound failed. (Ib) and (IIe) (heated under reflux in benzene for 3 h) gave exclusively (IVe), m.p. 123—124°.

These observations show clearly the qualitative differences between the reactivities of the 1,3-dienes (II) as a dienophile and as a diene in Diels–Alder reactions.

When (Ib) functions as a dienophile, the reaction occurs only at its 5,6-double bond to give a tetrahydrocoumarin (IV). Tetrahydroisocoumarin (VII), which might result from the addition to the 3,4-double bond of (Ib), was never detected. These facts are consistent with the net atomic charge of (Ib)cal culated by meanso f the extended Hückel method.[5]

We thank Emeritus Professor K. Sisido and Professor H. Nozaki for help and encouragement, and Mr. H. Tsukuni for a gift of dicyclopentadiene.

(*Received, 24th January* 1972; *Com.* 100.)

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† Elemental analyses and spectral data were consistent with the suggested structures for all new compounds and are available from the authors.

‡ Unless otherwise stated, all reaction products were oily compounds.

[1] T. Imagawa, M. Kawanisi, and K. Sisido, *Chem. Comm.*, 1971, 1292.

[2] A. K. Bahl and W. Kemp, *J. Chem. Soc.* (*C*), 1971, 2268; and references cited therein.

[3] B. T. Gillis and J. D. Hagarty, *J. Org. Chem.*, 1967, **32**, 330.

[4] For the stereochemistry, see A. B. Evnin, D. R. Arnold, L. A. Karnischky, and E. Strom, *J. Amer. Chem. Soc.*, 1970, **92**, 6218.

[5] J. A. Reed, C. L. Schilling, jun., R. F. Tarvin, T. A. Rettig, and J. K. Stille, *J. Org. Chem.*, 1969, **34**, 2188.