Double Diels–Alder Reactions of Coumalic Acid with Buta-1,3-dienes: a Single-step Synthesis of Tricyclo[3,2,1,$0^{2,7}$]oct-3-ene Derivatives

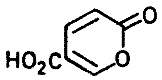
By TAKESHI IMAGAWA, MITUYOSI KAWANISI,* and KEIITI SISIDO

(*Department of Industrial Chemistry, Kyoto University, Kyoto, Japan*)

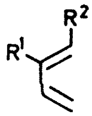
Summary Reaction of coumalic acid with buta-1,3-dienes gave (IIIa—c) *via* double Diels–Alder reaction; this represents the simplest synthesis of the tricyclo[3,2,1,-$0^{2,7}$]oct-3-ene ring system.

ALTHOUGH Diels–Alder reactions of α-pyrones and alkyl coumalates have been reported,[1] the reaction of coumalic acid (I) seems not to have been studied. It has been found that the double Diels–Alder reaction between (I) and buta-1,3-dienes (II) proceeds in such a way[2] as to yield the tricyclo[3,2,1,$0^{2,7}$]oct-3-ene derivatives (IIIa—c) in a single step. This reaction represents the simplest synthesis of the tricyclo[3,2,1,$0^{2,7}$]oct-3-ene yet reported.[3]

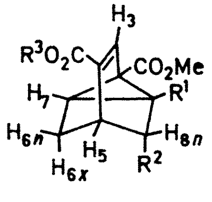
Heating a solution of (I) and (II; $R^1=R^2=H$) in MeOH in a pressure bottle at 100° for 6 h gave, after treatment of the product with ethereal diazomethane, (IIIa) (70%), m.p. 101—102°. The structure of (IIIa) is based principally upon spectroscopic data. The mass spectrum [m/e 222 (M^+), 207, 191, 163 (100%), 131, 119, 103, 91, 77, and 59] establishes (IIIa) $C_{12}H_{14}O_4$,† to be a dimethyl ester of a dicarboxylic acid. The n.m.r. spectrum (CCl_4) has signals at δ 0·84 (2H, d, J 12·3 Hz, 6n-H, 8n-H), 1·74 (2H, q, J 12·3 Hz, J' 4·9 Hz, 6x-H, R^2=8x-H), 2·28 (2H, bs, R^1=1-H, 7-H), 3·27 (1H, bt, J 4·9 Hz, J' 1·8 Hz, 5-H), 7·36 (1H, d, J 1·8 Hz, 3-H), and 3·70 and 3·73 (3H each, s,



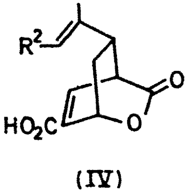
(I)



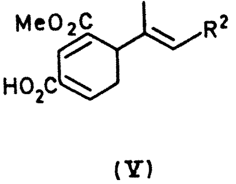
(II)



(III) a; $R^1=R^2=H$, $R^3=Me$
b; $R^1=R^2=R^3=H$
c; $R^1=R^3=Me$, $R^2=H$
d; $R^1=H$, $R^2=R^3=Me$



(IV)



(V)

---

† All new compounds gave satisfactory analyses.

CO_2Me); the assignment was confirmed by double resonance experiments and comparison with the spectrum of benzo-[6,7]tricyclo[3,2,1,$0^{2,7}$]octene.[3a] The u.v. maximum (EtOH) at **243** nm (ϵ **12,500**) indicates a β-cyclopropylacrylic ester chromophore.[4]

Without diazomethane treatment, the reaction gave a half-ester (IIIb), m.p. 178—178·5°, which showed i.r. bands (Nujol) at 1680 and 1740 cm^{-1}, indicating the presence of conjugated carboxylic acid and saturated ester groups. Esterification by means of diazomethane converted (IIIb) into (IIIa). Similar reaction of (I) with (II; R^1=Me, R^2=H) at 100° for 6 h gave (IIIc) (23%), b.p. 132—136°/5 mm, and with (II; R^1=H, R^2=Me) afforded (IIId) (21%), m.p. 98·5—99·5°.‡

These results can be explained by assuming that the first Diels–Alder reaction between the diene moiety of (I) and the ene part of (II) as the dienophile occurs with inverse electron demand to give (IV), a strained lactone, which is transformed into a half-ester with the diene structure (V) after methanolysis and subsequent dehydration. The second, intramolecular, Diels–Alder reaction also takes place with inverse electron demand, giving the product (III; R=H). This (4 + 2)-cycloaddition step leading to cyclopropane ring formation has some precedents in the literature.[3b,5]

We thank Prof. H. Nozaki for stimulating discussion and encouragement, and Dr. H. Takahasi for a gift of butadiene.

(*Received, August 5th,* 1971; *Com.* 1373.)

---

‡ The n.m.r. spectra of these adducts have been reasonably assigned, as in the case of (IIIa).

[1] H. Behringer and P. Heckmaier, *Chem. Ber.*, 1969, **102**, 2835; J. A. Reed, C. L. Schiling, jun., R. F. Tarvin, T. A. Rettig, and J. K. Stille, *J. Org. Chem.*, 1969, **34**, 2188; and refs. cited therein.

[2] R. Huisgen, R. Grashey, and J. Sauer, "The Chemistry of Alkenes", ed. S. Patai, Interscience, New York, 1964, p. 922.

[3] (a) R. C. Hahn and L. J. Rothman, *J. Amer. Chem. Soc.*, 1969, **91**, 2409; (b) C. F. Huebner, E. Donoghue, L. Dorfman, F. A. Stuber, N. Danieli, and E. Wenkert, *Tetrahedron Letters*, 1966, 1185; (c) C. A. Grob and J. H. Hostynek, *Helv. Chim. Acta*, 1963, **46**, 1676; (d) W. von E. Doering, E. T. Fossel, and R. L. Kaye, *Tetrahedron*, 1965, **21**, 25; (e) R. R. Sauers, J. A. Beisler, and H. Feilich, *J. Org. Chem.*, 1967, **32**, 569; (f) T. J. Katz and S. Cerefice, *J. Amer. Chem. Soc.*, 1969, **91**, 2405.

[4] M. J. Jorgenson and T. Leung, *J. Amer. Chem. Soc.*, 1968, **90**, 3769.

[5] W. von E. Doering and W. R. Roth, *Tetrahedron*, 1963, **19**, 715; E. N. Marvell and J. Seubert, *Tetrahedron Letters*, 1969, 1333.