Tricyclo[4,4,0,$0^{2,5}$]deca-3,7,9-triene

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Summary A new method for converting quinone Diels–Alder adducts into cyclohexadiene derivatives is used for the synthesis of tricyclo[4,4,0,$0^{2,5}$]deca-3,7,9-triene, which rearranges to tricyclo[4,2,2,$0^{2,5}$]deca-3,7,9-triene at 70°.

TRICYCLO[4,4,0,$0^{2,5}$]DECA-3,7,9-TRIENE (I) is a key intermediate in thermal rearrangements of several of the $(CH)_{10}$ isomers.[1,2] We now describe the synthesis and isolation of (I) and its Cope rearrangement to tricyclo[4,2,2,$0^{2,5}$]deca-3,7,9-triene (VIII) (Nenitzescu's hydrocarbon).

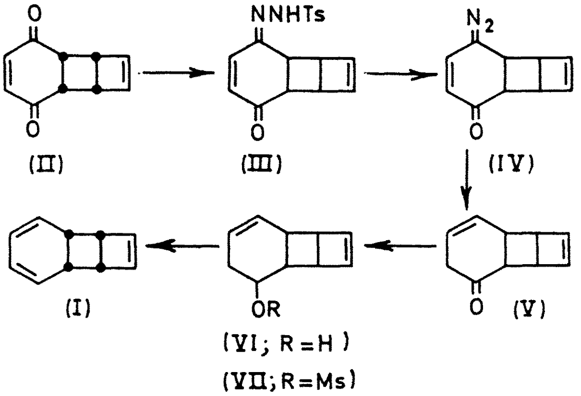
The quinone–cyclobutadiene adduct (II)[3] was converted into the toluene-*p*-sulphonylhydrazone (III), m.p. 158—159° (decomp.), and treatment of (III) with sodium carbonate afforded the sensitive diazoenone (IV), a red oil, 40% yield, preparative layer chromatography (p.l.c.) over silica gel; (IV): ν_{max} (neat) 4·88, 6·14, and 6·50 μm; δ (CCl_4) 7·06 (1H, d, *J* 9·7 Hz), 6·35 (2H, m), 5·25 (1H, d, *J* 9·7 Hz), and 3·3—4·1 (4H, m) p.p.m. Reduction of (IV) with zinc in acetic acid–tetrahydrofuran at 0° afforded the $\beta\gamma$-unsaturated ketone (V), (50% yield after p.l.c. over silica gel); (V): ν_{max} (neat) 5·87 μm; δ (CCl_4) 6·17br (2H, s), 5·72br (2H, s), 3·0—3·7 (4H, m), and 2·63br (2H, s) p.p.m. The final transformations into (I) were carried out by standard methods without isolation of the intermediate alcohol (VI) or the methanesulphonate (VII). Potassium t-butoxide in ether–dimethyl sulphoxide converted (VII) into the desired hydrocarbon tricyclo[4,4,0,$0^{2,5}$]deca-3,7,9-triene (I). Owing to the instability of (IV)—(VII) and the final product (I), all operations were performed at 0—5°.

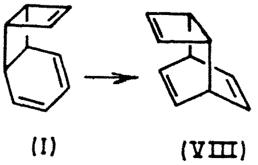
Purified (p.l.c.) (I) is stable in solution at room temperature, but neat samples decompose to an amorphous solid during several hours. A freshly chromatographed sample of (I) shows a u.v. maximum at 278 nm (ϵ 1750) and a minimum at 240 nm (ϵ 500).[4] The n.m.r. spectrum of (I) shows the characteristic broadened singlet for cyclobutene olefinic hydrogens 3- and 4-H at δ 6·26 p.p.m. and a broadened singlet at δ 5·52 p.p.m. for 7-, 8-, 9-, and 10-H. The aliphatic hydrogens appear as poorly resolved 2-H multiplets at δ 3·27 and 3·51 p.p.m.

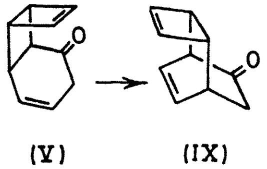
In dilute solution at 70° (I) rearranges smoothly to tricyclo[4,2,2,$0^{2,5}$]deca-3,7,9-triene (VIII) with a half-life of 28 min. Disappearance of the cyclohexadiene chromophore of (I) can be used to monitor the conversion of (I) into (VIII) and first-order kinetics are observed in the temperature range 55—75° ($E_a = 23{\cdot}5 \pm 1$ kcal mol^{-1}; log $A = 11{\cdot}5$). The ketone (V) also rearranges at 70° (half-life *ca.* 1 h) and the product is the known tricyclo-[4,2,2,$0^{2,5}$]deca-3,7-dien-9-one (IX).[5] Both (I) and (V) contain a *cis*-divinylcyclobutane moiety,[6] and the expected Cope rearrangement gives (VIII) and (IX), respectively.

Previous discussions[1] invoke a reversible interconversion of (I) and (VIII) to explain the transformation of (VIII) into 1,2-dihydronaphthalene and minor side-products at 280°. A necessary condition for these arguments is Cope rearrangement of (I) to (VIII) which we have now demonstrated to occur readily at 70°. The mechanism postulated[2] for conversion of basketene into (VIII) *via* (I) at 100° is also supported by our results.

The methods used for synthesis of (I) can be employed to solve the synthetic problem of converting Diels–Alder adducts of *p*-benzoquinone into cyclohexadiene derivatives which, in the formal sense, are Diels–Alder adducts of benzene. We are studying applications of this technique.







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