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The synthesis of the title compound, a previously unreported tri-cyclic benzofuran analog, and the preparation of some of its derivatives is reported

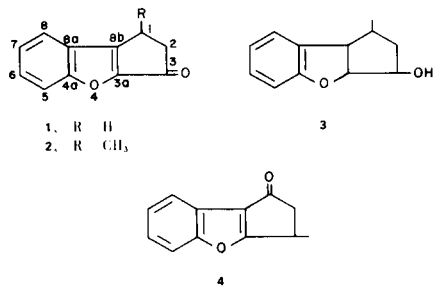
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Sir:

The benzofurocyclopentan-3-one system **1** does not appear to have been previously described in the chemical literature. Herein is described a simple procedure for the preparation in moderate yield of the racemic 1-methyl analog **2** from benzofuran and crotonic acid using a well known method employing polyphosphoric acid as solvent and catalyst (1).

The reaction of benzofuran with a 0.05 molar excess of crotonic acid was carried out as a well stirred solution in 10 volumes of commercial polyphosphoric acid. After heating for 30 minutes at 130° the resultant dark brown mixture was quenched in excess ice/water and extracted with ether. After extraction of the latter phase with sodium bicarbonate solution, evaporation of the ether afforded an oily mixture containing ca 85% (by glc) of a single major component which was obtained from the mixture by dry-column chromatography on alumina with methylene chloride as eluent [34% yield, b.p. 208-210° (1mm); ir (neat): 1717, 1595, 1255 cm⁻¹; ms: M⁺ 186.0682 (C₁₂H₁₀O₂); pmr (deuteriochloroform): 7.71 (m, 1H), 7.51 (m, 2H), 7.34 (m, 1H), 3.49 (m, 1H), 3.22 (q, 1H), 2.54 (q, 1H), 1.48 ppm (t, 3H); 2,4-dinitrophenylhydrazone m.p. 201-202°].

Reduction of **2** with Raney nickel catalyst (W2) proceeded with continuous uptake of 2 moles of hydrogen to afford a single product obtained pure by dry-column chromatography and assigned as the 3a,8b-dihydrobenzofurocyclopentan-3-ol **3** [95% yield, m.p. 84-86°; ir (nujol): 3400 (broad), 1590 cm⁻¹; ms: M⁺ 190; pmr (deuteriochloroform): 7.0 (m, 4H), 5.08 (q, 1H), 4.6-3.8 (broad, 1H), 4.3-4.0 (m, 1H), 3.9-3.04 (m, 1H), 2.85-1.15 (m, 3H), 1.02 ppm (t, 3H); *p*-phenyl benzoate m.p. 159-160°]. Stopping the hydrogenation after the uptake of one mole gave a mixture of partly reduced products.



The assignment of structure **2** to the product of the condensation of benzofuran and crotonic acid was based *inter alia* on the 270 MHz proton nmr and carbon-13 nmr spectra, with chemical shifts from the latter shown in Table I. The former yielded an essentially first order spectrum in which was observed the disappearance (with respect to benzofuran) of the two olefinic proton resonances of the furan ring and the appearance of three one proton multiplets (between 2.5-3.5 ppm) and a three proton doublet. The former set of signals formed a pseudo AMX spin system with one spin coupled additionally to a methyl group and attributed to the C-1 methine proton in **2**. The other two resonances in the group were quartets with geminal J value of 18 Hz and were attributed to the C-2 methylene protons in **2**. The remaining resonance in the aliphatic region was the three proton doublet (J = 7 Hz) at 1.32 ppm and this was attributed to the C-1 methyl group.

The carbon-13 nmr showed one carbonyl carbon and three sp³ hybridised carbons consistent with a methyl cyclopentanone ring fused to a conjugated π system [*cf.* indanone (2)]. Five quaternary carbons were revealed by off-resonance decoupling, four of which were readily attributable to C-3, 3a, 4a and C-8a. The low field resonance at ca 190 ppm was unambiguously assigned to the carbonyl carbon (C-3) while the resonance at 124.2 ppm was assigned to C-8a. The observation of the fifth signal at such a low field position as 155 ppm could only be reconciled with C-8b in structure **2** carrying a branched

Table I

C-13 Chemical Shifts of **2**

Ppm (from TMS)	Assignment (4)
20.0	C-1'
27.1	C-1
49.2	C-2
113.6	C-5
122.0	
123.9	C-6,7,8
129.1	
124.2	C-8a
155.1	
156.1	C-8b,4a
161.9	C-3a
189.9	C-3

alkyl substituent (3) and this permitted distinction between this structure and the possible alternative isomer 4. In the latter, the acyl substituted C-8b would not be predicted to give rise to a resonance as far downfield as observed (3). The possibility that compound 4 was present among the minor products of the condensation has yet to be investigated.

Acknowledgment.

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REFERENCES AND NOTES

- (1) J. M. Allen, K. M. Johnston, J. F. Jones and R. G. Schotter, *Tetrahedron*, **33**, 2083 (1977).
- (2) L. F. Johnson and W. C. Jankowski, "Carbon-13 NMR Spectra. A Collection of Assigned, Coded and Indexed Spectra.", Wiley-Interscience, New York, N. Y., 1972; H. G. Grant, unpublished results.
- (3) F. W. Wehrli and T. Wirthlin, "Interpretation of Carbon-13 NMR Spectra.", Heyden, 1976.
- (4) For other benzofuran C-13 shifts see also: N. Platzer, J. Basselier and P. Demerseman, *Bull. Soc. Chim. France*, 904 (1974).