

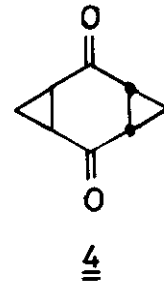
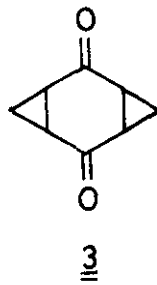
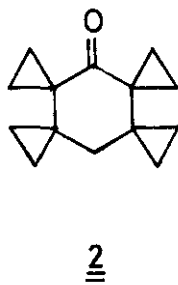
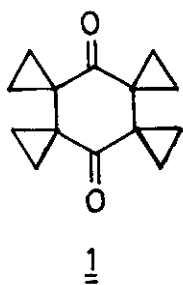
CONVENIENT SYNTHESIS OF TETRASPIRO[2.0.2.1.2.0.2.1]TETRADECANE-7,14-DIONE AND HEXASPIRO[2.0.2.0.2.0.2.0.2.0.2.0]OCTADECANE ("[6]-ROTANE")^[**]

Ehrhardt Proksch and Armin de Meijere^[*]

Organisch-Chemisches Institut der Universität, Tammannstraße 2,
D-3400 Göttingen, Germany

(Received in UK 11 October 1976; accepted for publication 14 November 1976)

As we have recently found^[1] cyclopropyl hydrocarbons are selectively oxidized by ozone in the α -position to give cyclopropyl alkyl ketones in high yields. This method offers itself for the synthesis of a number of otherwise inaccessible small ring molecules including the tetraspiro[2.0.2.1.2.0.2.1]-tetradecane-7,14-dione (1) and the tetraspiro[2.0.2.1.2.0.2.1]tetradecan-7-one (2), which are of interest in comparison to the known cis- (3) and trans-bis-homoquinone (4)^[2].



Wittig olefination^[3] of dispiro[2.2.2.2]decane-4,9-dione (5)^[4] lead to 4,9-dimethylenedispiro[2.2.2.2]decane (6)^[5] (liquid, 76 % yield), which upon cyclopropanation with the Simmons-Smith-reagent^[6] afforded tetraspiro[2.0.2.1.2.0.2.1]tetradecane (7)^[5] (mp. 94°C, 70 %). The signal of the cyclohexane protons of 7 at $\delta = 1.28$ ppm in the room temperature NMR spectrum appeared as a broad

singlet, which sharpened at higher temperatures and split into two multiplets at -20°C . This indicates, that the barrier for the cyclohexane inversion in 7 is higher by several kilocalories than the one for dispiro[2.2.2.2]decane^[7]. 7 was adsorbed on silica gel^[8] and treated with ozone to give 1^[5]. The reaction was followed by ~~gas chromatography~~ and carried to about 97 % conversion by repeated cycles of ozone adsorption at -78°C and warming up to room temperature. 1 was isolated in 61 % yield by elution from the silica gel with ether,

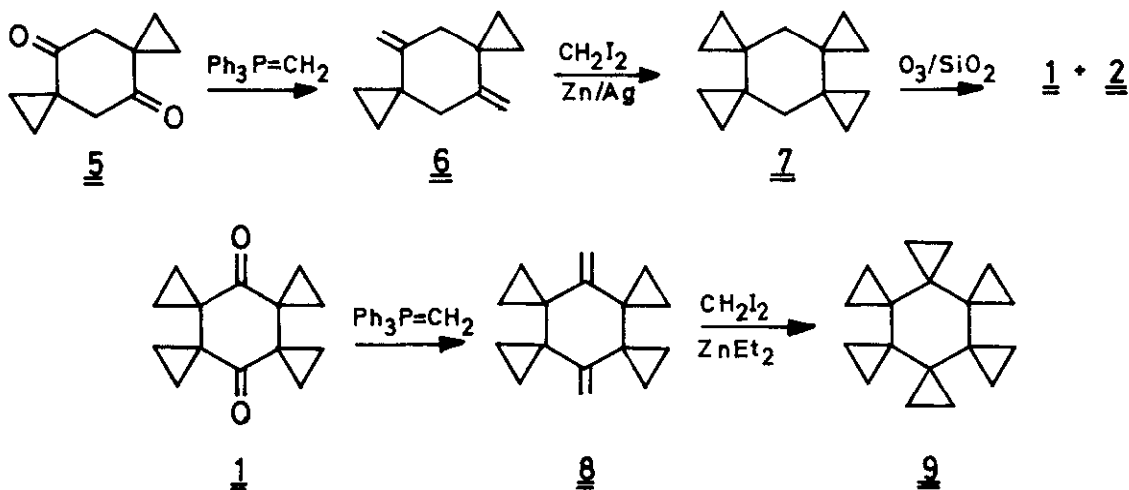


Table 1: $^1\text{H-NMR}$ spectral data for the new compounds

Compound	δ [ppm] (relative to TMS)
<u>6</u>	4.59 (A part, 2 H); 4.51 (B part of an AB system, 2 H); 2.08 (s, 4 H); 0.62 (AA' part, 4 H); 0.24 (BB' part of an AA'BB' system, 4 H)
<u>7</u>	1.28 (m, 4 H); 0.14 (m, 8 H)
<u>1</u>	1.19 (AA' part, 8 H); 0.45 (BB' part of an AA'BB' system, 8 H)
<u>2</u>	1.57 (s, 2 H); 1.10 (AA' part, 4 H); 0.39 (BB' part of an AA'BB' system, 4 H); 0.18 (s, 8 H)
<u>8</u>	4.42 (s, 4 H); 0.51 (AA' part, 8 H); 0.41 (BB' part of an AA'BB' system, 8 H)
<u>9</u>	0.47 (AA' part, 12 H); -0.38 (BB' part of an AA'BB' system, 12H)

evaporation of the solvent and subsequent sublimation of the residue. With a smaller excess of ozone the monoketone 2^[5] (m.p. 116°C) was formed predominantly and isolated by gas chromatography.

It is interesting to compare the carbonyl stretching frequencies and the UV absorptions of 1 and 2 with those of 3, 4 and cyclohexane-1,4-dione (see table 2). For 1 and 4 the bands of the $n \rightarrow \pi^*$ transitions exhibit a substantial hypsochromic shift relative to the parent diketone, whereas for 2 and 3 the shift is very small. This difference, which must be due to a difference in the electronic interaction between the carbonyl and the cyclopropyl groups^[9], is also reflected in the carbonyl stretching frequencies. However, the split between the antisymmetric and symmetric vibrational levels for 1 is surprisingly small, much smaller than for 3, 4 and the cyclohexane-1,4-dione.

Table 2: IR and UV spectral data for some cyclohexane-1,4-dione derivatives

Compound	$\nu\text{-C=O}$ [cm^{-1}]	λ_{max} [nm](solvent)	ϵ_{max} [$1 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$]
<u>1</u>	1688 (as)	271 (EtOH)	135
	1684 (s) ^[a]		
<u>2</u>	1667	279 (EtOH)	169
<u>3</u>	1701 (as)	280 (EtOH)	47
	1678 (s)		
<u>4</u>	1712 (as)	271 (EtOH)	57
	1668 (s)		
cyclohexane- -1,4-dione	1724 (as)	281 (EtOH)	29
	1709 (s) ^[a]		

[a] Taken from the Raman spectrum.

Olefination^[3] of the diketone 1 gave the 7,14-dimethylene-tetraspiro-[2.0.2.1.2.0.2.1]tetradecane (8)^[5] (67 %, isolated by sublimation). 8 upon cyclopropanation with methylene iodide/diethylzinc^[10] lead to [6]-rotane 9^[5] as the only product (m.p. 228°C, 72 %, isolated by sublimation). When the

cyclopropanation was carried out with methylene iodide/zinc-silver couple^[6] an unidentified second product was formed with 15 % relative yield, apparently arising from a zinc iodide catalyzed rearrangement of 9 or one of its precursors.

The five step sequence outlined above affords 9 with 16 % overall yield. It is therefore a convenient alternative to a method recently described^[11].

References and Footnotes

- [*] Author to whom correspondence should be addressed
- [**] This work was supported by the "Fonds der Chemischen Industrie" and the Höchst AG, Frankfurt/Main
- [1] E.Proksch and A.de Meijere, Angew. Chem. 88, in press (1976); Angew.Chem. Int. Ed. Engl. 15, in press (1976)
- [2] J.E.Heller, A.S.Dreiding, B.R.O'Connor, H.E.Simmons, G.L.Buchanan, R.A.Raphael, and R.Taylor, Helv. Chim. Acta 56, 272 (1973)
- [3] R.Greenwald, M.Chaykovsky, and E.J.Corey, J.Org.Chem. 28, 1128 (1963)
- [4] T.Tsuji, S.Nishida, and H.Tsubomura, J.C.S. Chem. Comm. 1972, 284. For a modified preparation of 5 see: P.Asmus, M.Klessinger, L.-U.Meyer and A.de Meijere, Tetrahedron Lett. 1975, 381
- [5] All new compounds were fully characterized by their IR, MS, ¹H-NMR spectra (see table 1) and elemental analysis.
- [6] J.M.Denis, C.Girard, and J.M.Conia, Synthesis 1972, 549
- [7] J.B.Lambert, J.L.Gosnell jr., and D.S.Bailey, J.Org.Chem. 37, 2814 (1972)
- [8] Z.Cohen, E.Keinan, Y.Mazur, and T.H.Varkony, J.Org.Chem. 40, 2141 (1975)
- [9] More detailed information about the transmission of electronic effects through the spirocyclopropyl groups in 1, 8 and 9 is expected from a photoelectron spectroscopic investigation, which is in progress in cooperation with Prof. R. Gleiter, Darmstadt.
- [10] J.Furukawa, N.Kuwabata, and J.Nishimura, Tetrahedron 24, 53 (1968); Tetrahedron Lett. 1968, 3495
- [11] L.Fitjer, Angew. Chem. 88, in press (1976)