Tetrahedron Letters,Vol.27,No.9,pp 1095-1098,1986 0040-4039/86 $3.00 + .00
Printed in Great Britain ©1986 Pergamon Press Ltd.

7,8-DIMETHOXYCARBONYL-10,11-DIMETHYL[5]PARACYCLOPHANE

G.B.M. Kostermans, W.H. de Wolf and F. Bickelhaupt*
Scheikundig Laboratorium, Vrije Universiteit
De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

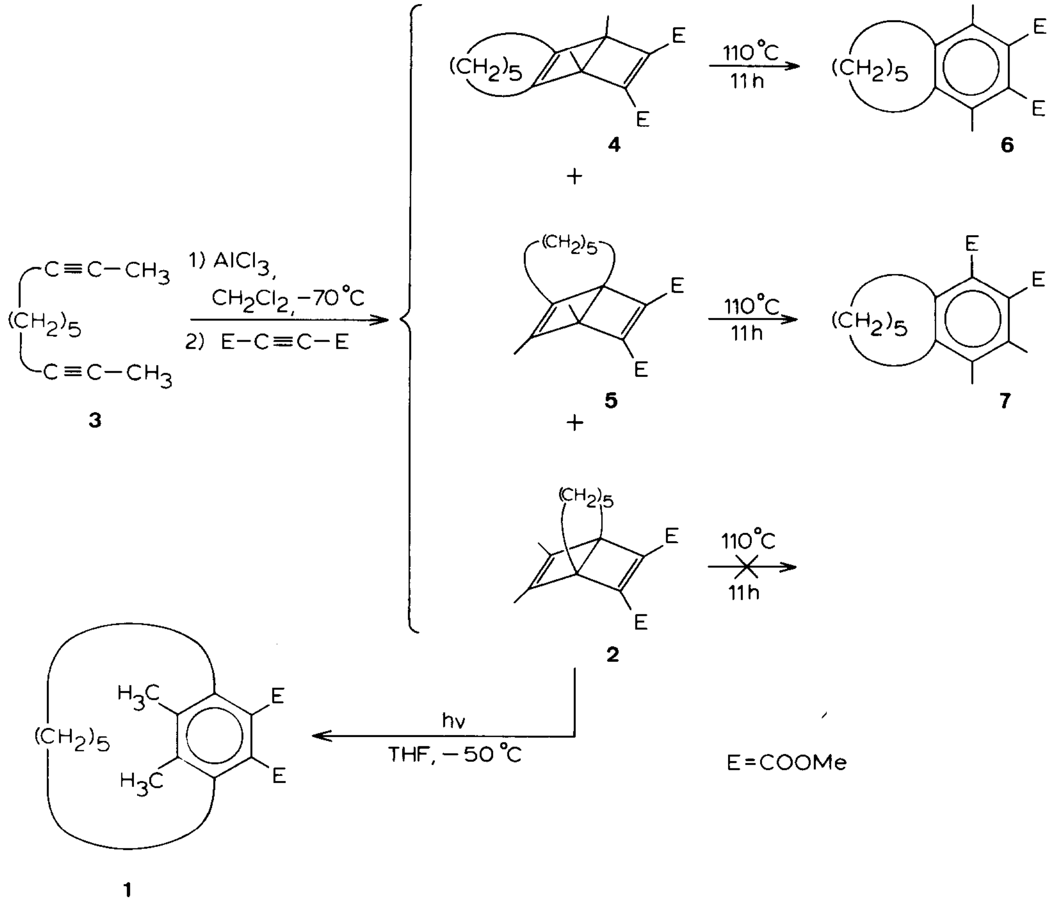
Abstract: The title compound (**1**) was obtained in 13% yield by UV irradiation of the corresponding Dewar benzene (**2**); it is considerably more stable than [5]paracyclophane itself.

Recently, we showed that [5]paracyclophane, the shortest representative of the simple paracyclophanes[1], is obtained in 7% yield on irradiation of the corresponding Dewar benzene[2]. In view of the instability of [5]paracyclophane at room temperature and because of the difficulties in preparing its precursor on a larger scale[3], we are presently engaged in developing more efficient synthetic routes to [5]paracyclophanes possessing a higher thermal stability with the goal of isolation and chemical investigations of these interesting compounds with a strongly bent benzene ring. We here report our first results in this direction by the preparation of 7,8-dimethoxycarbonyl-10,11-dimethyl[5]paracyclophane **1** (Scheme 1).

Precursor of **1** was **2**; this compound was synthesized from undeca-2,9-diyn (**3**) by the method of Hogeveen et al.[4]. This method furnishes a mixture of the three regioisomers **4**, **5** and **2** in a ratio of about 1:2:1[4]. Compound **2** can be isolated from this mixture by heating the crude mixture in toluene solution for 11 h at 110°C, whereupon **4** and **5** aromatize to **6** and **7**, respectively, while **2** remaines unchanged, followed by medium pressure column chromatography (silicagel 60, 15 µm, eluent petroleum ether 40-60 with 10% ethyl acetate). We obtained **2** as colourless crystals in 9% yield; it can thus easily be prepared on a gram scale. At 210 K, the ^{1}H- and ^{13}C-NMR spectra of **2** showed decoalescence phenomena[5] due to the presence of two conformers in a ratio of 61:39; this prevented a full assignment of the low temperature ^{1}H-NMR spectrum. Line shape analysis furnished $\Delta H^{\neq} = 10.8$ kcal·mol^{-1} and $\Delta S^{\neq} = -8.3$ cal·mol^{-1}·K^{-1} for the flipping motion of the bridge.

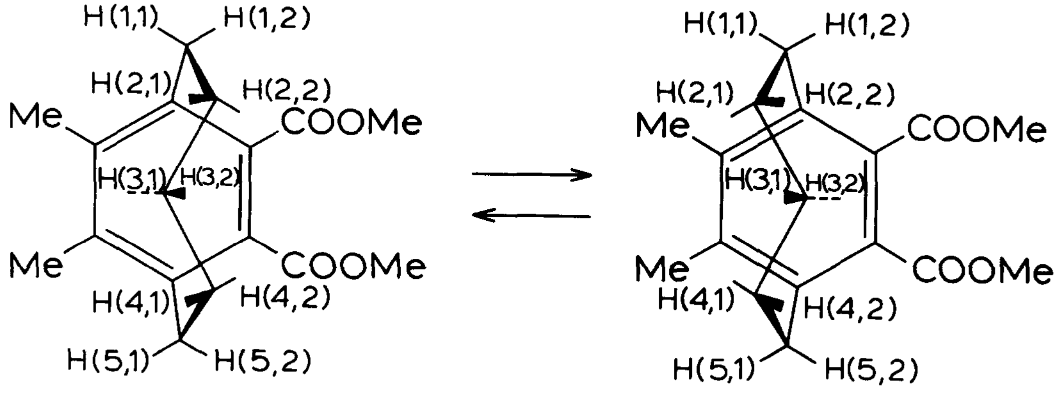
Irradiation of a degassed solution of ca. 20 mg of **2** in 0.4 ml THF-d_8 at -50°C in a quartz NMR tube with a low pressure mercury lamp (2537 Å) during 30 min yielded about 13% of **1**[6]; prolonged irradiation did not increase the ratio **1** : **2**. Like **2**, **1** occurs in two diastereomeric conformations, but the ratio (53:47) is close to unity. The ^{1}H-NMR spectrum identifies **1** as a cyclophane; in particular, the high-field shifts of two homobenzylic protons and of one of the central protons (in both conformers!) are diagnostic.

Scheme 1



In analogy to [5]paracyclophane and to the diester derived from [6]paracyclophane[7], the following assignments are made for the low temperature ^{1}H-NMR spectrum (Scheme 2): 1a: δH(3,1) = 0.06 ppm, δH(2,2) = δ(4,2) = 0.33 ppm; 1b: δH(3,2) = -0.55 ppm, δH(2,1) = δH(4,1) = 0.44 ppm[6]. Line shape analysis of the coalescing signals yielded $\Delta H^{\neq} = 11.2$ kcal·mol^{-1} and $\Delta S^{\neq} = -10.8$ cal·mol^{-1}·K^{-1} for the barrier of bridge flipping. The lower bridge barriers of 1 and 2 compared to the parent hydrocarbons are probably caused by unfavourable ground state interactions between bridge and the substituents at the benzene ring (COOMe; Me). The half life of 1 is concentration dependent, indicating a bimolecular or chain mechanism of polymerization. In THF (ca. 0.15 M), the half life is several hours at room temperature; this illustrates the stabilizing effect of the substituents, as the unsubstituted [5]paracyclophane rapidly decomposes above 0°C[9]. Attempts to separate 1 from 2 were, however, so far not succesful.

Scheme 2



1a **1b**

Of special interest are the chemical shifts of the arylmethyl groups of **1**' (**1a**: $\delta(CH_3)$ = 2.33 ppm, **1b**: $\delta(CH_3)$ = 2.31 ppm). They are exactly those expected for a planar, fully aromatic benzene ring[8]. Although the effects of steric compression and long range interactions remain to be analyzed, it is not expected that they will alter the conclusion that here again the "aromaticity" of **1** is essentially intact inspite of severe bending of the aromatic ring (cf. the "olefinic" value $\delta(CH_3)$ = 1.64 for **2**).

In contrast to the clean acid-catalyzed rearrangement of [5]paracyclophane to its ortho--isomer benzocycloheptene, **1** only gave polymeric, unidentified material, on treatment with CF_3COOD.

Acknowledgement. We gratefully acknowledge assistance and advice by Drs. H. Hofstraat (UV), Dr. F.J.J. de Kanter (NMR) and Drs. L.W. Jenneskens.

References and Notes

1. P.M. Keehn and S.M. Rosenfeld, Cyclophanes, Academic Press, New York (1983).
2. L.W. Jenneskens, F.J.J. de Kanter, P.A. Kraakman, L.A.M. Turkenburg, W.E. Koolhaas, W.H. de Wolf, F. Bickelhaupt, Y. Tobe, K. Kakiuchi and Y. Odaira, J. Am. Chem. Soc., 107, 3716 (1985).
3. J.W. van Straten, L.A.M. Turkenburg, W.H. de Wolf and F. Bickelhaupt, Recl. Trav. Chim. Pays-Bas, 104, 89 (1985).

4. (a) P.B.J. Driessen and H. Hogeveen, J. Am. Chem. Soc., 100, 1193 (1977). (b) P.B.J. Driessen and H. Hogeveen, J. Organomet. Chem., 156, 265 (1978).

5. Compound 2: m.p. 49-50°C; MS ($C_{17}H_{22}O_4$), 290 ($M^{+\cdot}$, 0.5%); HRMS ($C_{16}H_{19}O_4$), found 275.1289, cald.: 275.1284 ($M^{+\cdot}$, $-CH_3$), ^{1}H-NMR (400.1 MHz, $CDCl_3$, 297 K), δ = 1.3-1.6 (m, 6H, CH_2), 1.64 (s, 6H, Me), 1.8-2.1 (m, 4H, CH_2), 3.79 (s, 6H, OMe). ^{13}C-NMR (62.9 MHz, $CDCl_3$, 297 K), δ = 11.3 (q, $^1J_{CH}$ = 126 Hz, Me), 26.5 (t, $^1J_{CH}$ = 126 Hz, C(2,6)*), 27.4 (t, $^1J_{CH}$ = 125 Hz, C(3,5)*), 33.2 (t, $^1J_{CH}$ = 124 Hz, C(4)), 51.6 (q, $^1J_{CH}$ = 148 Hz, OMe), 61.9 (s, C(1,7)), 142.8 (s, C(10,11)), 151.2 (s, C(8,9)), 162.8 (s, CO). ^{13}C-NMR (62.9 MHz, $CDCl_3$, 210 K), δ = 11.5, 11.8 (q, $^1J_{CH}$ = 126 Hz, Me), 25.7, 26.6 (t, $^1J_{CH}$ ~ 126 Hz, C(2,6)*), 26.8, 27.4 (t, $^1J_{CH}$ ~ 126 Hz, C(3,5)*), 32.8, 33.0 (t, $^1J_{CH}$ ~ 125 Hz, C(4)), 52.2 (q, $^1J_{CH}$ = 147 Hz, OMe), 60.9, 62.0 (s, C(1,7)), 142.3 (s, C(10,11)), 151.2, 152.2 (s, C(8,9)), 162.4, 162.9 (s, CO). Assignments marked with an asterisk may have to be reversed. UV (2-methylbutane, 223 K): λ_{max} (log ε) = 250 nm (3.6).

6. Compound 1: ^{1}H-NMR (400.1 MHz, THF-d_8, 220 K), 1a, δ = 0.06, (dt, $^2J_{HH}$ = 17 Hz, $^3J_{HH}$ = 8 Hz, 1H, H(3,1)), 0.33 (m, $^3J_{HH}$ = 6 Hz, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 12 Hz, 2H, H(2,2), H(4,2)), 2.33 (s, 6H, Me), 2.87 (ddd, $^2J_{HH}$ = 13 Hz, $^3J_{HH}$ = 12 Hz, $^3J_{HH}$ = 5 Hz, 2H, H(1,1), H(5,1)), 2.99 (dd, $^2J_{HH}$ = 13 Hz, $^3J_{HH}$ = 6 Hz, 2H, H(1,2), H(5,2)), 3.72 (s, 6H, OMe), 1b, δ = -0.55 (dt, $^2J_{HH}$ = 16 Hz, $^3J_{HH}$ = 7 Hz, 1H, H(3,2)), 0.44 (m, $^3J_{HH}$ = 7 Hz, $^3J_{HH}$ = 5 Hz, 2H, H(2,1)), H(4,1)), 2.31 (s, 6H, Me), 3.22 (dd, $^2J_{HH}$ = 13 Hz, $^3J_{HH}$ = 5 Hz, 2H, H(1,1), H(5,1)), 3.73 (s, 6H, OMe). H(3,2), H(2,1), H(4,1) of 1a and H(3,1), H(2,2), H(4,2), H(1,2), H(5,2) of 1b are concealed under the multiplets of 2. Decoupling experiments indicated their chemical shifts at δ = 1.21 (H(3,2)) and δ = 1.59 (H(2,1), H(4,1) for 1a and δ = 1.32 H(3,1)), 1.59 (H(2,2), H(4,2)), 2.44 (H(1,2), H(5,2)) for 1b.

7. H. Günther, P. Schmitt, H. Fischer, W. Tochtermann, J. Liebe and C. Wolff, Helv. Chim. Acta, 68, 801 (1985).

8. (a) Y. Kashman, I. Wagenstein and A. Rudi, Tetrahedron, 32, 2427 (1976). (b) D.R. MacAlister, J.E. Bercaw and R.G. Bergman, J. Am. Chem. Soc., 99, 1666 (1977).

9. A comparable degree of stabilization has very recently been reported for the 7-carbomethoxy derivative of [5]paracyclophane: Y. Tobe, T. Kaneda, K. Kakiuchi and Y. Odaira, Chemistry Lett. 1985, 1301.

(Received in UK 12 December 1985)