A Formal [4 + 2] Dimerization of 9-Cyclopropylidene-9*H*-fluorene

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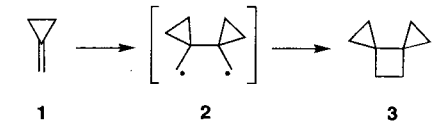
Received April 9, 1996

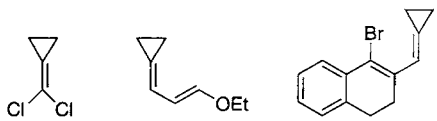
Key Words: Methylenecyclopropanes / Diradicals / Dimerization / Cycloaddition / Spirocycles

The methylenecyclopropanes **7** and **8**, with aryl substituents fixed in a coplanar conformation, show an extraordinary readiness to dimerize with formation of **10** and **11**, respectively.

Methylenecyclopropanes are well known for their pronounced reactivity, including their tendency to undergo a [2 + 2] dimerization at elevated temperatures. The parent hydrocarbon **1** dimerizes slowly at 240 °C to give the head-to-head dimer **3**, presumably via the diradical intermediate **2**[1]. The dichloro derivative **4**[1] and captodatively substituted methylenecyclopropanes[2] start to dimerize at about 100 °C, probably because of stabilizing effects of the substituents on radical intermediates. Even more reactive is the conjugated derivative **5**; in this case a reaction temperature of 50 °C is sufficient for dimerization[3]. A [2 + 2] dimerization at −78 °C occurs upon bromine-lithium exchange for compound **6**[4]; a special mechanism involving single-electron transfer has been suggested to explain this surprisingly low dimerization temperature.



1 **2** **3**

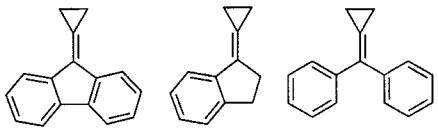


4 **5** **6**

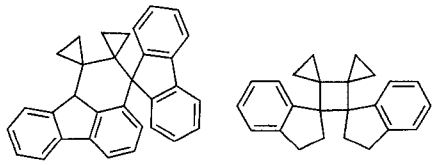
We report here on the remarkable reactivity of two aryl-substituted methylenecyclopropanes, which dimerize at room temperature.

Results and Discussion

An attempt to synthesize the fluorene system **7** at 20 °C by a Wittig reaction of fluorenone with cyclopropylidenetriphenylphosphorane[5] (generated in situ from (3-bromopropyl)triphenylphosphonium bromide) led to the isolation of the unusual spirocycle **10** (20% yield)[6], obviously the product of a [4 + 2] cyclodimerization with a subsequent 1,3-H-shift under rearomatization. The constitution has been confirmed by an X-ray structure analysis (Figure 1). A characteristic feature of the ^{1}H-NMR spectrum of this compound is a ^{1}H multiplet at $\delta = -0.5$, caused by a cyclopropyl hydrogen, whose signal is shifted upfield by the magnetic anisotropy of the fluorene moiety.

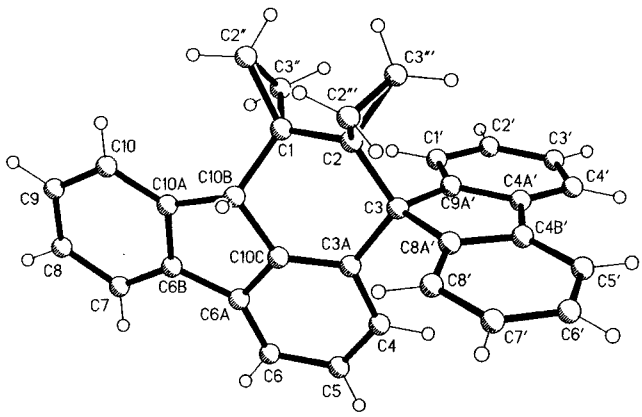


7 **8** **9**



10 **11**

Figure 1. Molecular structure of **10**



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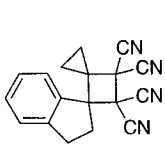
In a second experiment we tried to isolate the fluorene system **7** from the crude reaction mixture by Kugelrohr distillation at 90°C/0.3 Torr. Here also, the dimer **10** was isolated instead (47% yield) besides some fluorenone starting material (36% recovered). As the dimer **10** is insufficiently volatile to distil under these conditions, we assume that the monomer **7** dimerizes rapidly in the receiver.

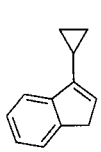
In contrast, the aryl-substituted methylenecyclopropanes **8** and **9** are efficiently accessible from indanone and benzophenone under similar reaction conditions[5]. Whereas **9** is stable under moderate conditions, **8** dimerizes slowly in the condensed phase even at −25°C. In contrast to the dimerization of **7**, no [4 + 2] dimers have been observed in this case. According to the ^{1}H-NMR spectra two isomeric head-to-head dimers **11** are formed in a 1:1 ratio by a [2 + 2] cycloaddition: the C_s-symmetrical *syn* isomer and the *anti* isomer with C_2 symmetry. Both the *syn*- and the *anti*-head-to-tail dimers corresponding to **11** would furnish AA'BB'-type absorptions in their ^{1}H-NMR spectra for the CH_2CH_2 fragments of the cyclopropane and of the indane ring systems. As this is not found experimentally, these head-to-tail dimers can be ruled out. Moreover, the *anti*-head-to-tail dimer would only give a single ^{13}C-NMR signal for its four cyclopropane CH_2 groups. In the head-to-head dimers **11** there is, in each isomer, one ABCD spin system for the protons of the two cyclopropane rings and one KLMN system for the protons of the two five-membered rings of the indane moieties. The *syn* and *anti* diastereomers of **11** can, in principle, be distinguished by H,H-NOE measurements. However, the experiments gave no conclusive results.

Obviously, the extraordinary reactivity of **7** and **8** is associated with the coplanarity of the phenyl rings and the olefinic double bond. This structural feature minimizes steric hindrance of reactions at the double bond and is suitable for stabilizing benzylic radicals[7] as reactive intermediates. Nevertheless, a concerted mechanism for the dimerization step cannot be ruled out: in comparison, the [4 + 2] dimerization of (*E*)-1,3-diphenyl-1,3-butadiene has been proven to proceed by a concerted mechanism, despite the fact that radical intermediates should be especially stabilized[8,9].

Some chemical properties of **8** have been tested: **8** does not react with furan or anthracene under moderate conditions, whereas with TCNE[10] a cycloadduct is obtained in excellent yield, whose spectroscopic data are in accord with structure **12**. By adsorptive filtration through neutral alumina, **8** is efficiently converted to its double bond isomer **13**[11].



12



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In conclusion, methylenecyclopropanes with aryl substituents fixed in a coplanar conformation exhibit pronounced reactivity, as seen in their dimerization reactions.

Financial support of the *Dr. Otto Röhm Gedächtnisstiftung* and *Fonds der Chemischen Industrie* is gratefully acknowledged.

Experimental

Melting points are uncorrected. – IR: Nicolet 320. – UV/Vis: HP 8452 A. – NMR: Bruker AM 400. ^{1}H-NMR spectra were recorded at 400.1 MHz using $CDCl_3$ as the solvent and TMS as the internal standard. ^{13}C-NMR spectra were recorded at 100.6 MHz using $CDCl_3$ as the solvent and the internal standard (δ = 77.05). – MS: Finnigan MAT 8430, 70 eV, electron impact.

Trispiro[Biscyclopropane-1,1':1",2'-fluoranthene-3'(10b'H),9"'-9H-fluorene] (**10**). – *Method A:* A mixture of 4.64 g (10.0 mmol) of (3-bromopropyl)triphenylphosphonium bromide and 3.99 g (20.0 mmol) of potassium bis(trimethylsilyl)amide in 20 ml of dry THF under N_2 was stirred for 3 h at 20°C. A solution of 1.80 g (10.0 mmol) of fluorenone and 0.32 g (1.0 mmol) of tris[2-(2-methoxyethoxy)ethyl]amine (TDA-1)[5] in 20 ml of THF was added and the resulting reaction mixture stirred for 2 d at 20°C. After dilution with 200 ml of *n*-pentane and adsorptive filtration through silica, the solvent was removed in vacuo. Flash chromatography of the residue (silica, hexanes/diethylether 50:1) afforded 414 mg (20%) of **10** (R_f = 0.29) as colorless crystals with m.p. 178°C (from 2-propanol) and 817 mg (45%) of fluorenone (R_f = 0.09) as recovered starting material.

Method B: A mixture of 6.49 g (14.0 mmol) of (3-bromopropyl)triphenylphosphonium bromide, 0.65 g (27 mmol) of NaH, and 2 drops of ethanol in 110 ml of dry THF/toluene (6:5) under N_2 was stirred for 6 h at 66°C. After addition of 1.80 g (10.0 mmol) of fluorenone, the solvent was removed in vacuo and the residue distilled in a Kugelrohr apparatus at 90–95°C/0.3 Torr. Flash chromatography of the sublimate (silica, hexanes/ether, 50:1) afforded 959 mg (47%) of **10** (R_f = 0.29) as colorless crystals with m.p. 178°C (from 2-propanol) and 652 mg (36%) of fluorenone (R_f = 0.09) as recovered starting material. – **10**: IR (KBr): $\tilde{\nu}$ = 3062 cm^{-1}, 3048, 3012, 3005, 1446, 1429, 1022, 757, 751, 739. – UV (acetonitrile): λ_{max} (lg ε) = 214 nm (4.82), 272 (4.48), 282 (4.33, sh), 304 (4.02). – ^{1}H NMR ($CDCl_3$): δ = −0.50 (m, 1H), 0.09 (m, 1H), 0.16 (m, 1H), 0.34 (m, 1H), 0.56 (m, 1H), 0.69–0.78 (m, 2H), 0.91 (m, 1H), 4.57 (s, 1H), 6.18 ("d", *J* = 7.9 Hz, 1H), 7.03 (m, 1H), 7.10–7.14 (m, 2H), 7.20 (m, 1H), 7.27–7.34 (m, 4H), 7.42 (m, 1H), 7.52 (m, 2H), 7.68 (m, 2H), 7.82 ("d", *J* = 7.5 Hz, 1H). – ^{13}C NMR ($CDCl_3$): δ = 5.0 (t), 7.1 (t), 7.4 (t), 17.1 (t), 25.8 (s), 28.3 (s), 49.0 (d), 60.1 (s), 117.3 (d), 119.2 (d), 120.6 (d), 125.2 (d), 125.7 (d), 126.0 (d), 126.5 (d), 126.9 (d), 127.0 (d), 127.2 (d), 127.4 (d), 127.5 (d), 127.5 (d), 127.7 (d), 139.1 (s), 139.4 (s), 140.0 (s), 141.2 (s), 143.0 (s), 143.7 (s), 146.0 (s), 151.4 (s), 154.7 (s). – MS (70 eV), *m/z* (%): 409 (20), 408 (48) [M$^+$], 381 (31), 380 (100), 379 (91), 365 (49), 363 (35), 354 (31), 352 (51), 217 (53), 215 (21), 205 (24), 203 (23), 202 (25), 165 (33). – $C_{32}H_{24}$ (408.5): calcd. C 94.08, H 5.92; found C 93.99, H 5.89.

Crystal-Structure Analysis of Compound **10**[12]: *Crystal data:* $C_{32}H_{24}$, M_r = 408.51, monoclinic, $P2_1/n$, *a* = 1314.5(2), *b* = 1252.8(2), *c* = 1331.9(2) pm, β = 94.366(10)°, *V* = 2.1869 nm^3, *Z* = 4, D_x = 1.241 Mg m^{-3}, λ(Mo-K_α = 71.073 pm, μ = 0.07 mm^{-1}, *F*(000) 0 864, *T* = −100°C. – *Data Collection:* Colorless irregular prism 0.6 × 0.3 × 0.25 mm, Siemens P4 diffractometer, 7845 intensities (3849 unique, R_{int} 0.031) to 2Θ 50°. – *Structure Refinement:* On F^2 using SHELXL-93 (G. M. Sheldrick, University of Göttingen). H atoms riding. Final $wR(F^2)$ 0.087, conventional $R(F)$ 0.038, for 289 parameters; *S* = 0.91, max. Δρ = 183 e nm^{-3}.

1-Cyclopropylidene-2,3-dihydro-1H-indene (**8**)[5]: A mixture of 4.64 g (10.0 mmol) of (3-bromopropyl)triphenylphosphonium bro-

mide and 3.99 g (20.0 mmol) of potassium bis(trimethylsilyl)amide in 20 ml of dry THF under N_2 was stirred for 3 h at 20°C. A solution of 0.99 g (7.5 mmol) of 1-indanone and 0.24 g (0.75 mmol) of tris[2-(2-methoxyethoxy)ethyl]amine (TDA-1)[5] in 15 ml of THF was added, and the resulting reaction mixture stirred for 24 h at 20°C. After dilution with 150 ml of *n*-pentane and adsorptive filtration through silica gel, the solvent was removed in vacuo. Kugelrohr distillation of the residue at 35°C/0.1 Torr provided 960 mg (82%) of **8** as a colorless oil, slightly impure because of the proceeding dimerization reaction. – ^{1}H NMR ($CDCl_3$): δ = 1.08–1.13 (m, 2H), 1.30–1.35 (m, 2H), 2.82–2.87 (m, 2H), 3.01–3.04 (m, 2H), 7.15–7.19 (m, 3H), 7.57–7.61 (m, 1H). – ^{13}C NMR ($CDCl_3$): δ = 1.0 (t), 2.8 (t), 30.3 (t), 30.3 (t), 112.0 (s), 121.5 (d), 125.2 (d), 126.4 (d), 127.3 (d), 131.1 (s), 142.1 (s), 146.1 (s).

anti- and syn-2‴,2⁗,3‴,3⁗-Tetrahydrotetraspiro[biscyclopropane-1,1′:1″,2′-cyclobutane-3′,1‴:4′,1⁗-di-1H-indene (**11**): 0.96 g (6.1 mmol) of **8** were refrigerated for 24 h at −25°C. Besides polymeric material, flash chromatography (silica gel, *n*-pentane) gave enriched fractions of *anti*-**11** as colorless solids, pure enough for analysis of NMR data (abbreviations: cp = cyclopropane, in = indane). 1. Fraction with R_f = 0.24: 146 mg (15%): ^{1}H NMR ($CDCl_3$): δ = 0.13 (ddd, 2H, cp-H_a), 0.27 (ddd, 2H, cp-H_b), 0.57 (ddd, 2H, cp-H_c), 0.78 (ddd, 2H, cp-H_d); $J_{a,b}$ = (−) 5.4, $J_{a,c}$ = 6.7, $J_{a,d}$ = 10.0, $J_{b,c}$ = 9.9, $J_{b,d}$ = 6.3, $J_{c,d}$ = (−) 4.7 Hz; δ = 1.41, 1.56 (m_c, 2H each, in-2-H), 2.45 (m_c = 4H, in-3-H), 7.12 (br. d, $J \approx 7$ Hz, 2H, in-4-H), 7.17 (td, $J \approx 7.3$, 7.3, and 1.3 Hz, 2H, in-5-H), 7.26 (br. t, $J \approx 7$ and 7 Hz, 2H, in-6-H), 7.67 (br. d, $J \approx 8$ Hz, 2H, in-7-H). – ^{13}C NMR ($CDCl_3$): δ = 4.8, 8.5 (both t, cp-C-2,3), 30.7 (t, in-C-3), 30.9 (s, cp-C-1), 31.9 (t, in-C-2), 62.4 (s, in-C-1), 124.2 (d, in-C-4), 125.9 (d, in-C-7), 126.0 (d, in-C-6), 126.5 (d, in-C-5), 143.9 (s, in-C-3a*), 148.2 (s, in-C-7a*); assignments from homonuclear decoupling, H,H-and C,H-COSY. 2. Fraction with R_f = 0.17: 151 mg (16%): ^{1}H NMR ($CDCl_3$): δ = 0.29 (m_c, 2H, cp-H), 0.51, 0.54, 0.57 (m_c, total of 6H, cp-H), 1.87, 2.61 (m_c, 2H each, in-2-H), 2.65 (m_c, 4H, in-3-H), 6.95, 6.969, 6.974 (m_c, total of 6H, in-H), 7.23 (m_c, 2H, in-H); chemical shift values from C,H-COSY. – ^{13}C NMR ($CDCl_3$): δ = 5.7, 6.3 (both t, cp-C-2,3), 30.8 (t, in-C-3), 31.3 (s, cp-C-1), 34.9 (t, in-C-2), 61.9 (s, in-C-1), 123.9, 125.0, 126.1, 126.3 (all d, in-C-4,5,6,7), 144.5, 145.2 (both s, in-C-3a,7a).

3′,3′,4′,4′-Tetracyano-2″,3″-dihydrodispiro[cyclopropane-1,1′-cyclobutane-2′,1″-1H-indene] (**12**): To 90 mg (0.58 mmol) of **8** in 0.6 ml of $CHCl_3$, 74 mg (0.58 mmol) of tetracyanoethene (TCNE) were added. After 5 min at room temperature the solvent was removed in vacuo and the residue crystallized from 2-propanol: 147 mg (90%) of **12** as colorless crystals with m.p. 165°C. – IR (KBr): $\tilde{\nu}$ = 3095 cm^{-1}, 3028, 2981, 2969, 2940, 2863, 2248, 1479, 1463, 1450, 1439, 1419, 1036, 992, 780, 748. – UV (acetonitrile): λ_{max} (lg ε) = 194 nm (4.57), 214 (4.02, sh), 222 (3.90, sh), 270 (3.17), 276 (3.15). – ^{1}H NMR ($CDCl_3$): δ = 1.14 (m, 1H), 1.24 (m, 1H), 1.34 (m, 1H), 1.53 (m, 1H), 2.34 (m, 1H), 2.97 (m, 1H), 3.12 (m, 2H), 7.33 (m, 1H), 7.38–7.45 (m, 2H), 7.67–7.69 (m, 1H). – ^{13}C NMR ($CDCl_3$): δ = 11.0 (t), 13.7 (t), 29.8 (t), 35.6 (s), 36.9 (t), 42.1 (s), 45.6 (s), 62.3 (s), 109.4 (s), 109.5 (s), 109.7 (s), 110.5 (s), 125.6 (d), 126.3 (d), 127.6 (d), 131.0 (d), 136.8 (s), 144.7 (s). – MS (70 eV): *m/z* (%): 285 (6), 284 (24) [M^+], 157 (14), 156 (100), 155 (43), 153 (15), 152 (14), 141 (93), 129 (15), 128 (61), 116 (16), 115 (51), 77 (10). – $C_{18}H_{12}N_4$ (284.3): calcd. C 76.04, H 4.25, N 19.71; found C 75.83, H 4.28, N 19.74.

3-Cyclopropyl-1H-indene (**13**): A solution of 592 mg (3.79 mmol) of **8** in 100 ml *n*-pentane was passed through a column containing 5 g of neutral aluminium oxide. The solvent was then removed in vacuo affording 570 mg (96%) of colorless oil **13**, the NMR spectra of which were in accord with reported data[11].

[1] W. R. Dolbier, Jr., D. Lomas, T. Garza, C. Harmon, P. Tarrant *Tetrahedron* **1972**, *28*, 3185–3189.

[2] [2a] A. de Meijere, H. Wenck, F. Seyed-Mahdavi, H. G. Viehe, V. Galez, I. Erden *Tetrahedron* **1986**, *42*, 1291–1297. – [2b] T. Liese, S. Teichmann, A. de Meijere *Synthesis* **1988**, 25–32.

[3] [3a] F. Kienzle, J. Stadlwieser *Tetrahedron Lett.* **1991**, *32*, 551–552. – [3b] J. Stadlwieser, F. Kienzle, W. Arnold, K. Gubernator, P. Schönholzer *Helv. Chim. Acta* **1993**, *76*, 178–186.

[4] T. Thiemann, B. Gehrke, A. de Meijere *Synlett* **1993**, 483–485.

[5] J. A. Stafford, J. E. McMurry *Tetrahedron Lett.* **1988**, *29*, 2531–2534.

[6] Functionalized methylenecyclopropanes in [4 + 2] cycloaddition reactions: [6a] F. Zutterman, A. Krief *J. Org. Chem.* **1983**, *48*, 1135–1137. – [6b] L. A. Paquette, G. J. Wells, G. Wickham, *J. Org. Chem.* **1984**, *49*, 3618–3621. – [6c] T. Tsuji, R. Kikuchi, S. Nishida *Bull. Chem. Soc. Jpn.* **1985**, *58*, 1603–1604. – [6d] F. Kienzle, J. Stadlwieser, I. Mergelsberg *Helv. Chim. Acta* **1989**, *72*, 348–352. – [6e] T. Thiemann, S. Kohlstruck, G. Schwär, A. de Meijere *Tetrahedron Lett.* **1991**, *32*, 3483–3486. – [6f] T. Heiner, S. Michalski, K. Gerke, G. Kuchta, M. Buback, A. de Meijere *Synlett* **1995**, 355–357.

[7] W. R. Roth, V. Staemmler, M. Neumann, C. Schmuck *Liebigs Ann.* **1995**, 1061–1118.

[8] J. Mulzer, K. Melzer *Angew. Chem.* **1995**, *107*, 981–984; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 895.

[9] For the formation of **10** a [2 + 2]-dimer might be an intermediate, that could undergo cycloreversion even at moderate temperatures: W. von E. Doering, K. D. Belfield, J. He *J. Am. Chem. Soc.* **1993**, *115*, 5414–5421.

[10] [10a] R. Noyori, N. Hayashi, M. Kato *J. Am. Chem. Soc.* **1971**, *93*, 4948–4950. – [10b] A. de Meijere, I. Erden, W. Weber, D. Kaufmann *J. Org. Chem.* **1988**, *53*, 152–161.

[11] R. A. Caldwell, L. Zhou *J. Am. Chem. Soc.* **1994**, *116*, 2271–2275.

[12] Further details of the crystal structure investigation are available on request from Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-405025 the names of the authors and the journal citation.

[96099]