## Preparation of 2,3-Dialkylcyclohexa-1,3-dienes by the Bis-Wittig Reaction

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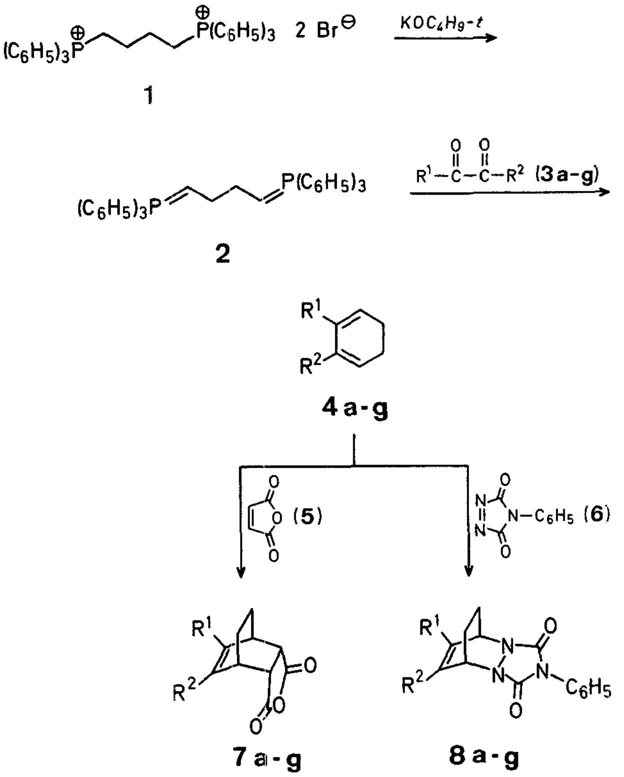
Alkyl-substituted cyclohexa-1,3-dienes are usually prepared by elimination reactions, which often lead to mixtures of isomers[1]. Only few 2,3-dialkylcyclohexa-1,3-dienes are known. The synthesis of 2,3-dimethylcyclohexa-1,3-diene (**4a**) was accomplished by fragmentation of 4-hydroxy-2,3-dimethylcyclohex-2-enecarboxylic acid[2]. Bicyclo[4.4.0]deca-1,5-diene (**4c**)[3] and the monosubstituted 2-phenylcyclohexa-1,3-diene (**4g**)[4] have only been prepared by reactions leading to diene mixtures.

One of the main advantages of the Wittig reaction lies in the fact that the double bond formed does not isomerize under the reaction conditions. Intramolecular Wittig reactions[5] have been successfully applied in the synthesis of 1-, 5-, and 6-substituted cyclohexa-1,3-dienes[6]. We report here a simple and short preparation of cyclohexadienes **4** by a bis-Wittig reaction[7].

Butane-1,4-bis[triphenylphosphonium] bromide (**1**) reacts with potassium *t*-butoxide to give the diphosphorane **2**, which was treated with a number of α-dicarbonyl compounds **3a–g**. The bis-Wittig reaction was best performed in tetraglyme[9], which allows the isolation of the volatile cyclohexadienes **4a–f** by distillation from the reaction mixture. This crude product containing some benzene, *t*-butanol, and tetraglyme is suitable for most purposes without further purification. Extraction with water and redistillation gave the highly oxygen-sensitive cyclohexa-1,3-dienes **4a–g** of 90–95% purity (as determined by G. L. C.), the remainder being the corresponding substituted benzene and oxygen-containing compounds, but none of the isomeric cyclohexadienes.



| | $R^1$ | $R^2$ |
|---|---|---|
| a | $CH_3$ | $CH_3$ |
| b | $CH_3$ | $C_2H_5$ |
| c | $-(CH_2)_4-$ | |
| d | $-(CH_2)_3-$ | |
| e | $-(CH_2)_2-\underset{CH_3}{\underset{\vert}{CH}}-$ | |
| f | $-(CH_2)_2-$ | |
| g | $C_6H_5$ | H |

0039-7881/80/0332-0238 $ 03.00

The yields are fairly low, especially for the strained cyclohexadienes **4d**, **4e**, and **4f**, however, due to the ready availability of the diphosphonium salt **1**[8] and of diketones **3**[10], this preparation still remains attractive. Whereas phenylglyoxal (**3g**) reacts with the diphosphorane **2** to give 2-phenylcyclohexa-1,3-diene (**4g**), aliphatic ketoaldehydes such as methylglyoxal did not yield any diene.

*Cyclohexadienes* **4a–g** *readily undergo Diels-Alder reactions* with maleic anhydride (**5**) and 4-phenyl-4*H*-1,2,4-triazolin-3,5-dione (**6**) to give adducts **7** and **8**, respectively, in high yield.

**Cyclohexa-1,3-dienes 4; General Procedure:**

Butane-1,4-bis[triphenylphosphonium] bromide[8] (**1**; 7.40 g, 10 mmol) and freshly sublimed potassium *t*-butoxide (2.24 g, 20 mmol) are suspended in dry tetraglyme (30 ml; tetraethyleneglycol *dimethyl ether, distilled from lithium aluminium hydride) at 0 °C* under nitrogen. The mixture is stirred at 0 °C for 2 h and the *t*-butanol formed distilled off at 0.02 torr. The α-diketone **3**[10] (10 mmol) dissolved in dry tetraglyme (10 ml) is added from a syringe under nitrogen. After stirring for 30 min at 25 °C, the reaction mixture is heated at 100–120 °C, and all volatile products collected at 12 torr in a cold trap during 3–4 h. Prolonged heating (6 h at 140 °C) is necessary for the formation of *7-methylbicyclo[4.3.0]nona-1,5-diene* (**4e**). The distillate is diluted with pentane, *extracted several times with water to remove t-butanol and traces*

**Table 1.** Cyclohexa-1,3-dienes **4a–g**

| Product | Yield[a] [%] | b.p. [°C][b]/ torr | $^1$H-N.M.R. ($CCl_4$) δ [ppm] | $^{13}$C-N.M.R. ($CDCl_3$) δ [ppm] | U.V. (c-$C_6H_{12}$) $\lambda_{max}$ [nm] (ε) | M.S. (70 eV) m/e (rel. int. %) |
|---|---|---|---|---|---|---|
| **4a**[2] | 26 (30) | 90/120 | 5.47 (bs, 2H, =CH); 1.98 (s, 4H, $CH_2$); 1.73 (bs, 6H, $CH_3$) | 133.7 (s, C-2,3); 122.0 (d, C-1,4); 23.0 (t, C-5,6); 19.7 (q, $CH_3$) | 261 (3330) | 108 (34, $M^+$); 93 (100); 91 (75); 77 (45); 65 (14) |
| **4b** | 14 (15) | 50/12 | 5.50 (bs, 2H, =CH); 2.0 (bs, 6H, $CH_2$); 1.77 (s, 3H, $CH_3$-1″); 1.02 (t, 3H, $CH_3$-2′) | 139.6 (s, C-2); 133.5 (s, C-3); 122.5 (d, C-4); 120.0 (d, C-1); 25.7 (t, C-1′); 22.9 (t, C-5,6); 19.3 (q, C-1″); 13.4 (q, C-2′) | 258 (2760) | 122 (45, $M^+$); 107 (50); 105 (22); 93 (100); 91 (41); 79 (37); 77 (29) |
| **4c** | 22 (25) | 80/12 | 5.39 (bs, 2H, =CH); 2.23 (bs, 4H, $CH_2$); 1.95 (bs, 4H, $CH_2$); 1.54 (m, 4H, $CH_2$-8,9) | 135.5 (s, C-1,6); 120.0 (d, C-2,5); 31.4 (t, C-7,10); 25.0 (t, C-8,9); 22.7 (t, C-3,4) | 263 (2970) | 134 (24, $M^+$); 119 (10); 108 (27); 105 (12); 91 (48); 78 (34); 43 (100) |
| **4d** | 4 (9) | 50/12 | 5.40 (bs, 2H, =CH); 2.2 (m, 8H, $CH_2$); 1.8 (m, 2H, $CH_2$-8) | 140.2 (s, C-1,6); 115.6 (d, C-2,5); 31.3 (t, C-7,9); 25.1 (t, C-8); 23.2 (t, C-3,4) | 267 (3300) | 120 (56, $M^+$); 118 (36); 117 (54); 105 (27); 92 (68); 91 (100); 79 (26) |
| **4e** | 6 (7) | 70/12 | 5.35 (bs, 2H, =CH); 1.7–2.6 (m, 9H, $CH_2$, CH); 1.08 (d, 3H, $CH_3$) | 145.3 (s, C-6); 140.4 (s, C-1); 115.5 (d, C-2); 114.5 (d, C-5); 37.6 (d, C-7); 34.2 (t, C-8); 29.7 (t, C-9); 23.1 and 22.9 (t, C-3,4); 18.2 (q, $CH_3$) | 266 (2940) | 134 (55, $M^+$); 119 (70); 117 (54); 108 (26); 105 (29); 91 (100); 78 (30) |
| **4f** | 3 (16) | 100/100 | 5.20 (bs, 2H, =CH); 2.73 (bs, 4H, $CH_2$-7,8); 2.17 (bs, 4H, $CH_2$-3,4) | 141.4 (s, C-1,6); 112.2 (d, C-2,5); 28.4 (t, C-7,8); 23.0 (t, C-3,4) | 267 (3560) | 106 (47, $M^+$); 105 (37); 104 (27); 103 (25); 91 (100); 89 (22); 78 (63); 59 (96) |
| **4g** | 17 (25) | 130/12 | 7.1 (m, 5$H_{arom}$); 5.9–6.3 (m, 3H, =CH); 2.20 (bs, 4H, $CH_2$) | 140.8 (s, C-1′); 136.0 (s, C-2); 128.4 (d, C-3′); 127.7 (d, C-3); 126.8 (d, C-4′); 125.8 (d, C-4); 125.4 (d, C-2′); 122.8 (d, C-1); 23.0 and 22.0 (t, C-5,6) | 228 (17600)<br>272 sh (3800) | 156 (96, $M^+$); 154 (100); 141 (34); 128 (21); 115 (31); 91 (26); 77 (23) |

[a] Redistilled product. Figures in brackets refer to crude yields determined by $^1$H-N.M.R.

[b] Oven temperature (Kugelrohr).

**Table 2.** *endo*-Bicyclo[2.2.2]oct-2-ene-5,6-carboxylic *Acid Anhydrides* **7a–g**

| Product | Yield [%] | m.p. [°C] | Molecular formula[a] | $^1$H-N.M.R. ($CDCl_3$) δ [ppm] |
|---|---|---|---|---|
| **7a** | 92 | 125–126 | $C_{12}H_{14}O_3$ (206.2) | 3.10 (t, J=1 Hz, 2H, CHCOO); 2.80 (bs, 2H, CH); 1.65 (s, 6H, $CH_3$); 1.4 (m, 4H, $CH_2$) |
| **7b** | 96 | 33–34 | $C_{13}H_{16}O_3$ (220.3) | 2.97 (t, J=1 Hz, 2H, CHCOO); 2.90 (bs, 2H, CH); 2.10 (q, J=7 Hz, 2H, $CH_2C{=}C$); 1.73 (s, 3H, $CH_3C{=}C$); 1.48 (m, 4H, $CH_2$); 0.95 (t, J=7 Hz, 3H, $CH_3$) |
| **7c** | 83 | 124–125 | $C_{14}H_{16}O_3$ (232.3) | 3.15 (t, J=1 Hz, 2H, CHCOO); 2.80 (t, J=1 Hz, 2H, CH); 2.0 (m, 4H, $CH_2C{=}C$); 1.5 (m, 8H, $CH_2$) |
| **7d** | 88 | 121–122 | $C_{13}H_{14}O_3$ (218.3) | 3.30 (bs, 2H, CH); 3.16 (t, J=1.5 Hz, 2H, CHCOO); 2.4 (m, 4H, $CH_2C{=}C$); 1.9 (m, 2H, $CH_2$); 1.48 (m, 4H, $CH_2$) |
| **7e** | 80 | 59–61[b] | $C_{14}H_{16}O_3$ (232.3) | 3.17 (bs, 4H, CH); 2.8–2.0 (m, 3H, $CH_2C{=}CCH$); 1.8–1.1 (m, 6H, $CH_2$); 1.02 (d, J=7 Hz, 3H, $CH_3$) |
| **7f** | 78 | 132–133 | $C_{12}H_{12}O_3$ (204.2) | 3.20 (bs, 2H, CH); 3.12 (s, 2H, CHCOO); 2.78 (s, 4H, $CH_2C{=}C$); 1.5 (m, 4H, $CH_2$) |
| **7g** | 93 | 122–123 | $C_{16}H_{14}O_3$ (254.3) | 7.25 (s, 5H, ArH); 6.45 (d d, J=8 Hz, J=2 Hz, 1H, =CH); 3.70 (bs, 1H, CH); 3.40 (m, 1H, CH); 3.25 (m, 2H, CHCOO); 1.60 (m, 4H, $CH_2$) |

[a] The microanalyses were in satisfactory agreement with the calculated values (C ±0.28, H ±0.19) except for **7c** (C −0.37, H +0.21).

[b] Presumably one isomer only; the configuration of the methyl group is not known.

**Table 3.** 4-Phenyl-2,4,6-triazatricyclo[5.2.2.0$^{2,6}$]undec-8-ene-3,5-diones **8a–g**

| Product | Yield [%] | m.p. [°C] (solvent) | Molecular formula[a] | $^1$H-N.M.R. (CDCl$_3$) δ [ppm] |
|---|---|---|---|---|
| **8a** | 98 | 170–171<br>(ligroin) | $C_{16}H_{17}N_3O_2$<br>(283.3) | 7.40 (s, 5H$_{arom}$); 4.67 (bs, 2H, CHN); 1.8 (m, 4H, CH$_2$); 1.80 (s, 6H, CH$_3$) |
| **8b** | 92 | 130–131<br>(ligroin) | $C_{17}H_{19}N_3O_2$<br>(297.4) | 7.32 (s, 5H$_{arom}$); 4.70 (m, 2H, CHN); 2.18 (q, 2H, $CH_2C{=}C$); 1.83 (s, 3H, $CH_3C{=}C$); 2.4–1.5 (m, 4H, CH$_2$); 1.03 (t, 3H, CH$_3$) |
| **8c** | 95 | 174–175<br>(ligroin) | $C_{18}H_{19}N_3O_2$<br>(309.4) | 7.32 (s, 5H$_{arom}$); 4.63 (bs, 2H, CHN); 2.17 (m, 4H, $CH_2C{=}C$); 2.4–1.5 (m, 8H, CH$_2$) |
| **8d** | 78 | 186–187<br>(CCl$_4$) | $C_{17}H_{17}N_3O_2$<br>(295.3) | 7.30 (s, 5H$_{arom}$); 5.00 (bs, 2H, CHN); 2.50 (t, $J=7$ Hz, 4H, $CH_2C{=}C$); 2.4–1.8 (m, 4H, CH$_2$); 1.8–1.4 (m, 2H, CH$_2$) |
| **8e** | 86 | 137–138<br>(ligroin) | $C_{18}H_{19}N_3O_2$<br>(309.4) | 7.30 (s, 5H$_{arom}$); 4.92 (bs, 2H, CHN); 2.90 (d q, $J=2$ Hz, $J=7$ Hz, 1H, $C\underline{H}CH_3$); 2.8–1.3 (m, 8H, CH$_2$); 1.05 (d, $J=7$ Hz, 3H, CH$_3$) |
| **8f** | 70 | 136–137<br>(CH$_2$Cl$_2$/PE) | $C_{16}H_{15}N_3O_2$<br>(281.3) | 7.35 (s, 5H$_{arom}$); 4.92 (bs, 2H, CHN); 2.90 (s, 4H, $CH_2C{=}C$); 2.5–1.5 (m, 4H, CH$_2$) |
| **8g** | 96 | 55–58<br>(CCl$_4$/PE) | $C_{20}H_{17}N_3O_2$<br>(331.4) | 7.35 (m, 10H$_{arom}$); 6.57 (d d, $J=5$ Hz, $J=2$ Hz, 1H, $=$CH); 5.40 (bs, 1H, CHN); 5.10 (bd, $J=5$ Hz, 1H, CHN); 2.4–1.5 (m, 4H, CH$_2$) |

[a] The microanalyses were in satisfactory agreement with the calculated values (C ±0.32, H ±0.22, N ±0.34).

of tetraglyme, dried, then carefully concentrated, and distilled in a Kugelrohr apparatus at reduced pressure. *2-Phenylcyclohexa-1,3-diene* (**4g**) is isolated by pentane extraction of the reaction mixture. The crude product is chromatographed through silica gel with petroleum ether to remove triphenylphosphine and triphenylphosphine oxide (Table 1).

***endo*-Bicyclo[2.2.2]oct-2-ene-5,6-dicarboxylic Acid Anhydrides 7:** Cyclohexadiene **4** (0.5 mmol) is treated with maleic anhydride (**5**; 0.10 g, 1.0 mmol) in dichloromethane (5 ml) at room temperature. After 4 h, the product (Table 2) is chromatographed through a short column of silica gel with dichloromethane and recrystallized from petroleum ether.

I.R. (CHCl$_3$): $\nu = 1870$ (w); 1840 (w); 1785; 1085; 950; 915; 900 cm$^{-1}$.

**4-Phenyl-2,4,6-triazatricyclo[5.2.2.0$^{2,6}$]undec-8-ene-3,5-diones 8:** Cyclohexadiene **4** (0.5 mmol) is treated with a solution of 4-phenyl-4*H*-1,2,4-triazolin-3,5-dione (**6**; 0.088 g, 0.5 mmol) in dichloromethane (20 ml) until a faint red colour persists. After evaporation in vacuo, the remaining solid is recrystallized from the appropriate solvent (Table 3).

I.R. (CHCl$_3$): $\nu = 1770$ (w); 1710; 1600; 1500; 1410; 1140; 1070; 1020; 870 cm$^{-1}$.

*Support of this work by the "Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung", project no. 2.148.0.78 and the CIBA foundation is gratefully acknowledged.*

Received: October 30, 1979

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