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THE INFLUENCE OF ENDOCYCLIC OXYGEN ATOMS ON THE CYCLOADDITION REACTIVITY OF *TRANS*-CYCLO-OCTENE

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Abstract—(5RS, 7RS)-1, 3-Dioxacyclo-oct-5(E)-ene **1a** proved to be considerably more reactive in [4+2]-, [3+2]-, and [2+2]-cycloadditions than its carbocyclic analogue **1b**.

cis, trans-1, 5-Cyclo-octadiene is considerably more reactive than *trans*-cyclo-octene,[1] although according to force field calculations, *trans*-double bond deformation is only slightly greater than for the latter compound.[2] Therefore, the main reason for the reactivity enhancement has to be seen in a through-space interaction of the *cis* and the *trans* double bonds, as a consequence of an unusually short intramolecular distance.[2]

Recently, (5RS, 7RS)-7-methoxy-1, 3-dioxacyclo-oct-5(E)-ene [(5RS, 7RS)-7-methoxy-7, 8-dihydro-2H, 4H-5(E)-1, 3-dioxocine] **1a** was synthesized in this laboratory.[3] Four of the five single bonds connecting the allylic carbon atoms in **1a** are shortened by the introduction of two endocyclic oxygen atoms (standard single bond lengths are : C–C 1.54Å; C–O 1.43Å[4]).

Through space and through bond distances between the *trans* double bond and the oxygen atoms are maximal, thus minimising resonance or inductive effects.

Cycloadditions of **1a** and its known carbocyclic analogue **1b**[5] were compared, seeking insight into the effect of chain shortening (enhancement of double bond deformation) on the reactivity of trans-cyclo-octene.

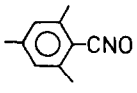
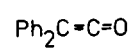
[4+2]-*Cycloadditions*

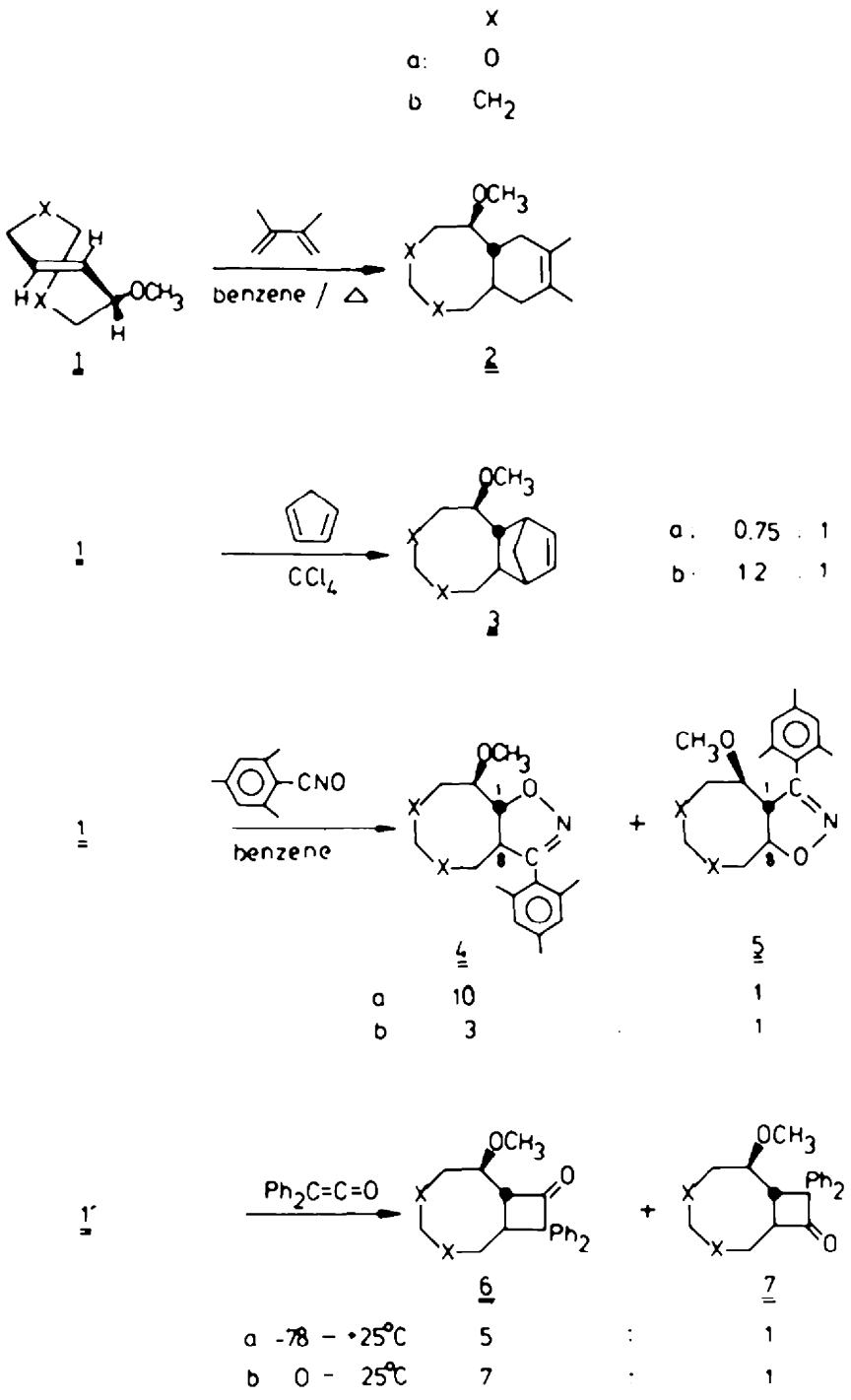
1a reacted with an excess of 2, 3-dimethyl-1, 3-butadiene quantitatively in 12 h at 60°.[3] **1b** did not react in refluxing benzene, but the reaction was successful at 120°. Accordingly, no trace of **2b** could be detected, when an equimolar mixture of **1a** and **1b** was heated one day with a slightly lower molar amount of 2, 3-dimethyl-1, 3-butadiene at 60°, and the reaction product was then analyzed by capillary GLC. The analytical detection limit of less than 0.1% **2b** results in a ratio of the reaction rates $k_a : k_b > 1000$ (Table 1). **1a** as well as **1b** formed the diels-alder adducts **3** with cyclopentadiene at ambient temperature. In both cases a mixture of two diastereomers was obtained (methylene bridge above or below the plane of the bicyclic framework). When the reaction was followed by ^{1}H-NMR, **1a** could be seen to disappear considerably faster than **1b**. When equimolar amounts of **1a** and **1b** competed for a limited amount of cyclopentadiene, no **3b** could be detected by capillary GLC despite the fact that **3b** had been obtained quantitatively under the same conditions with pure **1b**.

[3+2]-*Cycloadditions*

The stable 1, 3-dipole mesitonitrile oxide added to **1a** and **1b** at ambient temperature to give mixtures of regioisomers **4** and **5**. The regioselectivity of **1a** (**4a**:**5a** = 10) was more pronounced than that of the less reactive **1b** (**4b**:**5b** = 3). The regio- and stereochemistry of the adducts **4** and **5** could be established by three ^{1}H-NMR criteria: (a) The resonance of the deshielded bridgehead proton 1-H, is a "dd" in **4**, a "ddd" in **5**. $J_{1,8}$ confirms the *trans*-annelation (12.8 Hz in **4a**, 12.0 Hz in **4b**, 12.0 Hz in **5a**, 13.0 Hz in **5b**). (b) The methyl groups of the mesityl moiety give two singlets in a 2:1 ratio for **4** (magnetic equivalence of the ortho substituents), but

Table 1. Relative reactivity $k_a : k_b$ of **1a** and **1b** determined by competition experiments

enophil	temperature	mode of analysis	$k_a : k_b$
	60°C	glc	> 1000
	25°C	glc	> 300
	25°C	tlc / ^{1}H-nmr	> 100
	-50 - +25°C	tlc / ^{1}H-nmr	> 20



Scheme 1. [4 + 2]-, [3 + 2]- and [2 + 2]-cycloadditions of 1a and 1b

three singlets of equal intensity for 5 (presumably restricted rotation about the carbon-mesityl-single bond (c) The anisotropy of the mesityl group shields the methoxy group of 5 by about 1 ppm.

The adducts 4b and 5b could not be detected by ^{1}H-NMR or TLC in the crude reaction mixture of a competition experiment with 1a and 1b To obtain a better detection limit the main product 4a was separated by TLC. 5a and 4b, having only slightly different R_f-values were collected together. In this fraction small signals of 4b, constituting about 5% of 5a, were observed Thus $k_a : k_b$ is approx. 200. Considering the uncertainty of the analytical method, a ratio greater than 100 is stated in the Table.

[2 + 2]-Cycloadditions

Diphenylketene added to 1a and 1b even under cooling. There is a comparable degree of regioselectivity (5:1 and 7:1, respectively) The assignment of the regiochemical configuration to 6 and 7 is based on the shielding of the methoxy group in 7 and on the complete analysis of a 250 mHz-^{1}H-NMR spectrum of 6a

Competition experiments were performed by mixing the components at −40° or −78°C and smooth cycloaddition while slowly warming up to ambient temperature. The ^{1}H-NMR spectrum of the reaction mixture exhibited very weak signals for **6b** as well as the resonances of **6a** and **7a**. The components were separated by TLC, weighed and their purity checked by ^{1}H-NMR. Weight- and ^{1}H-NMR evaluation of two independent competition experiments gave ratios (**6a** + **7a**):**6b** = 23–34, assigning $k_{-} : k_{+}$ a lower limit of 20 (Table 1).

CONCLUSIONS

In [4 + 2]-, [3 + 2]- and [2 + 2]-cycloadditions, **1a** is considerably more reactive than **1b**. Even under conditions where pure **1b** undergoes clean cycloaddition, the corresponding adducts can only be found in traces or not at all, when **1b** has to compete with **1a**. All possible regioisomers have been observed (and isolated with the exception of **7b**) but no stereoisomer could be detected. Thus the *trans* olefins **1a** and **1b** react in a superfacial manner, giving *trans*-annellated adducts stereospecifically.

EXPERIMENTAL

All m.ps are uncorrected. IR spectra: Perkin–Elmer 397. ^{1}H-NMR spectra: Varian EM 390, 90 mHz, tetramethylsilane (TMS) as an internal standard. Mass spectra (MS): Varian Mat 311A, 70 eV. Analytical GLC: Siemens Sichromat 1 with flame ionisation detector, 90 ml N_2/min as carrier gas, 70 m glass capillary column, inner diameter 0.28 mm, very thinly coated with Carbowax 20 M. Preparative GLC: Varian Aerograph 920 with heat conductivity detector, 110 ml He/min as carrier gas; conditions A: 3 m 3/8 in. aluminium column filled with 17% Carbowax/3% KOH on Chromosorb W-AW 60/80 mesh, 180°, injector 200°, detector 210°, conditions B: 6 m 3/8 in. stainless steel column filled with 20% silicon OV 210 on Chromosorb W-AW DMCS 80/100 mesh, 140°, injector and detector 160°. Analytical TLC: 20 × 20 cm glass plates pre-coated with silica gel 60 F_{254}, layer thickness 0.25 mm (Merck). Preparative LC: 20 × 20 cm glass plates coated with 40 g silica gel 60 $F_{254+366}$ (Merck). The zones containing the individual components were scraped off, pulverized, filled in cylindrical glass columns and the compounds eluted with 100 ml of ethyl acetate. Microanalyses (EA) were performed by I. Radon with the elementaranalysator model 240B (Perkin-Elmer). **1b** was prepared according to the literature procedure[7]. Its purity was checked by capillary-GLC and ^{1}H-NMR.

Cycloadditions with 2, 3-dimethyl-1, 3-butadiene

(a) *With* **1a**. The reaction and isolation of **2a** and its spectra have been described elsewhere[1].

(b) *With* **1b**. The solution of 320 mg **1b** and 240 mg 2, 3-dimethyl-1, 3-butadiene in 1.5 ml benzene-d_6 containing 1 mg of sodium carbonate was refluxed under dry nitrogen for 12 h. No cycloadduct could be detected by capillary GLC and ^{1}H-NMR. 880 mg **1b**, 650 mg 2, 3-dimethyl-1, 3-butadiene, 3 g benzene and 1 mg of sodium carbonate were degassed and sealed under vacuum in a duran-D50 glass ampoule. It was dipped into an oil bath that was held at 120° for 12 h. The ampoule was chilled, opened and the cycloadduct **2b** (765 mg) was isolated by preparative GLC [condition A, t_{ret} (min): **1b** (3.8), **2b** (26.6)].

(1rH, 8tH)-2c-Methoxy-10, 11-dimethyl-bicyclo[6.4.0]dodec-10-ene (**2b**) showed ^{1}H-NMR (CCl_4): δ 3.25 (s, 3H, OCH_3), 2.90 (m, 1H, 2-H), 1.0–2.35 (m, 22H). IR (CCl_4): 2975, 2925, 2820, 1444, 1094 cm^{-1}. MS: *m/e* 222.1986 (M$^+$, calc. for $C_{15}H_{26}O$: 222.1984), 190 (M$^+$–CH_3OH), 120, 119 (base peak), 107, 105.

(c) *Competition*. 288.4 mg (2.0 mmol) **1a**, 281.0 mg (2.0 mmol) **1b**, 90.4 mg (1.1 mmol) 2, 3-dimethyl-1, 3-butadiene and 1 mg Na_2CO_3 in 2 ml C_6D_6 were warmed to 60° for 1d under nitrogen. Analysis was performed at 140° by capillary GLC, t_{ret} (min): **1b** (6.06), **1a** (7.47), **2b** (13.33, not detected), **2a** (20.25).

Cycloadditions with cyclopentadiene

(a) *With* **1a**. 90 mg **1a** and one drop of TMS in a ^{1}H-NMR tube were diluted with the necessary volume of CCl_4. An excess of freshly distilled cyclopentadiene was added and the tube was allowed to stand 12h at ambient temperature. A ^{1}H-NMR spectrum revealed the complete disappearance of **1a**. Capillary GLC (140°) indicated the formation of two cycloadducts **3a** with similar t_{ret}: 15.03 min (43%), 15.63 min (57%), that were purified by preparative GLC (condition B). (1rH, 2cH, 9tH, 10cH)-8t-Methoxy-4, 6-dioxatricyclo[8.2.1.0^{2,9}]tridec-11-ene and (1rH, 2tH, 9cH, 10cH)-8c-Methoxy-4, 6-dioxatricyclo[8.2.1.0^{2,9}]tridec-11-ene (mixture) **3a** showed ^{1}H-NMR (CCl_4): δ 5.80–6.36 (m, 2H, 11-, 12-H), 4.50–4.75 (m, 2H, 5-H), 3.50–4.10 (m, 2H, 3-, 7-H), 3.16–3.46 (m + s, 4H, 8-H and OCH_3), 2.76–3.16 (m, 2H, 3'-, 7'-H), 2.23–2.73 (m, 2H, 1-, 10-H), 1.63–2.15 (m, 1H, 9t-H and 2t-H), 0.73–1.53 (m, 3H, 13-H, 2c- and 9c-H). IR (CCl_4): 3055, 2930, 2876, 2816, 1565 (w), 1452, 1334, 1230, 1158, 1120, 1089, 1033, 1033, 1011, 934, 720 cm^{-1}. MS: *m/e* 210 (M$^+$), 135, 113, 91, 84 (base peak), 83, 69, 66 (Calc/found): C (68.55/68.20), H (8.63/8.52%).

(b) *With* **1b**. The reaction of **1b** with an excess of cyclopentadiene in CCl_4 was incomplete after 12 h at ambient temperature. After 36 hr **1b** had disappeared completely. Capillary GLC (140°) indicated the formation of two cycloadducts **3b** with similar t_{ret}: 10.18 min (54.7%), 10.37 min (45.3%), purified by preparative GLC (condition B). (1rH, 2tH, 9cH, 10cH)-3t-Methoxy-tricyclo[8.2.1.0^{2,9}]tridec-11-ene and (1rH, 2cH, 9tH, 10cH)-3c-Methoxy-tricyclo[8.2.1.0^{2,9}]tridec-11-ene (mixture) **3b** showed ^{1}H-NMR (CCl_4): δ 5.85–6.27 (m, 2H, 11-, 12-H), 3.26 (s, OCH_3, minor isomer), 3.22 (s, OCH_3, main isomer), 2.23–3.03 (m, 3H), 0.7–2.0 (m, 14H). IR (CCl_4): 3052, 2920, 2867, 2845, 2815, 1566 (w), 1458, 1441, 1335, 1196, 1094, 717 cm^{-1}. MS: *m/e* 206 (M$^+$), 174 (M$^+$–CH_3OH), 139, 97, 79, 67, 66 (Calc/found): C (81.50/81.08), H (10.75/10.67%).

(c) *Competition*. 316.10 mg (2.19 mmol) **1a** and 307.33 mg (2.19 mmol) **1b** were mixed with the solution of 132.20 mg (2.0 mmol) cyclopentadiene in 5 ml CCl_4 and allowed to stand at ambient temperature under nitrogen for 24 h. Capillary GLC indicated the exclusive formation of **3a**. **3b** could not be detected even in traces.

Cycloadditions with 2, 4, 6-trimethylbenzonitrile oxide (mesitonitrile oxide, MNO[8])

(a) *With* **1a**. 290 mg (1.8 mmol) MNO was added to the ice-cooled solution of 247 mg (1.7 mmol) **1a** in 10 ml benzene. The solution was shaken and allowed to stand at ambient temperature for 5 h. TLC with eluant benzene–ethylacetate (95:5) gave three spots: MNO (R_f = 0.79), **5a** (0.23), **4a** (0.16). The solution was concentrated to 3 ml *in vacuo* and separated on 10 LC plates by double development with benzene–ethylacetate (90:10). The lower zone had a width of approx. 1.5 cm and contained the main product **4a** (360 mg), the upper zone (0.5 cm broad) contained **4b** (37 mg).

4a was shaken with warm ether, the yellow suspension was cooled and decanted. The colourless solid was recrystallized from chloroform/pentane at −30°. (1rH, 8tH)-11-Mesityl-7t-methoxy-10-aza-3, 5, 9-trioxa-bicyclo[6.3.0]undec-10-ene (**4a**) showed m.p. 100°. ^{1}H-NMR ($CDCl_3$): δ 6.90 (s, 2H, mesityl-H), 4.67 (dd, $J_{1,9}$ = 12.8 Hz, $J_{1,8}$ = 7.5 Hz, 1H, 8-H), 4.65 (AB-system, J_{AB} = 6.1 Hz, 2H, 4-, 4'-H), 3.62 (s, 3H, OCH_3), 3.50–4.25 (m, 6H), 2.26 (s, 3H, p-CH_3), 2.23 (s, 6H, o-CH_3). IR (CCl_4): 2950, 2930, 2882, 1609 (w), 1453, 1170, 1121, 1095, 1033, 936, 868, 850 cm^{-1}. MS: *m/e* 305.16276 (M$^+$, Calc. for $C_{17}H_{23}NO_4$: 305.16269), 246, 244, 200 (base peak), 172, 158, 75, 58 (Calc/found): C (66.86/67.02), H (7.59/7.65), N (4.59/4.62%).

(1rH, 8tH)-9-Mesityl-7, t-methoxy-10-aza-3, 5, 11-trioxa-bicyclo[6.3.0]undec-9-ene (**5a**): m.p. 140° from $CHCl_3$-pentane at −30°. ^{1}H-NMR ($CDCl_3$): δ 6.88 (s, 2H, mesityl-H), 4.59–5.02 (m, 3H, 1-, 4-, 4'-H), 4.10 (dd, $J_{1,8}$ = 12.0 Hz, $J_{1,9}$ = 5.7 Hz, 1H, 8-H), 2.97–4.00 (m, 5H, 2-, 2'-, 6-, 6'-, 7-H), 2.67 (s, 3H, OCH_3), 2.31 (s, 3H, CH_3), 2.27 (s, 3H, CH_3), 2.23 (s, 3H, CH_3). IR (CCl_4): 2923, 2884, 1610 (w), 1453, 1268, 1215, 1169, 1130, 1095, 1030, 996, 942, 896, 870, 851 cm^{-1}. MS: *m/e* = 305 (M$^+$), 274 (M$^+$–OCH_3), 213, 202, 201, 187, 158, 91, 84 (base peak), 69, 58.

(b) *With* **1b** 2.2 g (13.6 mmol) MNO were added to the ice-cooled solution of 2.0 g (14.3 mmol) **1b** in 30 ml benzene. The solution was shaken and allowed to stand at ambient temperature for 15 h. TLC with the eluant benzene–ethylacetate (99:1) gave the following spots unidentified (R_f = 0.53), MNO (0.45), **5b** (0.32), **4b** (0.24). The solvent was removed *in vacuo* and the residue dissolved in petrol. 310 mg of MNO crystallized at −30°. The supernatant solution was decanted ans separated on 20 preparative LC-plates with the eluant benzene–ethyl acetate (99:1). 2.21 g **4b** and 0.70 g **5b** were obtained and recrystallized from chloroform–pentane at −30° and −78°, respectively.

(1rH, 8tH)-11-Mesityl-7t-methoxy-10-aza-9-oxa-bicyclo[6.3.0]undec-10-ene (**4b**), m.p. 104° showed ^{1}H-NMR ($CDCl_3$): δ 6.91 (s, 2H, mesityl-H), 4.63 (dd, $J_{1,8}$ = 12.0 Hz, $J_{1,7}$ = 7.5 Hz, 1H, 8-H), 3.53 (s, 3H, OCH_3), 3.16–3.80 (m, 2H, 1-, 7-H), 2.27 (s, 3H, p-CH_3), 2.22 (s, 6H, o CH_3), 1.06–2.06 (m, 10H). IR (CCl_4): 2922, 2853, 1609, 1460, 1443, 1373, 1198, 1107, 1089, 898, 868, 850 cm^{-1}. MS: *m/e* 301.2044 (M$^+$, Calc for $C_{19}H_{27}NO_2$: 301.2042), 286, 200, 172, 146, 119, 91, 71 (base peak). (Calc/found): C (75.71/75.91), H (9.03/9.02), N (4.65/4.73%).

(1rH, 8tH)-11-Mesityl-2c-methoxy-10-aza-9-oxa-bicyclo[6.3.0]undec-10-ene **5b**, m.p. 111° showed ^{1}H-NMR ($CDCl_3$): δ 6.87 (s, 2H, mesityl-H), 4.36 (ddd, $J_{1,8}$ = 13.0 Hz, $J_{1,9}$ = 9.6 Hz, $J_{1,7}$ = 3.7 Hz, 1H, 8-H), 3.57 (dd, $J_{1,8}$ = 13.0 Hz, $J_{1,7}$ = 9.6 Hz, 1H, 1-H), 3.05–3.35 (m, 1H, 2-H), 2.64 (s, 3H, OCH_3), 2.31 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 2.22 (s, 3H, CH_3), 1.10–2.10 (m, 10H). IR (CCl_4): 2922, 2856, 1609, 1458, 1444, 1378, 1323, 1193, 1107, 1089, 940, 900, 878, 866, 850 cm^{-1}. MS: *m/e* 301.2057 (M$^+$, Calc for $C_{19}H_{27}NO_2$: 301.2042), 286, 189, 188 (base peak), 187, 160, 159, 158, 144, 91, 71 (Calc/found): C (75.71/75.75), H (9.03/9.08), N (4.65/4.58).

(c) *Competition* 483.69 mg (3.00 mmol) MNO were given to the ice-cooled solution of 466.18 mg (3.23 mmol) **1a** and 452.75 mg (3.23 mmol) **1b** in 10 ml benzene. The solution was shaken and allowed to stand 2 days at ambient temperature. TLC indicated the presence of **4a** and **5a**. **4b** and **5b** could not be detected. Volatile components were removed at 60°/10^{-1} torr. The remaining solid (892 mg) was separated on 6 preparative LC-plates with eluant benzene–ethylacetate (92:8). 773 mg **4a** and 91 mg **5a** were obtained. The ^{1}H-NMR spectrum of the minor fraction showed that it contained approx. 5% of **4b** and 95% of **5a**. Thus 859.5 mg of **1a**-adducts and 4.5 mg of **1b**-adduct were obtained.

Cycloadditions with diphenylketene

(a) *With* **1a**. First run: 604.2 mg (4.19 mmol) **1a** were added by syringe to 1.000 g (5.15 mmol) diphenylketene at −78° under nitrogen. The reaction mixture was allowed to warm up slowly to ambient temperature. The viscous yellow oil was dissolved in ethylacetate and methanol was added until the solution became cloudy. At −30° colourless crystals separated and were filtered, washed with methanol and dried in vacuo (832.5 mg). Recrystallization from chloroform–ether at −30° afforded pure **6a**, m.p. 135° (1rH, 8tH)-7t-Methoxy-10, 10-diphenyl-3, 5-dioxa-bicyclo[6.2.0]decan-9-one (**6a**) showed ^{1}H-NMR (C_6D_6/250 mHz): δ 6.83–7.47 (m, 10H), 4.41 (AB-system, $J_{4a,4}$ = 6.3 Hz, 2H, 4-, 4-H), 3.92 (dd, J_{gem} = 11.0 Hz, $J_{6c,6t}$ = 4.5 Hz, 1H, 6c-H), 3.80 (t, $J_{1,8}$ = $J_{7,8}$ = 9.8 Hz, 1H, 8-H), 3.66 (dd, J_{gem} = 11.5 Hz, $J_{2,2c}$ = 4.3 Hz, 1H, 2c-H), 3.43 (dd, J_{gem} = 11.5 Hz, $J_{2,2t}$ = 6.1 Hz, 1H, 2t-H), 3.38 (s, 3H, OCH_3), 3.28 (ddd, $J_{6t,6c}$ = 11.0 Hz, $J_{6t,7}$ = 9.8 Hz, $J_{6t,6t}$ = 4.5 Hz, 1H, 7-H), 3.15 (t, J_{gem} = $J_{6t,6c}$ = 11.0 Hz, 1H, 6t-H), 3.12 (ddd, $J_{1,8}$ = 9.8 Hz, $J_{1,2t}$ = 6.1 Hz, $J_{1,2c}$ = 4.3 Hz, 1H, 1-H). Assignments were controlled by double resonance experiments. IR (CCl_4): 3080, 3055, 3022, 2930, 2880, 2825, 1776, 1598, 1492, 1444, 1155, 1115, 1084, 1067, 1026, 700 cm^{-1}. MS: *m/e* = 388 (w, M$^+$), 308 (w), 205, 193 (base peak), 192, 191, 165, 115, 103, 91, 85 (Calc/found): C (74.53/74.48), H (6.55/6.58%).

Second run: 485.7 mg (2.50 mmol) diphenylketene were cooled at −45° under nitrogen. The solution of 375.1 mg (2.6 mmol) **1a** in 500 μl benzene was added dropwise. The cooling bath was removed and the solid reaction mixture allowed to thaw. The deep yellow solution became pale when standing overnight at ambient temperature. Volatile components were removed at less than 100° bath temperature at 0.001 torr. The residue was dissolved in chloroform and analyzed by TLC (benzene–ethylacetate 92:8). R_f **6a** 0.18, **7a** 0.26). Preparative separation was performed on 6 LC-plates with the same eluant. 448 mg of **6a** and 69 mg of **7a** were obtained. **7a** was recrystallized twice from chloroform–ether at −30°.

(1rH, 8tH)-7t-Methoxy-9, 9-diphenyl-3, 5-dioxa-bicyclo[6.2.0]decan-10-one (**7a**) showed m.p. 155°. ^{1}H-NMR ($CDCl_3$): δ 7.00–7.75 (m, 10H), 4.70 (AB-system, $J_{4a,4}$ = 6.6 Hz, 2H, 4-, 4-H), 3.17–4.10 (m, 6H), 3.24 (s, 3H, OCH_3), 2.95 (ddd, $J_{1,8}$ = 10.0 Hz, $J_{1,2c}$ = 6.6 Hz, $J_{1,2t}$ = 4.1 Hz, 1H, 1-H). IR (CCl_4): 3060, 3022, 2938, 2884, 2824, 1777, 1600, 1494, 1447, 1236, 1153, 1111, 1082, 1030, 941, 703 cm^{-1}. MS: *m/e* 338.1501 (w, M$^+$). Calc for $C_{21}H_{22}O_4$: 338.1518), 293, 223.1118 (base peak, CH_3O^+=CH-CH=C(Ph)$_2$). Calc for $C_{16}H_{15}O$: 223.1123), 205, 191, 165, 91, 55 (Calc/found): C (74.53/74.46), H (6.55/6.58%).

(b) *With* **1b**. First run: 3.1 g (16 mmol) diphenylketene were cooled (−45°). 1.2 g (8.6 mmol) **1b** were added under dry nitrogen. The inner temperature rose quickly to +30°. After the exothermic reaction had ceased, the mixture was warmed to 60° for 1 h. A ^{1}H-NMR spectrum of the resulting viscous orange oil showed two methoxy singulets corresponding to the cycloadducts **6b** and **7b** in a ratio of 4.5:1. The excess diphenylketene was removed with short path distillation at 10^{-1} torr (70–120° bath temperature). 1.23 g of **6b** crystallized from an ether–pentane solution of the residue at −30°. After three additional recrystallizations from methanol it melted at 96°.

(1rH, 8tH)-2c-Methoxy-9, 9-diphenyl-bicyclo[6.2.0]decan-10-one (**6b**) showed ^{1}H-NMR ($CDCl_3$): δ 6.90–7.47 (m, 10H), 3.42 (s, 3H, OCH_3), 3.30–3.70 (m, 2H, 1-, 2-H), 2.87 (td, $J_{1,8}$ = $J_{2c,8}$ = 11.1 Hz, $J_{2c,1}$ = 3.6 Hz, 1H, 8-H), 0.80–2.24 (m, 10H). IR (CCl_4): 3082, 3060, 3030, 2980 (sh), 2933, 2857, 2828, 1777, 1601, 1496, 1462, 1448, 1108, 1090, 1023 (sh), 718 (sh), 704 cm^{-1}. MS: *m/e* 334 (M$^+$), 302 (M$^+$–CH_3OH), 274 (base peak, M$^+$–CH_3OH–CO), 217, 205, 193, 180, 167, 165, 115, 91, 85 (Calc/found): C (82.60/82.86), H (7.84/7.89%).

Second run: 3.48 g (18 mmol) diphenylketene were added to a solution of 1.26 g (9 mmol) **1b** in 10 ml benzene, cooled in ice. The solution was allowed to stand 12 h at ambient temperature. The solvent was removed in vacuo and the residue was analyzed by ^{1}H-NMR (**6b**:**7b** = 7:1) and by TLC (benzene–ethylacetate 92:8, R_f **6b** 0.48, **7b** 0.75). Preparative separation was performed on 10 LC plates with the same eluant. 2.294 g **6b** and 0.3071 g of crude **7b** (25% aromatic impurity) were obtained. Several recrystallizations of the latter fraction from methanol did not afford pure **7b**.

(1rH, 8tH)-2c-Methoxy-10, 10-diphenyl-bicyclo[6.2.0]decan-9-one (**7b**) showed ^{1}H-NMR (CCl_4): δ 6.80–7.68 (m, 10H), 3.02 (s, 3H, OCH_3), 2.65–3.27 (m, 3H, 1-, 2-, 8-H), 0.80–2.07 (m, 10H).

(c) *Competition*. First run. The solution of 422.67 mg (2.93 mmol) **1a** and 415.57 mg (2.96 mmol) **1b** in 500 μl benzene was dropped within 5 min to 489.60 mg (2.52 mmol) of diphenylketene, cooled to −40°. The cooling bath was removed and the solid reaction mixture allowed to thaw and to stand at ambient temperature (12 h). Volatile components, containing **1b** and **1a** in the ratio 2:1 (^{1}H-NMR) were removed at 10^{-1} torr (< 60° bath temperature). The residue was separated on 6 LC plates (benzene–ethylacetate 92:8). 448.5 mg **6a**, 90.7 mg **7a**, and 23.1 mg **6b** were obtained.

Second run. The solution of 422.67 mg (2.93 mmol) **1a** and 415.57 mg (2.96 mmol) **1b** in 5 ml of *n*-pentane was cooled to −78° under nitrogen. 489.60 mg (2.52 mmol) diphenylketene was added dropwise. The mixture was allowed to stand 12 h at ambient temperature. Work-up as above afforded 330.2 mg **6a**, 64.4 mg **7a**, and 11.5 mg **6b**.

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