Tetrahedron Vol. 45, No. 10, pp. 2887 to 2894, 1989
Printed in Great Britain.

0040-4020/89 $3.00+.00

5-ALKYLIDENE-HEXAHYDRO-1*H*-CYCLOPENTA[*c*]PYRROL-1,3-DIONES BY NICKEL(0) OR PALLADIUM(0) CATALYZED [3+2] CYCLOADDITION OF METHYLENECYCLOPROPANES WITH MALEIMIDES

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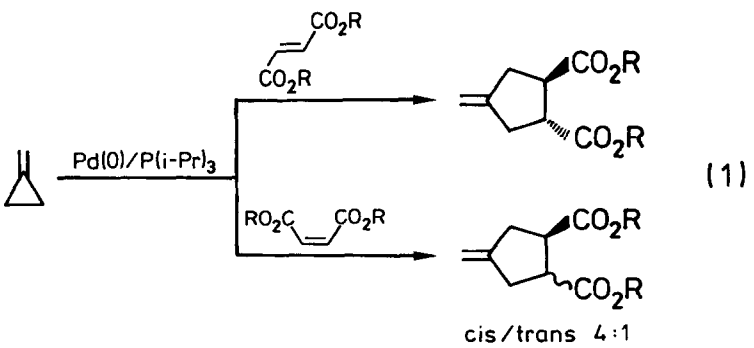
(*Received in Belgium* 27 *July* 1988)

Abstract - Nickel(0) catalyzed [3+2] cycloaddition of methylenecyclopropanes **1a - e** with N-substituted maleimide **3b** (R = CH_3) and **3c** (R = Ph) leads almost exclusively to the title compounds **6** and **7**. The same reaction occurs in the presence of a palladium(0) catalyst with lower selectivity. Neither unsubstituted maleimide (**3a**) nor maleic anhydride (**2a**) undergo this metal catalyzed cycloaddition. With isopropylidenecyclopropane (**1b**) an ene reaction takes place giving the codimers **4a,b**, whereas (diphenylmethylene)cyclopropane (**1c**) reacts in a Diels-Alder reaction with two equivalents of **2a**, affording the cotrimer **5**.

INTRODUCTION

Trimethylenemethane and its derivatives are excellent synthons for preparing a wide range of methylenecyclopentanes directly by [3+2] cycloaddition with suitable alkenes. Some of them are interesting building blocks for the synthesis of cyclopentanoid natural products[1]. Of the various precursors for trimethylenemethanes, methylenecyclopropane and its derivatives have attracted special attention because of their availability and versatile applications[1a]. Specially interesting is their ability to react chemoselectively either by proximal or distal opening of the three-membered ring; the course of the reactions depends on the metal catalyst and the substitution pattern of the methylenecyclopropane[1b].



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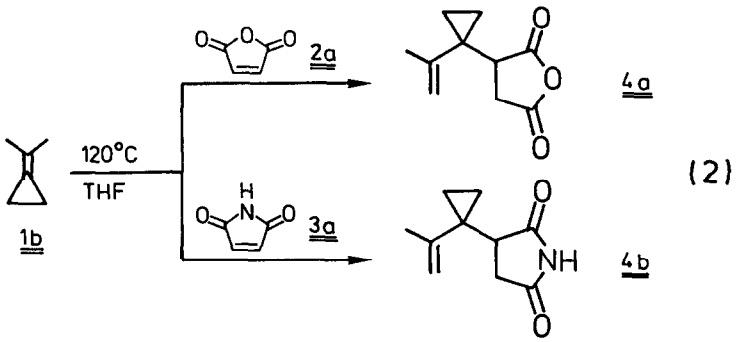
One unsolved problem is the stereoselective cis [3+2] cycloaddition of methylenecyclopropanes with electron deficient olefins. Whereas e. g. dialkylfumarates react in the presence of Ni(0) or Pd(0) catalyst with all kinds of methylenecyclopropanes to give 4-methylenecyclopentane-trans-1,2-dialkylcarboxylates, the corresponding reaction with dialkylmaleates always is accompanied by partial isomerization[2]. The best

studied example is the Pd(0) catalyzed cycloaddition of methylenecyclopropane **1a** and dimethylmaleate, which under suitable conditions yields a 4:1 cis/trans mixture of 4-methylenecyclopentane-1,2-dimethylcarboxylate. After ozonolysis, the pure cis-4-cyclopentanone derivative can be obtained in 50 % yield by simple crystallization[3].

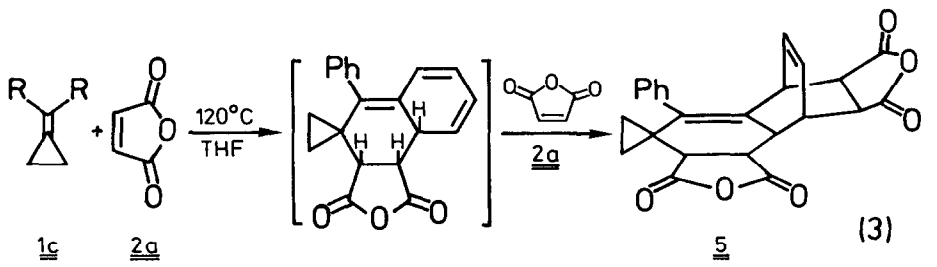
Surprisingly, no attempts to codimerize maleic anhydride with **1a** have been successful. One result of these earlier studies was that the combination of $Ni(COD)_2$ with maleic anhydride has been found to be one of the most effective catalyst for the cyclodimerization of **1a**[4]. On the other hand substituted methylenecyclopropanes like isopropylidenecyclopropane (**1b**) or (diphenylmethylene)cyclopropane (**1c**) are unable to cyclodimerize under the influence of a Ni(0) or Pd(0) catalyst, though they are slightly more reactive in the catalyzed codimerization with electron deficient olefins. Therefore we undertook an new study of their reactivity towards maleic anhydride (**2a**) and some maleimides (**3a - c**).

RESULTS

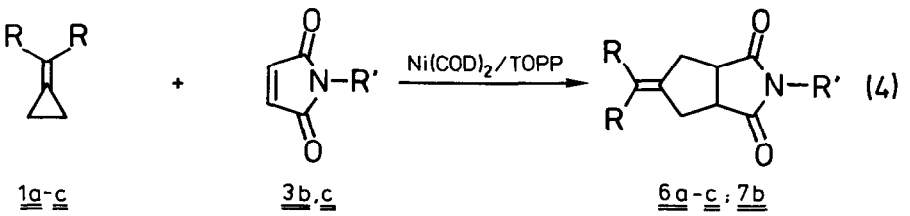
Prolonged heating of a 1:1 mixture of **1b** and **2a** to 120°C give raise to an ene reaction which leads to the codimer **4a** in 53 % yield; This ocurrs irrespective of whether a Ni(0) or Pd(0) compound is present or not. Maleimide **3a** reacts in the same manner giving **4b** in 94 % yield. The reaction conditions are quite moderate in comparison to known examples of ene reactions between alkenes and **2a**, which require temperatures of ca. 200°C[5]. No indication of a metal catalyzed cycloaddition between **1b** and **2a** or **3a** has ever been observed.



Similarly with (diphenylmethylene)cyclopropane (**1c**) and **2a** or **3a** no metal catalyzed reaction occurs. At 120°C only a thermally induced Diels-Alder reaction takes place. With two equivalents of the dienophile **2a** the cycloadduct **5** is obtained in 76 % yield. **5** must be formed by a reaction sequence involving two [4+2] cycloadditions. First **1c** and **2a** react to form an intermediate which is not isolated, and this in turn reacts with more **2a** to yield the final product **5**. Diels-Alder reactions of Arylethylenes were first discovered in 1931[6a] and have since been thoroughly explored[6b,c].



In the view of these results, it was surprising to discover that the N-substituted maleimides **3b** (R = CH_3) and **3c** (R = Ph) undergo the metal(0) catalyzed [3+2] cycloaddition with various methylenecyclopropanes, giving the desired 5-alkylidene-hexahydro-1*H*-cyclopenta[*c*]pyrrol-1,3-diones **6** and **7**, respectively (Table 1). In the presence of the Ni(0) catalyst $Ni(COD)_2$/TOPP (TOPP = tris(*o*-phenylphenyl)phosphite; molar ratio Ni:P = 1:1 - 1:4) isopropylidenecyclopropane (**1b**), (diphenylmethylene)cyclopropane (**1c**) and 1-methylene-2-phenylcyclopropane (**1d**) codimerize with the maleimides **3b** and **3c** regio- and stereospecifically to give **6b - d** and **7b** in 82 - 93 % yields. At 120°C the reactions are completed after 2 - 14 h, depending on the Ni:P ratio of the catalyst. Raising the Ni:P ratio prolongs the reaction time without having any influence on the regio- or stereoselectivity of the reaction (see entry 2 and 3 Table 1). Most of the codimerizations were performed in THF since this is a better solvent for **3b - c**. However, as shown in entry 5 (Table 1), toluene can also be used as solvent.



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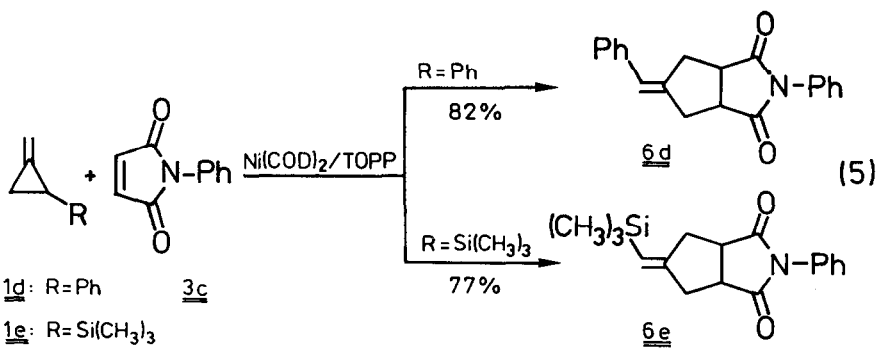

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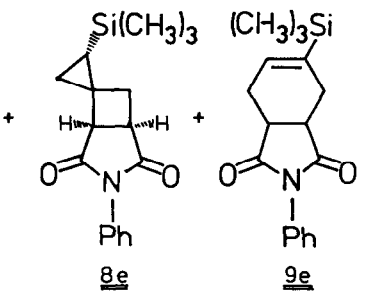
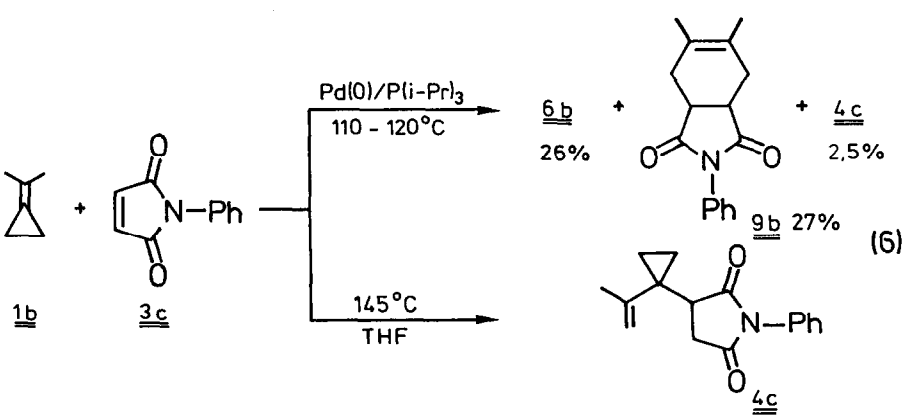


Table 1: *Ni(0) or Pd(0) catalyzed cyclodimerization of methylenecyclopropanes* **1a - e** *with maleimides* **3b, 3c**

entry	methylene-cyclopropane **1**	maleimide **3**	catalyst M(0)/ PR_3	ratio M:P	solvent	reaction conditions [h]	[°C]	codimers **6/7**	yield [%] isol.	(GC)
1	**1a**	**3c**	$Ni(COD)_2$/ TOPP[a]	1:1	THF	20	70	**6a**	7	(12)
2	**1b**	**3c**	"	1:1.5	"	5	120	**6b**	67	(90)
3	**1b**	**3c**	"	1:4	"	14	120	**6b**	84	–[c]
4	**1b**	**3b**	"	1:4.5	"	10	120	**7b**	87	(93)
5	**1c**	**3c**	"	1:2	toluene	2	120	**6c**	83	–[c]
6	**1d**	**3c**	"	1:1	THF	8	110	**6d**	23	(82)
7	**1e**	**3c**	"	1:1	"	8	120	**6e**	20	(44)[d]
8	**1b**	**3c**	Pd(0)/ $P(i\text{-}Pr)_3$ [b]	1:1	"	22	110	**6b**	–[c]	(27)[e]
9	**1c**	**3c**	"	1:1	"	5	120	**6c**	56	(67)

a) $Ni(COD)_2$ and TOPP are used in the given ratio. - b) The Pd(0)-catalyst is produced in situ from (η^3-allyl)(η^5-cyclopentadienyl)palladium. - c) Not determined. - d) The isomers **8** (9 %) and **9e** (16 %) as well as an unidentified codimer (8 %) are also formed; total yield (incl. **6e**): 77 %. - e) Further codimers: **9b** (27%), **4c** (2 %) and two unidentified codimers (Σ 6 %); total yield (incl. **6b**): 62 %.

When methylenecyclopropane (**1a**) or 1-methylene-2-(trimethylsilyl)cyclopropane (**1e**) are introduced into these Ni(0) catalyzed codimerizations, considerable lower yields of the cycloadduct, e. g. **6a** or **6e**, are observed. With **1a** the educts oligomerize mainly to undefined products, whereas with **1e** in addition to the [3+2] cycloadduct **6e** three isomeric compounds were obtained. Two of them could be isolated and identified as the [2+2] cycloadduct **8e** (9 %) and the [4+2] cycloadduct **9e** (16 %). The first originates from a nickelacyclopentane derivative generated by oxidative coupling of the two alkenes at the Ni(0) catalyst followed by reductive elimination[1b,7], whereas if the latter is formed by Diels-Alder reaction, then a Ni(0) catalyzed isomerization of **1e** to the 2-trimethylsilyl-1,3-butadiene has to be formulated[8].



Instead of the $Ni(COD)_2$/TOPP catalyst, trialkylphosphane modified Pd(0) catalysts [e. g. triisopropyl-

phosphane/(η^3allyl)(η^5cyclopentadienyl)palladium[2a)]] can be used for these codimerizations. However these catalysts are less effective and the selectivity of the product formation is considerably reduced (entry 8,9 Table 1). Thus the Pd(0) catalyzed reaction between **1b** and **3c** gives the [3+2] cycloadduct **6b** and the Diels-Alder product **9b** in equal amounts. The formation of **9b** incorporates the Pd(0) catalyzed isomerization of **1b** into 2,3-dimethylbutadiene[9]. Three further codimers were obtained, including **4c** (2.5 %). This is the product of an ene reaction. An additional experiment showed that the thermally induced ene reaction between **1b** and **3c** can take place at temperatures above 110°C; e. g. after heating **1b** and **3c** to 145°C for 44 h **4c** could be isolated in 90 % yield.

The easy formation of the hexahydro-1*H*-cyclopenta[*c*]pyrrol-1,3-diones by this method prompted us to examine possible derivatizations of the codimers **6b** and **7b**. Especially in the view of their potential as building blocks in organic synthesis, it is particularly important to be able to oxidize the isopropylidene group or to reduce the imide function. It was found that **6b** and **7b** can be easily converted by ozonolysis into the corresponding ketone derivatives in good yields (62 - 78 %). The reduction of **6b** is more complicated and leads to different products depending on the reducing reagent and the reaction conditions. With lithium alanat both carbonyl groups can be easily removed to give the saturated bicyclus (e. g. from **6b** crude yield: 98 %). The use of less active hydride reagents allows a stepwise reduction either to the hydroxylactam or lactam itself[10].

Structural related compounds containing a saturated 1*H*-cyclopenta[*c*]pyrrole skeleton are of interest with regard to their pharmacological activity[11]. 1*H*-Cyclopenta[*c*]pyrrole derivatives are usually prepared by reaction of amines or ammonia with 1,2-carboxylic acids or anhydrides[14]. Other approaches include the 1,3-dipolar cycloadditon of azomethine ylids with cycloalkenes[12] and atom transfer cyclization of alk-3-yne iodide with maleimides[13]. The metal catalyzed [3+2] cycloaddition of methylencyclopropanes with maleimides described in this paper provides an new approach to compounds of this class, particularly because it makes possible the preparation of 1*H*-cyclopenta[*c*]pyrroles with previously unknown substitution pattern.

EXPERIMENTAL SECTION

All reactions were performed under an argon atmosphere. - MS[15]: Varian CH-5 at 70 eV. - IR[16]: Nicolet FT 7199. - ^{1}H-NMR[17]: Bruker AM 200 FT at 200 MHz (internal standard: TMS). - ^{13}C-NMR[18]: Bruker AM 200 (50.3 MHz) and Bruker WM 300 FT (75.4 MHz); internal standard: TMS. - Analytical GC[19]: Becker Packard 417, SE-54; 60 - 280°C; 8°C/min; 1.2 bar He. - Preparative GC[20]: AMPG-60 (Gerstel, Mülheim a. d. Ruhr); detailed conditions see experiments. - Elementary analysis: Dornis + Kolbe, Mülheim a. d. Ruhr. - Commercial chemicals were distilled or recrystallized and stored under argon before using in catalysis: maleic anhydride, maleimide, N-methylmaleimide, N-phenylmaleimide (Fluka), triisopropylphosphane (Ventron). - Prepared by literature procedures: methylenecyclopropane (**1a**)[21], alkylidenecyclopropanes (**1b**,**1c**)[22], 1-methylene-2-phenylcyclopropane (**1d**)[23], 1-methylene-2-(trimethylsilyl)cyclopropane (**1e**)[24], (η^3-allyl)(η^5-cyclopentadienyl)palladium[25], bis(η^4-cycloocta-1,5-diene)nickel[26], tris(o-phenylphenyl)phosphite[27].

Reactions of Maleic anhydride (2a)

(a) Ene reaction with **1b**:
3-(1-Isopropenylcyclopropan-1-yl)tetrahydrofuran-2,5-dione **3a**: 1.85 g (18.9 mmol) **2a** and 3.28 g (39.9 mmol) **1b** in 30 ml THF are heated in an autoclave at 120°C for 24 h. After cooling the solvent is distilled of and recrystallization of the oily residue from ether/pentane gave 1.82 g (54 %) of **4a** as colorless needles, mp. 37°C. - MS: *m/z (%)* = 180 (17, M^+), 152 (5), 136 (26), 108 (22), 93 (100). -IR (neat): ν = 1864 (m), 1788 (s), 1642 (s) cm^{-1}. - ^{1}H-NMR ($CDCl_3$): δ = 0.42 - 0.72 (m, 4H, cyclopropane), 1.57 (s br., 3H, CH_3), 2.63 (m, 3H, pyrrole), 4.72 (m, 1H, C=CH_2), 4.82 (m, 1H, C=CH_2). - ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 10.69, 11.48 (t, cyclopropane), 20.96 (q, CH_3), 27.66 (s, cyclopropane), 33.19 (t, C-4), 46.07 (d, C-3), 116.28 (t, C=CH_2), 143.90 (s, C=CH_2), 170.13, 171.93 (s, C-2, C-5).

(b) Twofold Diels-Alder reaction with **1c**:
2.48 g (25.3 mmol) **2a** and 2.40 g (11.6 mmol) **1c** in 40 ml THF react under the same conditions as above. Concentration and recrystallization from acetone yield 3.52 g (76 %) of **5** as a white solid, mp. 315°C (dec.). - MS: *m/z (%)* = 402 (4, M^+), 374 (5), 358 (16), 330 (12), 231 (100). - IR (KBr): ν = 1859 (m), 1781 (s) cm^{-1}. - Raman: ν = 1656 cm^{-1}. - ^{1}H-NMR ([D_6]DMSO): δ = 0.39 (m, 1H), 0.50 (m, 1H), 0.94 (m, 2H), 3.02 (dd, J = 9.2 Hz, J' = 0.6 Hz, 1H), 3.06 (d, J = 9.4 Hz, 1H), 3.55 (m, 2H), 3.67 (m, 2H), 3.89 (dd, J = 9.4 Hz, J' = 9.2 Hz, 1H) 6.04 (m, J = 8.1 Hz, J' = 5.9 Hz), 6.16 (m, J = 8.1 Hz, J' = 6.3 Hz, 1H), 7.10 (m, 2H), 7.40 (m, 3H). - ^{13}C-NMR (50 MHz, [D_6]DMSO): δ = 10.60 (t), 22.60 (s), 35.77 (d), 37.22 (d), 40.50 (d), 44.72 (d), 45.19 (d), 46.05 (d), 50.81 (d), 127.41 (d), 128.28 (d), 128.73 (d), 130.7 (d), 132.90 (d), 135.49 (s), 135.70 (s), 135.86 (s), 172.37 (s), 172.52 (s), 172.73 (s), 173.91 (s). - Anal. Calcd. for $C_{24}H_{18}O_4$: C, 71.64; H, 4.51; Found: C, 71.48; H, 4.45.

Reactions of Maleimides

(a) Ene reaction of **3a** with **1b**:
Ene reaction of maleimide (**3a**) with **1b** was performed in a similar way as above yielding the corresponding vinylcyclopropane derivative:
3-(1-Isopropenylcyclopropan-1-yl)tetrahydropyrrol-2,5-dione **4b**: (67 %); white crystalline solid, mp. 113°C (recrystallized from ether). - MS: *m/z (%)* = 179 (58, M^+), 108 (12), 93 (100). - IR (KBr): ν = 3220 (s), 1785 (m), 1710 (s), 1645 (m) cm^{-1}. - ^{1}H-NMR ([D$_6$]DMSO): δ = 0.55 - 0.94 (m, 4H, cyclopropane), 1.73 (s, 3H, CH_3), 2.46 (m, 1H, pyrrole), 2.84 (m, 2H, pyrrole), 4.88 (m, 1H, C=CH_2), 4.95 (m, 1H, C=CH_2), 11.14 (s br., 1H, N-H). - ^{13}C-NMR (50 MHz,$CDCl_3$): δ = 10.26, 10.57 (t, cyclopropane), 21.03 (q, CH_3), 27.36 (s, cyclopropane), 34.65 (t, C-4), 45.50 (d, C-3), 114.19 (t, C=CH_2), 145.44 (s, C=CH_2), 177.89, 179.57 (s, C-2,C-5). - Anal. Calcd. for $C_{10}H_{13}O_2$: C, 67.02; H, 7.31; N, 7.82; Found: C, 66.86; H, 7.53; N, 7.77.

(b) Ene reaction of N-phenylmaleimide (**3c**) with **1b**:
3-(1-Isopropenylcyclopropan-1-yl)-1-phenyltetrahydropyrrol-2,5-dione **4c**: After 20 h at 115°C and 44 h additional heating at 145°C **4c** was obtained in 90 % yield; white solid, mp. 138 - 139°C (recrystallized from ether/dichlormethane 5:1). - MS: *m/z (%)* = 255 (56, M^+), 136 (15), 108 (30), 93 (100). - IR (KBr): ν = 1708 (s), 1642 (w) cm^{-1}. - ^{1}H-NMR ($CDCl_3$): δ = 0.64 - 0.96 (m, 4H, cyclopropane), 1.78 (s, 3H, CH_3), 2.71-2.96 (m, 3H, pyrrole), 4.93 (m, 1H, C=CH_2), 5.00 (m, 1H, C=CH_2), 7.27 (m, 2H, *o*-H, Ph), 7.31-7.51 (m, 3H, p+m-H, Ph). - ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 10.57, 11.16 (t, cyclopropane), 21.32 (q, CH_3), 28.14 (s, cyclopropane), 33.69 (t, C-4), 44.88 (d, C-3), 113.45 (t, C=CH_2), 126.35 (d, *o*-C, Ph), 128.49 (d, *p*-C, Ph), 129.09 (d, *m*-C, Ph), 132.00 (s, Ph), 144.72 (s, C=CH_2), 175.45, 176.86 (s, C-2, C-5). Anal. Calcd. for $C_{16}H_{17}NO_2$: C, 75.27; H, 6.71; N, 5.49; Found: C, 75.14 ; H, 6.75; N, 5.42.

(c) [3+2] Cycloadditions of maleimides (**3b, 3c**) with methylenecyclopropanes

General procedure: To approximately 2-3 mol% $Ni(COD)_2$/TOPP or 7 mol% (η^3-allyl)(η^5cyclopentadienyl)palladium/phosphane in 20 ml THF was added about 15-45 mmol of the maleimide at room temperature. The resulting solution was filled in an autoclave followed by the addition of methylenecyclopropane in a slight excess. Because of the low boiling point of **1a**, in this case it is necessary to cool the autoclave. After heating at almost 120°C, the end of reaction was determined by monitoring GC. The reaction mixture was chromatographed (CH_2Cl_2 on Florisil®) at once to separate the catalyst. Concentration and crystallization gave the products as crystalline solids. The detailed results are summarized in Table 2.

Table 2: *Ni(0) or Pd(0) catalyzed cyclodimerization of methylenecyclopropanes* **1a - e** *with maleimides* **3b, 3c**; *experimental data*

entry	methylene-cyclopropane **1** [g/mmol]	maleimide **3** [g/mmol]	catalyst [mol%] (M:P)	crude residue [g]	composition (% GC) codimer **6/7**	rest
1	**1a** 3.00 (55.46)	**3c** 4.24 (24.48)	A[a] 2.7 (1:1)	2.33[c]	**6a** 28.7	19 peaks (>1%) Σ 54.2%
2	**1b** 1.38 (16.80)	**3c** 2.91 (16.80)	A 8.9 (1:1.5)	4.10	**6b** 94.3	1 peak (>1%) 1.5%
3	**1b** 2.07 (25.26)	**3c** 3.15 (17.83)	A 3.3 (1:4)	5.62	**6b** 87.1	3 peaks (>1%) Σ 5%
4	**1b** 3.74 (45.59)	**3b** 4.91 (44.19)	A 0.5 (1:4.5)	8.07	**7b** 98.2	–
5	**1c** 2.90 (14.06)	**3c** 2.55 (14.55)	A 2.6 (1:2)	–	**6c** 88.1	4 peaks (>1%) Σ 9.6%
6	**1d** 2.60 (20.00)	**3c** 2.47 (14.30)	A 4.3 (1:1)	5.33	**6d** 66.6	8 peaks (>1%) Σ 20%
7	**1e** 2.89 (22.90)	**3c** 2.28 (13.20)	A 3.9 (1:1)	3.90	**6e** 44.7	**9e** 16.8%, **8** 9.6%, 7.7% [mol. mass 299], 6 peaks(>1%) Σ 14%
8	**1b** 3.30 (40.17)	**3c** 6.02 (34.76)	B[b] 7.0 (1:1)	6.35[d]	**6b** 37.5	**9b** 38%, **4c** 4.9%, 2.1% [mol. mass 255], 3.2% [257], 5 peaks (>1%) Σ 6.5%
9	**1c** 2.84[e] (13.80)	**3c** 2.40 (13.90)	B 7.5 (1:1)	4.71	**6c** 75.0	14.7% **1c**, 3 peaks(>1%) Σ 3.4%

a) A = $Ni(COD)_2$/TOPP. - b) B = Pd(0)/P(i-Pr)$_3$. - c) Obtained by distillation. - d) Weight too high. - e) Conversion of **1a**: 76 %.

Characterization of [3+2]-cycloaddition products

1) with methylenecyclopropane (**1a**):
Hexahydro-5-methylene-2-phenyl-1H-cyclopenta[c]pyrrol-1,3-dione **6a**: 0.36 g (7 %) of a white solid, mp. 94-95°C (recrystallization from ether/dichlormethan 2:1). - MS: *m/z (%)* = 227 (41, M^+), 80 (100), 79 (45). - IR (KBr): 1705 (s) cm^{-1}. - ^{1}H-NMR ($CDCl_3$): δ = 2.77 (m, 4H, 4-H, 6-H), 3.39 (m, 2H, 3a-H, 6a-H), 4.98 (m, 2H, C=CH_2), 7.25 (m, 2H, *o*-H, Ph), 7.4 (m, 3H, *m*+*p*-H, Ph). - Anal. Calcd. for $C_{14}H_{13}NO_2$: C, 73.99; H, 5.77; N, 6.16; Found: C, 72.52; H, 5.76; N, 5.79.

2) with isopropylidenecyclopropane (**1b**):
Hexahydro-5-isopropylidene-2-phenyl-1H-cyclopenta[c]pyrrol-1,3-dione **6b**: 2.85 g (entry 2: 67 %) resp. 3.82 g (entry 3: 84 %) of a white solid, mp. 101°C (recrystallization from ether). - MS: *m/z (%)* = 255 (100, M^+), 174 (10), 108 (43), 107 (66). - IR (KBr): ν = 1710 (s) cm^{-1}. - ^{1}H-NMR ($CDCl_3$): δ = 1.66 (s br., 6H, CH_3), 2.73 (m, 2H, 4-H, 6-H), 2.85 (m, J_{gem} = -16.0 Hz, 2H, 4-H, 6-H), 3.39 (m, 2H, 3a-H, 6a-H), 7.25 (m, 2H, *o*-H, Ph), 7.37 (m, 1H, *p*-H, Ph), 7.46 (m, 2H, m-H, Ph). - ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 21.24 (q, CH_3), 33.16 (t, C-4, C-6), 45.10 (d, C-3a, C-6a), 125.62 (s, C=$C(CH_3)_2$), 126.42 (d, *o*-C, Ph), 128.40 (d, *p*-C, Ph), 129.02 (d, *m*-C, Ph), 129.85 (s, C-5), 132.27 (s, Ph), 179.20 (s, C-1, C-3). - Anal. Calcd. for $C_{16}H_{17}NO_2$: C, 75.27; H, 6.71; N, 5.49; Found: C, 75.11; H, 7.19; N, 5.61.

Hexahydro-5-isopropylidene-2-methyl-1H-cyclopenta[c]pyrrol-1,3-dione **7b**: 7.39 g (87 %) of a white crystalline solid, mp. 83°C (recrystallized from ether). - MS: *m/z (%)* = 193 (62, M^+), 112 (34), 108 (64), 93 (100). - IR (KBr): ν = 1695 (s) cm^{-1}. - ^{1}H-NMR ($CDCl_3$): δ = 1.63 (s br., 6H), 2.50-2.82 (m, 4H), 2.94 (s, 3H), 3.28 (m, 2H). - ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 21.37 (q, CH_3), 25.07 (q, N-CH_3), 32.87 (t, C-4, C-6), 45.13 (d, C-3a, C-6a), 125.37 (s, C=$C(CH_3)_2$), 130.19 (s, C-5), 180.53 (s, C-1, C-3). - Anal. Calcd. for $C_{11}H_{15}NO_2$: C, 68.37; H, 7.82; N, 7.25; Found: C, 68.38; H, 7.86; N, 7.12.

[4+2] Cycloadduct:
1,3,3a,4,7,7a-Hexahydro-5,6-dimethyl-2-phenyl-1H-isoindol-1,3-dione **9b**: yellow oil enriched by preparative GC[20% SE-30 on Volaspher A 4; d = 20 mm; T = 220°C; N_2: 830 ml/min]; purity: 80.8 % (GC), rest: 2 peaks (> 1 %) 8.2 %. - MS: *m/z (%)* = 255 (63, M^+), 174 (14), 108 (79), 107 (100). - ^{1}H-NMR ($CDCl_3$): δ = 1.70 (s br., 6H, CH_3), 2.25 (m, J_{gem} = -14.6 Hz, 2H, 4-H, 7-H), 2.50 (m, J_{gem} = -14.6 Hz, 2H, 4-H, 7-H), 3.12 (m, 2H, 3a-H, 7a-H), 7.13-7.47 (m, 5H, Ph). - ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 19.20 (q, CH_3), 30.91 (t, C-4, C-7), 40.02 (d, C-3a, C-7a), 126.39 (d, *o*-C, Ph), 126.96 (s, C-5, C-6), 128.40 (d, *p*-C, Ph), 129.01 (d, *m*-C, Ph), 132.19 (s, Ph), 179.34 (s, C-1, C-3).

3) with (diphenylmethylene)cyclopropane (**1c**):
5-Diphenylmethylene-hexahydro-2-phenyl-1H-cyclopenta[c]pyrrol-1,3-dione **6c**: 4.45 g (entry 5: 83 %) resp. 2.60 g (entry 9: 56 %) of colorless plated crystals, mp. 129°C (recrystallized from ether/CH_2Cl_2 20:1). - MS: *m/z (%)* = 379 (65, M^+), 232 (41), 231 (100). - IR (KBr): ν = 1710 (s) cm^{-1}. - ^{1}H-NMR ($CDCl_3$): δ = 2.88 (m, 2H, 4-H, 6-H), 3.02 (m, 2H, 4-H, 6-H), 3.42 (m, 2H, 3a-H, 6a-H), 7.02-7.53 (m, 15H, Ph). - ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 34.79 (t, C-4, C-6), 44.04 (d, C-3a, C-6a), 126.26 (d, *o*-C, N-Ph), 126.82 (d, *p*-C, Ph), 128.08 (d, *m*-C, Ph), 128.48 (d, *p*-C, N-Ph), 128.91 (d, *o*-C, Ph), 129.06 (d, *m*-C, N-Ph), 131.86 (s, N-Ph), 135.36 (s, C=CPh_2), 137.88 (s, C-5), 141.51 (s, Ph), 178.62 (s, C-1, C-3). - Anal. Calcd. for $C_{26}H_{21}NO_2$: C, 82.30; H, 5.58; N, 3.69; Found: C, 81.83; H, 6.69; N, 3.81.

4) with 1-methylene-2-phenylcyclopropane (**1d**):
5-Benzylidene-hexahydro-2-phenyl-1H-cyclopenta[c]pyrrol-1,3-dione **6d**: 1.26 g (23 %) of a white solid, mp. 128°C (recrystallized from ether). - MS: *m/z (%)* = 303 (59, M^+), 156 (100). - IR (KBr): ν = 1704 (s) cm^{-1}. - ^{1}H-NMR ($CDCl_3$): δ = 2.81-3.03 (m, 3H, 4-H, 6-H), 3.09 (d, Jgem= -15.0 Hz, 1H, 4-H or 6-H), 3.26-3.53 (m, 2H, 3a-H, 6a-H), 6.47 (m, 1H, C=C(H)Ph), 7.14-7.47 (m, 10H, Ph). - ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 32.97 (t, C-4), 38.40 (t, C-6), 43.11, 45.22 (d, C-3a, C-6a), 124.74 (d, C=C(H)Ph), 126.42 (d, *o*-C, N-Ph), 126.86 (d, *p*-C, Ph), 128.32, 128.45 (d, *m*+*o*-C, Ph), 128.54 (d, *p*-C, N-Ph), 129.06 (d, *m*-C, N-Ph), 131.91 (s, N-Ph), 136.93 (s, C-5), 138.94 (s, Ph), 178.67, 178.73 (s, C-1, C-3). - Anal. Calcd. for $C_{21}H_{17}NO_2$: C, 79.19; H, 5.65; N, 4.62; Found: C, 78.97; H, 5.65; N, 4.26.

5) with 1-methylene-2-(trimethylsilyl)cyclopropane (**1e**):
Hexahydro-2-phenyl-5-(trimethylsilylmethylene)-1H-cyclopenta[c]pyrrol-1,3-dione **6e**: 0.80 g (20 %) of a white crystalline solid, mp. 140°C (third compound isolated by LC; ether/hexane 1:1). MS: *m/z (%)* = 299 (8, M^+), 284 (100). - IR (KBr): ν = 1705 (s), 1634 (w) cm^{-1}. - ^{1}H-NMR ($CDCl_3$): δ = 0.04 (s, 9H, $Si(CH_3)_3$)), 2.55-2.91 (m, 4H, 4-H, 6-H), 3.17-3.40 (m, 2H, 3a-H, 6a-H), 5.43 (m, 1H, C=C(H)$Si(CH_3)_3$), 7.11 (m, 2H, *o*-H, Ph), 7.28-7.39 (m, 3H, *m*+*p*-H, Ph). - ^{13}C-NMR (50 MHz, $CDCl_3$): δ = -0.47 (q, $Si(CH_3)_3$), 34.93(t, C-6), 40.14 (t, C-4), 43.23, 44.53 (d, C-3a, C-6a), 124.53 (d, C=C(H)$Si(CH_3)_3$), 126.27 (d, *o*-C, Ph), 128.37 (d, *p*-C, Ph), 128.91 (d, *m*-C, Ph), 131.87 (s, Ph), 153.77 (s, C-5), 178.65, 178.68 (s, C-1, C-3). - Anal. Calcd. for $C_{17}H_{21}NO_2Si$: C, 68.19; H, 7.07; N, 4.68; Found: C, 68.07; H, 7.11; N, 4.04.

[2+2] Cycloadduct:
(1S,5S,6R,2'R)-(±)-3-phenyl-2'-(trimethylsilyl)spiro{3-azabicyclo[3.2.0]heptan-6,1'-cyclopropane}-2,4-dione **8**: 0.12 g of a colorless oil (second compound isolated by LC; ether/hexane 1:1); purity: 91.8 %(GC), rest: 7.8% **9b**. - MS: *m/z (%)* = 299 (15, M^+), 73 (100). - ^{1}H-NMR ($CDCl_3$): δ = 0.08 (s, 9H, $Si(CH_3)_3$), 0.19 (dd, J_{cis} = 11.3 Hz, J_{trans} = 8.3 Hz, 1H, 2'-H), 0.61 (dd, J_{gem} = -4.3 Hz, J_{trans} = 8.3 Hz, 1H, 3'-H), 0.98 (dd, J_{gem} = -4.3 Hz, J_{cis} = 11.3 Hz, 1H, 3'-H), 2.42 (dd, J_{gem} = -12.8 Hz, $J_{7,1}$ = 3.9 Hz, 1H, 7-H, trans), 2.78 (dd, J_{gem} = -12.8 Hz, $J_{7,1}$ = 10.1 Hz, 1H, 7-H, cis), 3.32 (d, $J_{5,1}$ = 6.5 Hz, 1H, 5-H), 3.45 (m, $J_{1,5}$ = 6.5 Hz, $J_{1,7}$ = 10.1 Hz, $J_{1,7'}$ = 3.9 Hz, 1H, 1-H), 7.13-7.40 (m, 5H, Ph). - ^{13}C-NMR (50 MHz, $CDCl_3$): δ =

-1.72 (q, $Si(CH_3)_3$), 7.61 (d, C-2'), 16.69 (t, C-3'), 24.78 (s, C-6), 31.84 (t, C-7), 35.43, 47.15 (d, C-1, C-5), 126.40 (d, *o*-C, Ph), 128.50 (d, *p*-C, Ph), 129.12 (d, *m*-C, Ph), 132.13 (s, Ph), 177.06, 178.75 (s, C-2, C-4).

[4+2] Cycloadduct:
1,3,3a,4,7,7a-Hexahydro-2-phenyl-5-trimethylsilyl-1H-isoindol-1,3-dione **9e**: 0.37 g of a colorless oil (first compound isolated by LC; ether/hexane 1:1); purity (GC): 91.5 %, rest: 3.8 % fourth unidentified compound, 2.4 % **6e**. - MS: *m/z (%)* = 299 (31, M^+), 284 (17), 73 (100). - ^{1}H-NMR ($CDCl_3$): δ = 0.00 (s, 9H, $Si(CH_3)_3$), 1.58 (d, J_{gem} = -13.5 Hz, 1H, 7-H), 1.63 (d, J_{gem} = -13.5 Hz, 1H, 7-H), 2.75 (m, 2H, 4-H), 3.46 (m, $J_{6a,3a}$ = 7.4 Hz, $J_{3a,4}$ = 4.1 Hz, $J_{3a,4}$ = 8.2 Hz, 1H, 3a-H), 3.90 (d, $J_{7a,3a}$ = 7.4 Hz, 1H, 7a-H), 5.26 (m, 1H, 6-H), 7.20 (m, 2H, *o*-H, Ph), 7.32 (m, 1H, *p*-H, Ph), 7.41 (m, 2H, *p*-H, Ph). - ^{13}C-NMR (50 MHz, $CDCl_3$): δ = -1.66 (q, $Si(CH_3)_3$), 21.01, 40.01 (t, C-4, C-7), 43.32, 53.13 (d, C-3a, C-7a), 117.27 (d, C-6), 126.24 (d, *o*-C, Ph), 128.11 (d, *p*-C, Ph), 128.78 (d, *m*-C, Ph), 131.89 (s, Ph), 145.60 (s, C-5), 177.20, 179.26 (s, C-1, C-3).

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