Data of **7**: colourless liquid. IR (film): 1680*s*. MS: 191 (3, *M*), 148 (100), 130 (13), 149 (11), 120 (9), 92 (7), 118 (6), 133 (5), 65 (4). ^{1}H-NMR (360 MHz, $CDCl_3$): 0.97, 1.01 (2*t*, *J* = 7, 2×CH_3); 1.62 (*m*, CH_2); 1.76 (*m*, CH_2); 2.80 (*m*, CH_2); 2.90 (*t*, *J* = 7, CH_2); 7.19 (*d*, *J* = 5, H–C(5)); 8.54 (*d*, *J* = 5, H–C(6)); 8.82 (*s*, H–C(2)).

1-(4-Propylpyridin-3-yl)butan-1-ol (**8**). A soln. of $NaBH_4$ (10 g, 0.26 mol) in H_2O (100 ml) was added at r.t. to a soln. of **7** (19.1 g, 0.10 mol) in MeOH (120 ml). The mixture was stirred for 4 h at r.t., the solvents evaporated, and the residue dissolved in H_2O. The product was isolated by extraction with Et_2O followed by bulb-to-bulb distillation (130°/0.01 Torr). Yield: 16 g (83%) of **8**.

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Pyrolysis of Acetate **9**. A soln. of acetate **9** (6.47 g, 27.5 mmol) in toluene (30 ml) was pyrolyzed at 500° at *ca.* 20 Torr in a slow stream of Ar in a pyrolysis tube packed with quartz fragments. The crude pyrolysate was subjected to bulb-to-bulb distillation to give 3.5 g (72%) of **3**/**4** (1:5). The pure isomers were isolated by GC (silicone, 200°), **3** being eluted first.

Data of **3**: colourless oil. IR (film): 1630*w*, 1580*m*, 1545*w*, 825*m*. MS: *Fig. 2*. ^{1}H-NMR (360 MHz, $CDCl_3$): 0.94 (*t*, *J* = 7, CH_3(3")); 1.01 (*t*, *J* = 7.5, CH_3(4')); 1.59 (*m*, CH_2(2")); 2.13 (*m*, CH_2(3')); 2.54 (*t*, *J* = 7.5, CH_2(1")); 5.82 (*td*, *J* = 7.5, 11, H–C(2')); 6.37 (br. *d*, *J* = 11, H–C(1')); 7.09 (*d*, *J* = 5, H–C(5)); 8.34 (*s*, H–C(2)); 8.37 (*d*, *J* = 5, H–C(6)).

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Ernest Wenkert[a])*, **Christian Vial**[b]), and **Ferdinand Näf**[b])*

Abstract. Acetoxymaleic anhydride (AMA) has been shown to be a versatile ketene equivalent in the *Diels-Alder* reaction for the conversion of 1,3-dienes into cyclohexanones. The new transformation has been applied to an alternate synthesis of methyl *cis*-dihydrojasmonate, an important jasmine fragrance, and to several model systems.

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In this publication, we describe the use of acetoxymaleic anhydride (AMA, **1**) [2] as ketene equivalent in the *Diels-Alder* reaction (*Scheme 1*).

The known reaction of AMA (**1**) with cyclopentadiene **2** gave the adduct **3** (82%) [3]. It was assumed that acetoxyglutaric anhydride **3** or its dihydro derivative **4** would undergo hydrolytic decarbonylation in analogy to the behavior of α-oxy-acids, which lose CO upon acid treatment forming carbonyl compounds [4] (*Scheme 2*). When the saturated acetoxyglutaric anhydride **4** [5] was treated with 96% H_2SO_4 between 5 and 20°, a 42:58 mixture (57%) of **5a** and **5b**, was obtained (*Scheme 1*). Acid-catalysed decarboxylation of the

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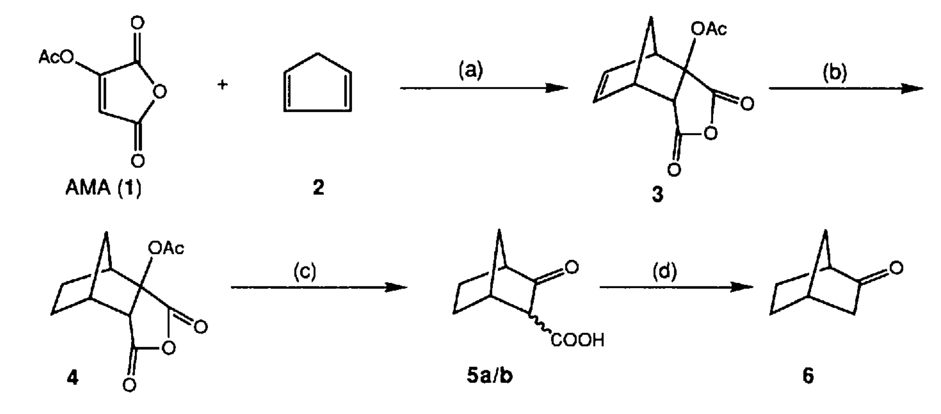

Reagents: a) 24 h/25°, benzene; b) H_2/Pd-C; c) 96% H_2SO_4/5° → 25°; d) AcOH, 2 h reflux.

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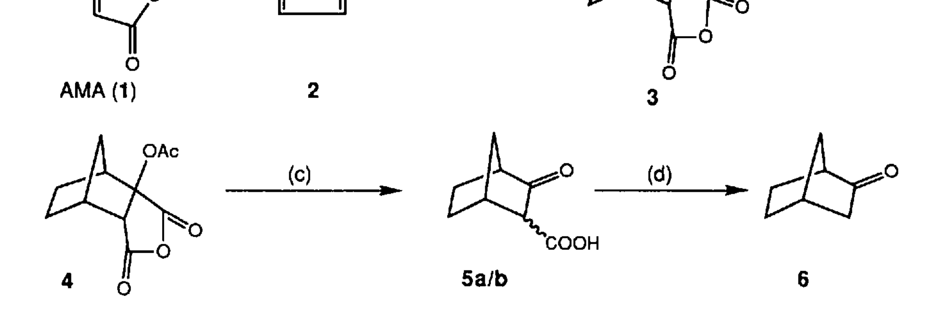

Reagents: a) 24 h/25°, benzene; b) H_2/Pd-C; c) 96% H_2SO_4/5° → 25°; d) AcOH, 2 h reflux.

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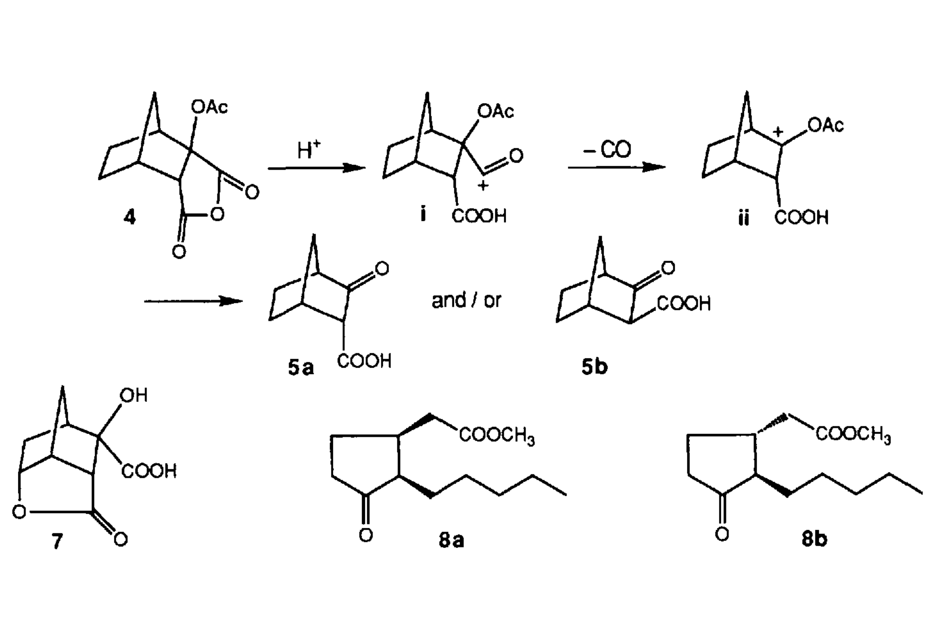
5a/b mixture produced norbornan-2-one **6** (72%).

Unfortunately, the initial *Diels-Alder* adduct **3** gave no decarbonylation and furnished only lactone **7**, m.p. 180–184° (dec.).

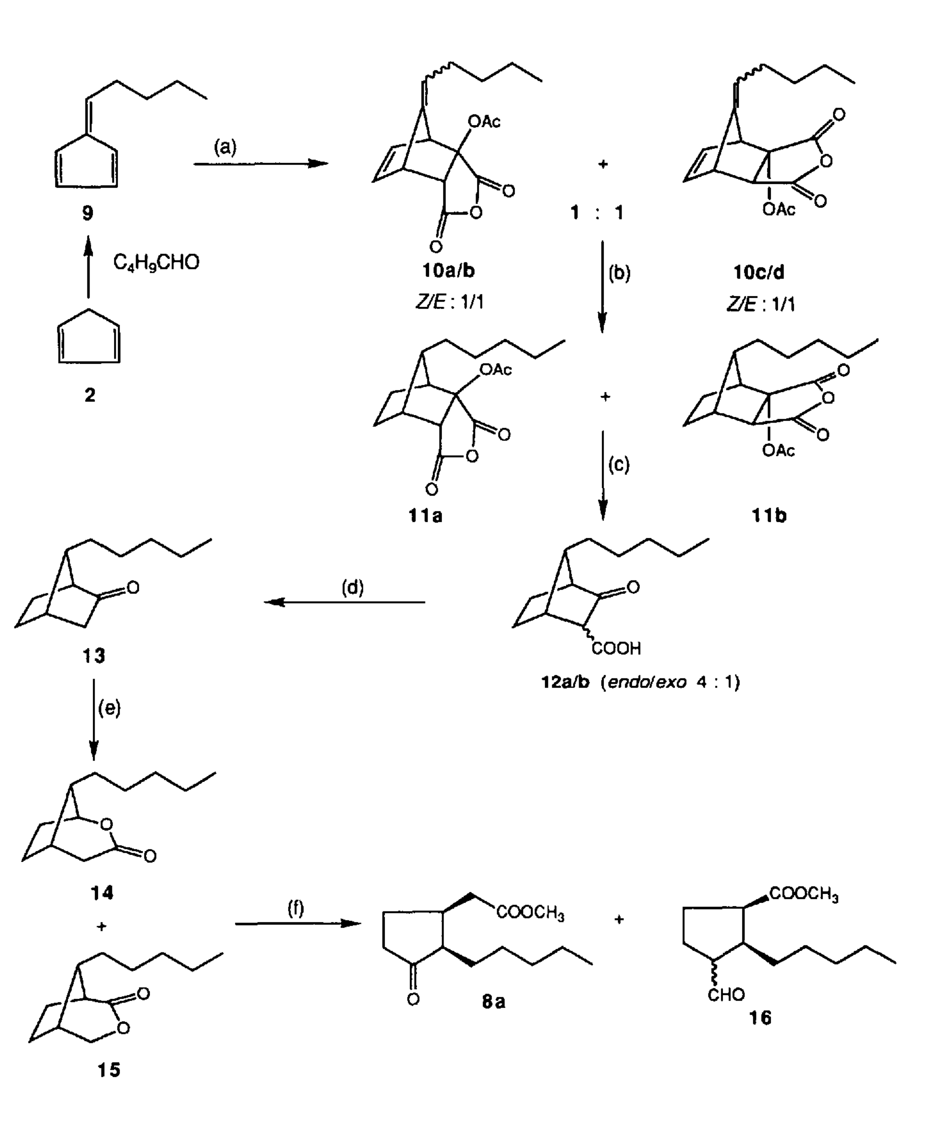
To illustrate the utility of the new method (*Scheme 1*), it was applied to the synthesis of methyl *cis*-dihydrojasmonate, a key constituent of the commercial jasmine fragrance *Hedione*® [6], the thermodynamic mixture of methyl *cis*- and *trans*-dihydrojasmonate (**8a** and **8b** ~96:4) [7]. Odor evaluation has demonstrated clearly the *cis*-isomer to be much stronger, thus emphasizing the importance of direct access to **8a** [8].

Diels-Alder reaction of fulvene **9** [9] [10] and AMA (**1**) in benzene furnished in 65% yield a mixture of the four isomeric cycloadducts **10a**, **10b**, **10c**, and **10d** (1:1:1:1; *Scheme 3*). Subsequent catalytic hydrogenation gave the two isomers **11a** and **11b** (1:1) which, upon treatment with 96% H_2SO_4 followed by decarboxylation, led to 98% pure *syn*-7-pentylnorbornan-2-one (**13**) [11] (the yields being 68% from pure **11a** and 74% from pure **11b**). *Bayer-Villiger* reaction (40% AcO_2H (10 equiv.), 96% H_2SO_4 (3.4 equiv.), 18 h at room temperature) of ketone **13** gave in 67% yield an inseparable mixture (7:3) of desired lactone **14** [11] and undesired lactone **15**. Alternative methods (*m*-chloroperbenzoic acid/$CHCl_3$, reflux; 35% $AcOOH/AcOH/CH_2Cl_2$) left the starting material unchanged. A reaction sequence [11] of saponification, esterification, and oxidation finally led to an easily separable mixture (by flash chromatotography on silica gel) of methyl *cis*-dihydrojasmonate **8a** (containing 6% **8b**, 57% yield of **8a/b** based on **14**) and **16**.

Scheme 2



Scheme 3



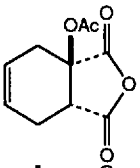
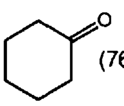
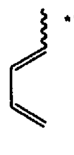
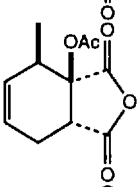
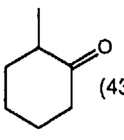
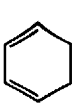
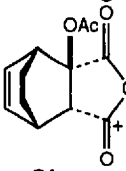
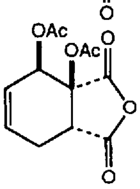
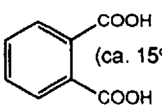
Reagents: a) AMA (**1**), 13 h/50° and 19 h/80°; b) H_2/Pt, 60 psi, AcOH; c) 96% H_2SO_4, 5° → 25°; d) AcOH, 2 h reflux; e) 40% AcOOH (10 equiv.)/AcOH/H_2SO_4 (3.4 equiv.), 18 h/25°; f) KOH/CH_3OH, → CH_2N_2 → PCC/CH_2Cl_2/AcONa.

To further test the scope and limitation of the reaction sequence of *Scheme 1*, it was applied to various 1,3-dienes. The results are summarised in the *Table*. The following general experimental procedures were used.

A) Diels-Alder Step. AMA (**1**; 0.1 mol) was added at room temperature to a solution of the diene (0.2 mol) in 250 ml of solvent (benzene or toluene) under Ar. The mixture was stirred either at room temperature, at reflux temperature, or in a sealed tube for a given time (for specific conditions see *Table*). The reaction mixture was concentrated under vacuum and chromatographed over silica gel (hexane/Et_2O).

B) Hydrogenation Step. A mixture of the *Diels-Alder* adduct (0.2 mol) and *ca.* 5

Table. *Reaction of AMA* (**1**) *with Various Dienes, Followed by a Hydrogenation/Decarbonylation-Hydrolysis/Decarboxylation Reaction Sequence*

Entry	Diene	Method	*Diels-Alder* Adduct [yield]	Method	Final Product [yield]
1		A: 26 h/110° benzene, sealed tube	 (49%)	B, C	 (76%)
2	 a)	A: 24 h/110° benzene, sealed tube	 (31%)	B,C	 (43%)
3		A: 24 h/110° benzene, sealed tube	 (4-7%) + polymers	-	-
4	 b)	A: 5 h/110° toluene, reflux	 (76%)	B, C	 (ca. 15%)

a) *Z/E* ratio 1:2.
b) *Z/E* ratio 3:7.

mg of 5% Pd/C in 200 ml of AcOEt was hydrogenated at room temperature and atmospheric pressure. It was filtered, concentrated and, if necessary, chromatographed.

C) Decarbonylation and Decarboxylation Steps. The hydrogenated *Diels-Alder* adduct (0.05 mol) was added at once to a stirred solution of 96% H_2SO_4 (100 ml) at 5°. The temperature was allowed to rise to 20° and stirring was continued until gas evolution had stopped completely (after formation of *ca.* 0.05 mol CO). The mixture was poured onto crushed ice, extracted (AcOEt), washed (brine), dried (Na_2SO_4), and concentrated under vacuum. The resulting keto-acid was dissolved in glacial AcOH (120 ml) and heated at reflux temperature for 2 h. The mixture was diluted with pentane and the layers were separated. The pentane phase was washed with sat. Na_2CO_3 and brine to neutrality. The pentane extract was dried (Na_2SO_4), concentrated and distilled.

It follows from the *Table* and from the preceeding experiments that AMA (**1**) is only a moderately reactive dienophile not undergoing any preparatively useful reactions with unreactive dienes such as cyclohexa-1,3-diene, but reacting well with reactive dienes such as cyclopentadiene and 1-acetoxybuta-1,3-diene. Attempts to prepare the presumably more reactive dienophiles tosyloxymaleic anhydride and trifluoroacetoxymaleic anhydride failed. The relatively vigorous conditions needed for the decarbonylation of the acetoxyglutaric anhydrides is not compatible with labile structures such as in *Entry 4*. In the latter case only double elimination of AcOH and hydrolysis of the anhydride, giving phthalic acid was observed. Reagents alternative to 96% H_2SO_4 (*e.g.* various Pd^{II}, Rh^{I}, Ru^{III} complexes) were also tried, but gave unfavourable results.

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