Cycloadditions of Substituted 1,2-Dimethylenecyclopentanes. — The Influence of Methyl Groups on the Rate of Diels-Alder Reactions

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The preparation of methyl-substituted 1,2-dimethylenecyclopentanes and their reactivity in (4 + 2) cycloadditions with α,β-unsaturated carboxylic esters and nitriles is studied. In kinetic measurements the methyl groups show a moderately rate-enhancing effect. The results are compared with those for analogously substituted butadienes. Whereas 1,1-dimethylbutadiene reacts with TCNE to form a mixture of (2 + 2) and (4 + 2) cycloadducts, the correspondingly substituted 1,2-dimethylenecyclopentane gives only the (4 + 2) adduct.

Cycloadditionen von substituierten 1,2-Dimethylencyclopentanen. — Der Einfluß von Methyl-Gruppen auf die Geschwindigkeit von Diels-Alder-Reaktionen

Es wird über die Synthese Methyl-substituierter 1,2-Dimethylencyclopentane und deren Cycloadditionen mit α,β-ungesättigten Carbonsäureestern und Nitrilen berichtet. Die Methyl-Gruppen zeigen in kinetischen Messungen einen schwach aktivierenden Einfluß. Die Resultate werden mit analog substituierten Butadienen verglichen. Während 1,1-Dimethylbutadien mit TCNE unter Bildung einer Mischung von (2 + 2)- und (4 + 2)-Cycloaddukten reagiert, ergibt das entsprechend substituierte 1,2-Dimethylencyclopentan nur das (4 + 2)-Addukt.

Introduction

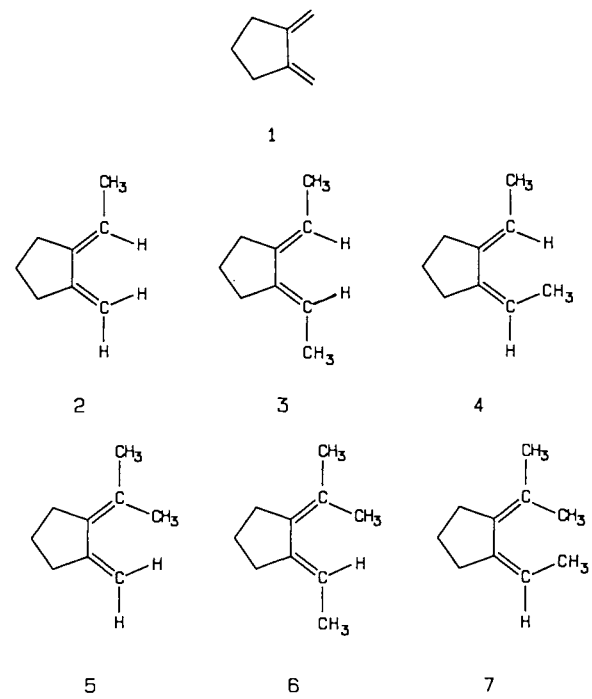
(4 + 2) cycloadditions of 1,2-dimethylenecyclopentane (**1**) have been investigated several times in connection with the mechanism of the Diels-Alder reaction. As a diene fixed in a *syn*-periplanar conformation, it has the advantage of excluding the influence of the equilibrium *s-cis/s-trans* on the course of the cycloaddition. Bartlett[1] used this diene to study the competition of olefins for (2 + 2) and (4 + 2) cycloadditions. Its reactivity was also compared with other dienes fixed in a *cisoid* conformation[2], and we used it as one of several model dienes for investigating the influence of the 1,4 distance in a diene on the rate of the Diels-Alder reaction[3]. Knowledge about the electronic structure of this diene results from spectroscopical studies and from theoretical investigations[4-7].

Most (4 + 2) cycloadditions between electron-rich dienes and electron-deficient dienophiles seem to proceed by a concerted, but not necessarily synchronous, pathway. Two-step reactions can be detected only with special substitution patterns of diene and dienophile and in cases where a synperiplanar conformation of the diene can not be reached easily. In this context a one-step reaction is expected for the cycloaddition of 1,2-dimethylenecyclopentane (**1**) and electron-deficient dienophiles. A change of mechanism should also not occur if hydrogen atoms in **1** are replaced by methyl groups. Therefore, besides synthetic aspects, cycloadditions of methylated **1** should be good models to show the influence of methyl groups on Diels-Alder reactions.

This publication describes cycloadditions of the substituted 1,2-dimethylenecyclopentanes **2**–**7** with cyano- and methoxycarbonyl-substituted dienophiles. Rate measurements are carried out for the reactions with methyl propiolate and dimethyl acetylenedicarboxylate in order to determine the influence of methyl groups in a *syn*-periplanar diene on the rate of Diels-Alder reactions. Differences to correspondingly substituted open dienes will be discussed.

Preparation of Dienes 1–7

The parent compound **1** has been prepared by several routes. Three procedures start from cyclopentane-1,2-dicarboxylic acid, which is readily available by a straightforward but long route, and convert it by conventional methods to **1**[9-11]. A fourth method involves a cyclization of the dianion



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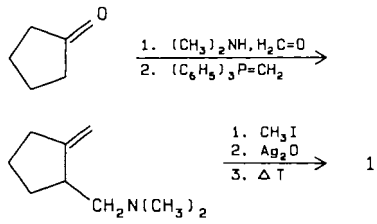
of 2,3-dimethylbutadiene with methylene chloride[12]. We followed a proposal of Bickelhaupt for the preparation of higher homologues of **1**[13]. In an overall yield of 13%, which is higher than in any of the other procedures, cyclopentanone is converted by Mannich and a Wittig reaction to **8**, and then by Hofmann degradation to **1**. A very pure product, which does not need further purification, is obtained after pyrolysis.



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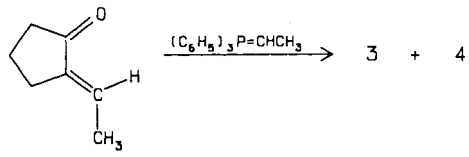
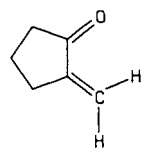
Diene **2** is prepared by an optimized Wittig reaction of **9**. It is essential to use tetrahydrofuran (THF) as solvent and *n*-butyllithium as base in order to reach a 30% yield of **2**. Only the (*E*) isomer is formed. A synthesis of **3** based on a titanium-mediated diyne cyclization[14] was described recently. A simpler route to **3** was found to be the Wittig reaction of **9** which under proper conditions leads to a mixture of **3** and **4** in 60% yield and in a ratio of 8:1. *n*-Butyllithium as base for the in situ generation of the ylide is crucial, since use of potassium *tert*-butoxide replaces the olefination by a Michael addition to the α,β-unsaturated enone[15]. The separation of **3** and **4** was performed by column chromatography.



9

A similar Michael-type addition was found[16] when the synthesis of **5** was attempted by a Wittig reaction of **10** with isopropylidenetriphenylphosphorane. If, instead, **11** and methylenetriphenylphosphorane is used, it is possible to isolate **5** in 63% yield after optimization.



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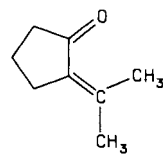


11

Again, the reaction conditions are very important. Thus, THF and potassium *tert*-butoxide are essential.

A mixture of **6** and **7** is generated in a 60:40 ratio if **11** is treated with ethylidenetriphenylphosphorane, prepared in THF with potassium *tert*-butoxide as base. The two isomers can be separated by column chromatography on silica gel with *n*-pentane as eluent. The isolated yields of **6** and **7** are 30% and 16%, respectively.

Photoelectron (PE) Spectra of 1–3 and 5–7

The PE spectra of the dienes were recorded in order to deduce the influence of the methyl groups on the π electrons in the diene system. In Table 1 we compare the first and second vertical ionization potentials of **2**–**7** with those of **1**.

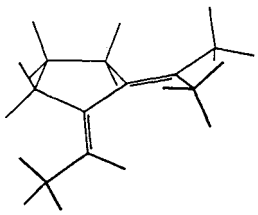
Table 1. First and second vertical ionization potentials [eV] for dienes **1**–**3** and **5**–**7**; values in brackets (**6** and **7**) are from MNDO calculations (see text)

IP [eV]	1	2	3	5	6		7	
First	8.54	8.32	7.95	8.09	7.79	(8.97)	8.00	(9.05)
Second	10.16	10.08	9.65	9.77	9.40	(10.46)	9.30	(10.32)
ΔIP	1.62	1.76	1.70	1.68	1.61	(1.49)	1.30	(1.27)

The diene part of **1** assumes a planar conformation according to the analysis of Pfeffer and Klessinger[7]. The interaction of the double bonds in **1** leads to a $\Delta IP_{1,2}$ = 1.62 eV between the two occupied π-MOs of **1**. If methyl groups are introduced in *trans* positions (**2** and **3**) we do not expect the planar arrangement of the double bond to be disturbed. $\Delta IP_{1,2}$ in **2** and **3** remains similar to that of **1**. A shift to lower ionization potentials is caused by the hyperconjugative effect of the methyl groups. It is only for **4**–**7** that one might expect a deviation from planarity which should lead to a weaker interaction of the double bonds. However, one methyl group in a *cis* position leads only to a small, almost negligible reduction in $\Delta IP_{1,2}$ (**5** and **6**). The first and second *IP*s of **5** are very similar to those of **3**, i.e. it does not make a big difference whether a second methyl group is attached to C-1 or C-4 of the diene moiety. The shift of the *IP*s by about 0.3 eV is caused by the third methyl group. Thus, we observe an almost additive substituent effect for each additional methyl group. The only deviation from this rule is found for **7**, where ΔIP is only 1.30 eV. Steric crowding with the consequence of a reduced ΔIP leads to a deviation from planarity. In order to obtain further information about this process we carried out MNDO calculations with complete geometry optimization for **6** and **7**. The structures obtained are displayed in **12** and **13**. Dihedral angles of 35° for **12** and 51° for **13** between the double bonds are evaluated, and the calculated ΔIP is smaller for **13** than for **12** (Table 1). However, it could be that MNDO overemphasizes the steric crowding, leading to exaggerated dihedral angles. The comparison of our result with that for 1,2-Dimethylenecyclohexane, where a dihedral angle of 55° and an experimental ΔIP of 0.93 eV has been established[17], indicates that the torsional angles in **6** and **7** should be smaller than found by MNDO.

A distortion of the π system of **7**, as compared to **6**, follows also from the UV spectra. For **6** we recorded a λ_{max} (lg ε) in *n*-hexane of 250 nm (4.068), close to the data for **5** [λ_{max} (lg ε) = 251 nm (4.033)]. In **7** λ_{max} suffers a hypsochromic

shift [λ_{max} (*n*-hexane) = 238 nm] and a reduction of the molar extinction coefficient (lg ε = 3.986).



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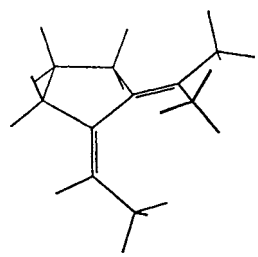
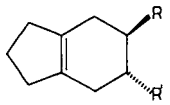


13

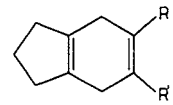
Cycloadditions

1,2-Dimethylenecyclopentane reacted at room temperature in THF or 1,4-dioxane with acrylonitrile, fumaronitrile, methyl propiolate and dimethyl acetylenedicarboxylate in high yields to give the cycloadducts **14** – **17**. Reaction times varied between 7 days for acrylonitrile and 1 day for dimethyl acetylenedicarboxylate. The compounds were characterized by spectroscopic techniques.



14 R=H, R'=CN

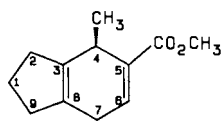
15 R=R'=CN



16 R=CO_2CH_3, R'=H

17 R=R'=CO_2CH_3

The reaction of diene **2** with methyl propiolate can lead to two regioisomeric products **18** and **19**. GLC analysis of the crude reaction mixture revealed the presence of two new compounds in a ratio of 7:1. The mixture was isolated as a colorless oil after two weeks at room temperature in 89% yield. Separation of the isomers was not attempted.



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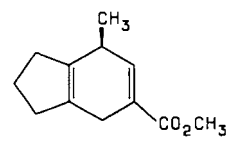
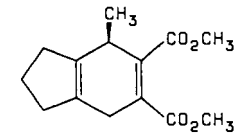


19

The major isomer can be identified by ^{1}H-NMR spectroscopy unambiguously as **18**. The vinylic proton at C-6 shows a doublet splitting of 1.0 Hz due to an allylic coupling with the proton at C-4 and a triplet splitting of 3.7 Hz with the protons at C-7. Due to heavy overlapping of the signals of **18** and **19** no complete signal assignments could be made for **19**. Its nature as a cycloadduct follows from the MS data, recorded individually for **18** and **19** by GC/MS. The predominant formation of the *ortho* isomer is in agreement with the results for the reaction of *trans*-piperylene and methyl propiolate[18] and with the expectation from FMO theory[19]. Dimethyl acetylenedicarboxylate and **2** lead to **20** in 91% isolated yield as a low-melting solid (mp 42°C).



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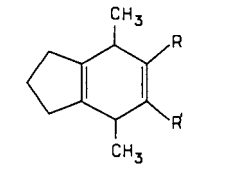
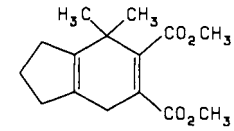


21 R=CO_2CH_3, R'=H

22 R=R'=CO_2CH_3

The symmetrically substituted diene **3** reacts with methyl propiolate and dimethyl acetylenedicarboxylate to give a single cycloadduct in high yield, 84% for **21** and 86% for **22**. Due to the small quantities of **4** which could be isolated, no cycloadditions of this diene were studied.

The geminal dimethyl-substituted diene **5** needs longer reaction times for the cycloaddition. The presence of a *syn*-periplanar methyl group, which hinders the approach of the dienophile, accounts for the lower reactivity. Thus, a 1:1 mixture of dimethyl acetylenedicarboxylate and **5** (each 1 M) took 22 days to react at room temperature in THF. The less reactive methyl propiolate required the same time but a temperature of 65°C. **23** is obtained in 86% yield as colorless crystals, **24** (78% yield) is a low-melting solid (mp 20°C).



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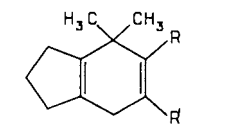


24a R=CO_2CH_3, R'=H

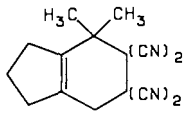
24b R=H, R'=CO_2CH_3

The crude reaction mixture of **24a, b** was carefully analyzed in order to find possible regioisomers. GLC and ^{1}H-NMR analyses provided evidence that both **24a** and **24b** were present in a ratio of 94:6. Assignment rests on the ^{1}H-NMR data for the single vinylic protons. One signal (major isomer) appears as a triplet at δ = 6.97 (J = 3.7 Hz), and the signal for the second isomer can be identified after blow-up of the spectrum at δ = 6.77 (J = 1.9 Hz). A singlet at δ = 1.12 appears for the 6 methyl protons of **24b**. This is found at δ = 1.33 for **24a**. The larger triplet splitting of the signal for the vinylic proton of the major isomer is interpreted as originating from a vicinal position of the coupling nuclei. For **24b** this splitting stems from allylic protons and should therefore be smaller. As compared to diene **2** one might have assumed that a second methyl group at the same diene carbon would have increased the portion of the *meta* isomer. However, on the contrary, the percentage of the *meta* isomer is even reduced. This means that steric factors do not influence the regiochemistry noticeably.

5 was also treated with tetracyanoethylene, because the antiperiplanar 1,1-dimethylbutadiene in this case leads to a mixture of (2 + 2) and (4 + 2) adducts. In a fast reaction even at −60°C only the (4 + 2) adduct **25** is formed in almost quantitative yield. ^{1}H-NMR spectroscopy of the crude reaction mixture gave no indication for the presence of a (2 + 2) adduct.

A mixture of dienes **6** and **7** (ratio 60:40) was treated with only 0.55 equivalents of tetracyanoethylene (TCNE) in order to show the influence of a second *cis*-periplanar methyl group on the reactivity. The reaction with **6** is fast at room temperature and leads to 83% of isolated cycloadduct (relative to added TCNE). The excess diene remaining in solution is the less reactive isomer **7**. As pure **6** and **7** were obtained by chromatography we also treated **7** with TCNE separately. Solutions of TCNE (0.1 M) and **7** in THF gave on mixing a deeply red colored charge transfer (CT) complex. In methylene dichloride the complex shows a deep blue color (λ_{max} = 620–630 nm, broad band). The color disappears completely after the reaction is finished. While a rapidly disappearing CT complex can also be observed for **6**, it is the steric inhibition of the reaction due to the two *cis*-methyl groups which makes the analysis of the CT complex for **7** possible.

The reactivity difference between **6** and **7** is also apparent in the reaction with dimethyl acetylenedicarboxylate. At 65°C a 0.4 M THF solution of **6** gave 92% of cycloadduct **26**. Diene **7** on the other hand gave no product under the same conditions after 28 days. After a 1 M solution of **7** is heated to 110° for 5 days, it is possible to detect by GC/MS the formation of three products in very low yield, one of which is identical to the compound formed from **6** and dimethyl acetylenedicarboxylate. The second compound has the same M^+ peak (m/z = 278) and is assumed to be an isomerized compound. An M^+ peak of m/z = 276 for the third compound points to dehydrogenation of the primary product.



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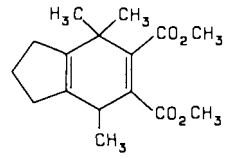
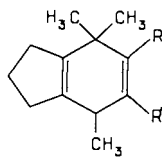


26

The low reactivity of methyl propiolate prevented its reaction with **7**. However, a 0.8 M THF solution of **6** at 65°C (15 days) led to 76% of isolated product. The ^{1}H-NMR spectrum showed the presence of two isomers. In particular the vinylic region with a triplet at δ = 6.84 (J = 3.8 Hz) and another one at δ = 6.74 (J = 0.7 Hz) made an assignment possible. From a separate run on a ^{1}H-NMR scale the ratio of **27a** and **27b** was determined to 68:32.

27a and **27b** could be separated by column chromatography and were identified independently.



27a R=CO_2CH_3, R=H

27b R=H, R=CO_2CH_3

Kinetic Measurements

For methyl propiolate and dimethyl acetylenedicarboxylate the rate constants for cycloadditions to **1**–**3**, **5**, and **6** were determined at 80°C. The data are collected in Table 2.

Table 2. Rate constants for cycloadditions of **1**–**3**, **5**, and **6** to methyl propiolate (A) and dimethyl acetylenedicarboxylate (B) at 80°C in 1,4-dioxane

diene	dienophile	$k_2 \times 10^7$ [l/mol · s]
1	A	2850 ± 61
	B	123000 ± 3700
2	A	6500 ± 280
	B	675000 ± 290
3	A	16000 ± 710
	B	408000 ± 210
5	A	90 ± 1
	B	7240 ± 180
6	A	113 ± 3
	B	2100 ± 56

The cycloadditions of dimethyl acetylenedicarboxylate are faster than those of methyl propiolate. This demonstrates that these cycloadditions are typical representatives of normal Diels-Alder reactions. Depending on the substitution pattern of the 1,2-dimethylenecyclopentanes a rate acceleration factor of 20–100 is observed. Diene **2** reacts 72 times faster with methyl propiolate than **5**, and 93 times faster with dimethyl acetylenedicarboxylate. A second methyl group in position 4 of the diene is slightly activating for methyl propiolate but deactivating for dimethyl acetylenedicarboxylate (compare **2** and **3**). In the case of **6** as compared to **5** almost no effect is detectable. The difference in reactivity between **2** and **5** can be attributed to a steric effect of the *cisoid*-methyl group which hinders the approach of the dienophile. Similarly, two methyl groups in *cis* positions (diene **7**), made kinetic measurements under identical conditions impossible. The reaction becomes too slow.

Due to the important influence of steric crowding it is not possible to correlate the rate data with the first ionization potentials as a measure of the HOMO energies of the diene. Even though the $HOMO_{diene}/LUMO_{dienophile}$ separation is the more important FMO interaction, no quantitative correlation with the rate data can be observed. A confirmation, at least qualitatively, of the FMO model follows from the reactivity difference between methyl propiolate and dimethyl acetylenedicarboxylate. For each diene the dimethoxycarbonyl-substituted acetylene is more reactive than methyl propiolate.

In general, methyl groups in the diene do not influence the reactivity appreciably by electronic effects. In those cases (**1**–**3**) where steric effects can be excluded a rate increase by a factor of 2–3 for each additional methyl group is found. In a study of cycloadditions of dienes not fixed in a *syn*-periplanar conformation a similarly small influence of a methyl group was observed for maleic anhydride as dienophile[20]. A stronger differentiation is observed for the

more reactive TCNE[20]. This is in line with the fact that higher reactivity goes parallel with higher selectivity in concerted cycloadditions.

A mechanistically revealing result follows from a comparison of the cycloaddition of TCNE with **5** and 1,1-dimethylbutadiene. The latter, having an energetically difficult to reach *syn*-periplanar conformation, gives a mixture of (4 + 2) and (2 + 2) adducts[20,21]. The (2 + 2) route, which does not require the *s-cis* conformation, becomes competitive. The formation of the four-membered ring almost certainly involves a zwitterionic intermediate. Also the formal Diels-Alder adduct could evolve from a two-step process. Ring closure to the (2 + 2) adduct and rotation of the zwitterion to the favorable conformation for the (4 + 2) product might be competitive. If, however, attack of TCNE occurs at a *syn*-periplanar conformation as in **5**, no (2 + 2) adduct can be diagnosed although the formation of a zwitterion should still be feasible. This observation could indicate an interesting difference in the behavior of zwitterions and biradicals.

This contrasts results obtained by Bartlett on the cycloaddition of **1** to 1,1-dichloro-2,2-difluoroethylene where a ratio of 2.3 in favor of the (2 + 2) adduct was found. With the assumption that the (2 + 2) adduct is formed in a two-step reaction via biradicals one might argue that a biradical intermediate is more reactive and, therefore, less selective than a zwitterionic intermediate in the reaction of TCNE with **5**.

Similarly, the comparison with the dimerization of methyl-substituted *o*-xylylenes allows interesting mechanistic conclusions[22].

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Experimental

Analytical instruments: ^{1}H- and ^{13}C-NMR spectra (internal standard TMS): Varian XL 200 and EM 360 A. – Mass spectra: Finnigan MAT 312/188. – IR spectra: Perkin-Elmer 397. – UV spectra: Varian Cary 219. – PE spectra: Leybold-Heraeus UGP 200. – Melting points are uncorrected.

1,2-Dimethylenecyclopentane (**1**) was prepared according to an adapted procedure for higher homologues[13]. 2-(Dimethylamino)-methylcyclopentanone[23] (56.4 g, 0.4 mol), dissolved in 100 ml of THF was slowly added dropwise to a solution of triphenylphosphonium methylide at room temp. This solution had been prepared by suspending 285.0 g (0.80 mol) of triphenylmethylphosphonium bromide in 600 ml of THF and adding 90.0 g (0.80 mol) of potassium *tert*-butoxide. After 15 h at room temp. a sufficient amount of water was added to dissolve all the precipitate. The organic layer was dried with magnesium sulfate and the reaction product directly methylated by adding 200 g (1.4 mol) of methyl iodide. Within 3 h a colorless solid separated, which was filtered and dried at 60°C (13 Pa); yield 110.0 g (98%).

48.0 g (1.20 mol) of sodium hydroxide in 120 ml of water was added within 5 min to a solution of 200.0 g (1.18 mol) of silver(I) nitrate in 500 ml of water. The dark brown precipitate was filtered and washed with water until the filtrate remained neutral. This silver hydroxide was added to a suspension of trimethyl[(2-methylenecyclopentyl)methyl]ammonium iodide in 500 ml of water within 30 min. After 2 h the solution was filtered, and the water was removed under vacuum at 20–25°C and 27 hPa. The remaining 30 ml were heated slowly to 120°C (15 Pa) in a vessel attached to a distillation bridge. The product was collected in a bulb cooled with liquid nitrogen. The product was dissolved in 50 ml of pentane and dried with magnesium sulfate. After removing the solvent using a 15-cm Vigreux column under normal pressure the product was collected by bulb-to-bulb condensation; yield 15.0 g (40%). The spectral properties were identical with those reported[9–11].

1-Ethylidene-2-methylenecyclopentane (**2**): To a suspension of methyltriphenylphosphonium bromide (250 g, 0.7 mol) in 750 ml of THF under argon was added 280 ml of a 2.5 M solution of *n*-butyllithium in hexane within 1 h. After 1 h a 50% solution of 2-ethylidenecyclopentanone[24–26] (55 g, 0.5 mol) in THF was added dropwise to the solution within 1 h. During this time the solution boiled moderately under reflux. The cooled solution was filtered over a 5-cm layer of silica gel (diameter 20 cm). After removing the solvent at a bath temp. of 30°C under vacuum the product was isolated by bulb-to-bulb condensation; yield 16 g (30%), purity 95% by GLC. – IR (film): $\tilde{\nu}$ = 1625 cm^{-1} (C=C). – UV (1,4-dioxane): λ_{max} (lg ε) = 254 nm (3.985). – ^{1}H NMR ($CDCl_3$): δ = 1.66 (quint, *J* = 7 Hz, 2H), 1.69 (d, *J* = 7 Hz, 3H, H_3CCH=), 2.3–2.43 (m, 4H), 4.74 (s, 1H), 5.17 (s, 1H), 5.90 (tq, *J* = 7 Hz, *J* = 2.5 Hz, 1H). – ^{13}C NMR (C_6D_6): δ = 14.97 (q, CH_3), 24.26 (t), 30.09 (t), 34.97 (t), 100.92 (t), 114.65 (d), 141.12 (s), 149.61 (s). – MS (70 eV): *m/z* (%) = 108 (48) [M$^+$], 93 (100), 92 (31), 79 (50), 78 (35), 67 (13), 53 (12), 39 (26), 16 (23).

1,2-Diethylidenecyclopentane (**3** and **4**): 278 g (0.75 mol) of ethyltriphenylphosphonium bromide was suspended in 700 ml of THF, and 280 ml of a 2.5 M solution of *n*-butyllithium in hexane was added within 1 h. The solution warmed to 50°C and was stirred for 5 h at room temp. To this dark-red solution was added dropwise within 30 min 55 g (0.50 mol) of 2-ethylidenecyclopentanone in 100 ml of THF. The mixture began to boil and was kept for 2 h at room temp. Then 500 ml of water was added to dissolve the precipitate, and the organic layer was dried with magnesium sulfate. The solvent was removed under normal pressure at a bath temp. of 90°C. The residue was purified by bulb-to-bulb condensation. 42 g (60%) of a mixture of the (*E,E*) and (*E,Z*) isomers were obtained. The pure (*E,Z*) isomer **3** could be obtained by column chromatography on silica gel with pentane as eluent. **4** was characterized from the mixture.

3: IR (film): $\tilde{\nu}$ = 1665 cm^{-1} (C=C). – UV (1,4-dioxane): λ_{max} (lg ε) = 256.5 nm (4.003). – ^{1}H NMR (C_6D_6): δ = 1.53 (quint, *J* = 7 Hz, 2H), 1.63 (d, *J* = 7 Hz, 6H, 2 CH_3), 2.24 (t, *J* = 7 Hz, 4H), 5.81 (tq, *J* = 7 Hz, *J* = 2.6 Hz, 2H). – ^{13}C NMR (C_6D_6): δ = 14.94 (q, CH_3), 23.99 (t), 30.35 (t), 111.59 (d), 141.88 (s). – MS (70 eV): *m/z* (%) = 122 (100) [M$^+$], 107 (88), 105 (25), 94 (37), 93 (81), 91 (85), 80 (30), 79 (78), 77 (78), 67 (33), 65 (32), 55 (25), 53 (36), 51 (29), 41 (44), 39 (51).

4: ^{1}H NMR ($CDCl_3$): δ = 1.61 (quint, *J* = 7 Hz, 2H), 1.72 (d, *J* = 7 Hz, 3H, CH_3), 1.79 (d, *J* = 7 Hz, 3H, CH_3), 2.20–2.42 (m, 4H), 5.48 (mq, *J* = 1 Hz, *J* = 7 Hz, 1H), 5.77 (tq, *J* = 2.7 Hz, *J* = 6 Hz, 1H). – ^{13}C NMR ($CDCl_3$): δ = 15.08 (q), 15.36 (q), 23.78 (t), 31.08 (t), 36.42 (t), 116.06 (d), 120.35 (d), 141.10 (s). – MS/GC (70 eV): *m/z* (%) = 122 (100) [M$^+$], 107 (61), 105 (14), 94 (22), 93 (100), 91 (55), 80 (17), 79 (89), 77 (49), 67 (20), 65 (16), 55 (16), 53 (20), 51 (16), 41 (32), 39 (36).

1-Isopropylidene-2-methylenecyclopentane (**5**): In a two-necked flask, equipped with stirrer and dropping funnel 26.9 g (0.24 mol) of potassium *tert*-butoxide was suspended in 800 ml of THF and stirred together with 89.3 g (0.25 mol) of methyltriphenylphosphonium bromide for 3 h at room temp. Then 19.2 g (0.15 mol) of

2-isopropylidenecyclopentanone[27-29] in 50 ml of THF was added slowly. After 1 additional h at room temp. 800 ml of pentane was added and the mixture hydrolyzed with 100 ml of water. After drying the organic layer, the solvents were removed under vacuum, and the residue was taken up in 800 ml of pentane. A colorless precipitate was filtred off and the solvent removed under vacuum. Bulb-to-bulb distillation (ca. 0.5 mbar) gave 15.3 g of a colorless liquid, 85% in **5** according to GC. Further purification yielded 11.5 g (63%) of **5**. – IR (film): $\tilde{\nu}$ = 1650 cm^{-1} (C=C), 1615 cm^{-1} (C=C). – UV (hexane): λ_{max} (lg ε) = 251 nm (4.033). – ^1H NMR ($CDCl_3$): δ = 1.65 (quint, *J* = 7 Hz, 2H), 1.77 (s, 3H, CH_3), 1.94 (s, 3H, CH_3), 2.39 (m, 4H), 5.00 (s, 1H), 5.04 (s, 1H). – ^{13}C NMR ($CDCl_3$): δ = 22.3 (q), 23.7 (q), 23.8 (t), 32.2 (t), 37.0 (t), 107.3 (t), 128.3 (s), 133.5 (s), 150.1 (s). – MS (70 eV): *m/z* = 122 (66) [M^+], 107 (100), 105 (10), 93 (35), 91 (32), 81 (18), 80 (13), 79 (62), 77 (20), 67 (13), 53 (11), 41 (20) 39 (20).

(E)- and (Z)-1-Ethylidene-2-isopropylidenecyclopentane (**6** and **7**): 74.30 g (0.20 mol) of ethyltriphenylphosphonium bromide in 400 ml of THF was stirred for 2 h at room temp. with 22.4 g (0.20 mol) of potassium *tert*-butoxide. 19.20 g (0.15 mol) of 2-isopropylidenecyclopentanone in 50 ml of THF was added slowly, the mixture stirred for 1 h, 400 ml of petroleum ether (bp 40–60°C) added, and then 100 ml of water for hydrolysis. The organic layer was dried with magnesium sulfate and the solvent removed. A colorless precipitate was filtered off after adding 100 ml of petroleum ether. Removal of solvent and bulb-to-bulb condensation at 0.2 mbar gave 16.03 g (79%) of an (*E*/*Z*) mixture showing a 60:40 ratio for **6**:**7**. Chromatography of 3.00 g on silica gel (column 50 cm, diameter 3 cm) with pentane gave first 0.63 g of **7**, then a mixture of **6** and **7**, and afterwards 1.13 g of **6**.

6: IR (film): $\tilde{\nu}$ = 1650 cm^{-1} (C=C). – UV (hexane): λ_{max} (lg ε) = 250 nm (4.068). – ^1H NMR ($CDCl_3$): δ = 1.64 (quint, *J* = 7 Hz, 2H), 1.74 (d, *J* = 7 Hz, 3H), 1.76 (s, 3H), 1.90 (s, 3H), 2.34 (t, *J* = 7 Hz, 4H), 5.61 (q, *J* = 7 Hz, 1H). – ^{13}C NMR ($CDCl_3$): δ = 15.4 (q), 22.3 (q), 23.3 (t), 23.8 (q), 30.8 (t), 32.2 (t), 118.4 (d), 124.5 (s), 134.7 (s), 142.3 (s).

7: IR (film): $\tilde{\nu}$ = 1655 cm^{-1} (C=C). – UV (hexane): λ_{max} (lg ε) = 238 nm (3.986). – ^1H NMR ($CDCl_3$): δ = 1.56 (d, *J* = 7 Hz, 3H), 1.63 (m, 2H), 1.66 (m, 3H), 1.71 (s, 3H), 2.2 (m, 4H), 5.25 (q, *J* = 7 Hz, 1H). – ^{13}C NMR ($CDCl_3$): δ = 17.0 (q), 21.6 (q), 22.4 (t), 23.8 (q), 29.6 (t), 35.3 (t), 116.2 (d), 125.0 (s), 133.0 (s), 142.7 (s).

Cycloadditions

Methyl 4,7-Dihydroindan-5-carboxylate (**16**): 0.94 g (10 mmol) of **1** and 0.84 g (10 mmol) of methyl propiolate were each dissolved in 5 ml of 1,4-dioxane and allowed to react for 5 h. After removal of the solvent the product was recrystallized from diethyl ether; yield 1.60 g (90%), mp 49°C. – IR (film): $\tilde{\nu}$ = 1730 cm^{-1} (C=O), 1650 (C=C). – ^1H NMR ($CDCl_3$): δ = 1.89 (quint, *J* = 7 Hz, 2H), 2.29 (m, 4H), 2.86 (m, 4H), 3.76 (s, 3H), 7.04 (m, 1H). – ^{13}C NMR ($CDCl_3$): δ = 21.73 (t), 26.91 (t), 28.54 (t), 34.91 (t), 35.28 (t), 51.57 (q), 128.36 (s), 130.01 (s), 132.31 (s), 137.35 (d), 167.77 (s). – MS (70 eV): *m/z* (%) = 178 (42) [M^+], 177 (23), 176 (16), 145 (42), 119 (40), 117 (52), 115 (36), 105 (15), 91 (100), 77 (12), 65 (13), 59 (11), 51 (11), 41 (12), 39 (13).

$C_{11}H_{14}O_2$ (178.2) Calcd. C 74.13 H 7.92
Found C 74.09 H 7.56

Dimethyl 4,7-Dihydroindan-5,6-dicarboxylate (**17**): 0.94 g (10 mmol) of **1** and 1.42 (10 mmol) of dimethyl acetylenedicarboxylate, dissolved in 5 ml of 1,4-dioxane each, reacted exothermally at room temp. Removal of the solvent after 24 h and recrystallization from diethyl ether gave 2.03 g (86%) product with m.p. 54°C. – IR (film): $\tilde{\nu}$ = 1730 cm^{-1} (C=O), 1655 (C=C). – ^1H NMR ($CDCl_3$): δ = 1.86 (quint, *J* = 7.2 Hz, 2H), 2.26 (t, *J* = 7.2 Hz, 4H), 2.94 (s, 4H), 3.75 (s, 6H). – ^{13}C NMR ($CDCl_3$): δ = 21.66 (t), 29.19 (t), 34.80 (t), 52.12 (q), 130.27 (s), 133.37 (s), 168.72 (s). – MS (70 eV): *m/z* (%) = 236 (8) [M^+], 204 (24), 203 (42), 177 (19), 176 (100), 145 (29), 118 (12), 117 (37), 116 (28), 105 (37), 91 (29), 77 (49), 59 (41), 41 (15).

$C_{13}H_{16}O_4$ (236.3) Calcd. C 66.09 H 6.83
Found C 65.82 H 6.67

Methyl 4-Methyl-4,7-dihydroindan-5-carboxylate (**18**) *and Methyl 4-Methyl-4,7-dihydroindan-6-carboxylate* (**19**): 1.08 g (10 mmol) of **2** and 0.84 g (10 mmol) of methyl propiolate were allowed to react in 10 ml of 1,4-dioxane at room temp. After 15 d the reaction was complete. By GC and ^1H NMR a 7:1 ratio for **18**:**19** was determined. After removal of the solvent the product was purified by bulb-to-bulb condensation at 13 Pa and 50°C bath temp.; 1.70 g (89%) oily product was obtained. – IR (film): $\tilde{\nu}$ = 1725 cm^{-1} (C=O), 1645 (C=C). – ^1H NMR ($CDCl_3$) (major isomer): δ = 1.15 (d, *J* = 7 Hz, 3H), 1.88 (quint, *J* = 7 Hz, 2H), 2.1–2.5 (m, 4H), 2.79 (m, 2H), 3.20 (m, 1H), 3.76 (s, 3H), 6.99 (dt, *J* = 1 Hz, *J* = 3.7 Hz, 1H). – ^{13}C NMR ($CDCl_3$) (major isomer): δ = 19.70 (q), 22.03 (t), 28.39 (t), 31.53 (d), 33.36 (t), 35.13 (t), 51.40 (q), 129.37 (s), 134.20 (s), 136.75 (d), 137.71 (s), 167.69 (s). – MS/GC (70 eV) (major isomer): *m/z* (%) = 192 (38) [M^+], 177 (35), 164 (7), 161 (11), 145 (11), 133 (46), 131 (11), 117 (15), 115 (20), 105 (100), 91 (29), 79 (8), 77 (14), 59 (27), 41 (15). – MS/GC (70 eV): (minor isomer): *m/z* (%): 192 (26) [M^+], 177 (20), 132 (82), 131 (11), 117 (24), 115 (19), 105 (100), 91 (30), 77 (15), 59 (25), 41 (18).

$C_{12}H_{16}O_2$ (192.3) Calcd. C 74.97 H 8.39
Found C 74.51 H 8.61

Dimethyl 4-Methyl-4,7-dihydroindan-5,6-dicarboxylate (**20**): The reaction of 1.08 g (10 mmol) of **2** and 1.42 g (10 mmol) of dimethyl acetylenedicarboxylate in 10 ml of 1,4-dioxane was complete after 180 h at room temp. The crude product, obtained after removal of the solvent, was recrystallized from diethyl ether; yield 2.25 g (91%), mp 42°C. – IR (film): $\tilde{\nu}$ = 1740 cm^{-1} (C=O), 1655 (C=C). – ^1H NMR ($CDCl_3$): δ = 1.10 (d, *J* = 7 Hz, 3H), 1.88 (quint, *J* = 7 Hz, 2H), 2.1–2.4 (m, 4H), 2.90 (m, 2H), 3.17 (m, 1H), 3.73 (s, 3H), 3.77 (s, 3H). – ^{13}C NMR ($CDCl_3$): δ = 18.17 (q), 21.73 (t), 28.38 (t), 32.90 (t), 34.11 (d), 51.87 (q), 129.81 (s), 129.96 (s), 135.06 (s), 141.16 (s), 167.77 (s), 169.32 (s). – MS (70 eV): *m/z* (%) = 250 (8) [M^+], 203 (100), 191 (50), 190 (50).

$C_{14}H_{18}O_4$ (250.3) Calcd. C 67.18 H 7.25
Found C 67.17 H 7.46

Methyl 4,7-Dimethyl-4,7-dihydroindan-5-carboxylate (**21**): The reaction of 0.70 g (5.7 mmol) of **3** and 0.48 g (5.7 mmol) of methyl propiolate at 80°C in 5 ml of 1,4-dioxane was terminated after 200 h. After removal of the solvent 1.00 g (84%) oily product was obtained by bulb-to-bulb condensation at 13 Pa and 50°C bath temp. – IR (film): $\tilde{\nu}$ = 1725 cm^{-1} (C=O), 1645 (C=C). – ^1H NMR ($CDCl_3$): δ = 1.13 (d, *J* = 7 Hz, 3H), 1.14 (d, *J* = 7 Hz, 3H), 1.93 (m, 2H), 2.20 (m, 2H), 2.48 (m, 2H), 2.89 (m, 1H), 3.14 (m, 1H), 3.76 (s, 3H), 6.92 (d, *J* = 4.4 Hz, *J* = 0.6 Hz, 1H). – ^{13}C NMR ($CDCl_3$): δ = 19.72 (q), 20.75 (q), 22.31 (t), 31.82 (d), 33.26 (d), 33.32 (t), 33.73 (t), 51.42 (q), 133.40 (s), 134.74 (s), 137.43 (s), 142.58 (d), 167.76 (s). – MS (70 eV): *m/z* (%) = 206 (32) [M^+], 191 (37), 147 (100), 119 (90).

$C_{13}H_{18}O_2$ (206.3) Calcd. C 75.69 H 8.80
Found C 75.33 H 8.83

Dimethyl 4,7-Dimethyl-4,7-dihydroindan-5,6-dicarboxylate (**22**): 0.60 g (5.0 mmol) of **3** and 0.71 g (5.0 mmol) of dimethyl acetylenedicarboxylate reacted at room temp. in 5 ml dioxane for 20 h. After removal of the solvent at room temp. (13 Pa) the product was

recrystallized from diethyl ether; yield 1.10 g (86%), mp 33°C. – IR (film): $\tilde{\nu}$ = 1740 cm^{-1} (C=O), 1645 (C=C). – ^1H NMR ($CDCl_3$): δ = 1.21 (d, *J* = 7 Hz, 6H), 1.93 (m, 2H), 2.1–2.3 (m, 2H), 2.4–2.6 (m, 2H), 3.11 (q, *J* = 7 Hz, 2H), 3.79 (s, 6H). – ^{13}C NMR ($CDCl_3$): δ = 20.30 (q), 22.80 (t), 33.68 (t), 34.64 (t), 51.58 (q), 136.04 (s), 139.32 (s), 168.42 (s). – MS (70 eV): *m/z* (%) = 263 (3) [M^+], 216 (100).

$C_{15}H_{20}O_4$ (264.3) Calcd. C 68.16 H 7.63
Found C 68.19 H 7.15

Dimethyl 4,4-Dimethyl-4,7-dihydroindan-5,6-dicarboxylate (**23**): 2.00 g (16.0 mmol) of **5** in 10 ml of THF were allowed to react for 22 d at room temp. with 2.33 g (16.0 mmol) of dimethyl acetylenedicarboxylate. After removal of the solvent and addition of 15 ml of pentane slightly yellow crystals were obtained. Further purification by filtering a diethyl ether pentane solution (1 : 1, 30 ml) over silica gel and crystallization from methanol gave 3.74 g (86%) colorless crystals with mp 60°C. – IR (KBr): $\tilde{\nu}$ = 1720 cm^{-1} (C=O), 1630 (C=C). – ^1H NMR ($CDCl_3$): δ = 1.23 (s, 6H), 1.87 (quint, *J* = 7 Hz, 2H), 2.3 (m, 4H), 2.93 (m, 2H), 3.75 (s, 3H), 3.82 (s, 3H). – ^{13}C NMR ($CDCl_3$): δ = 21.8 (t), 26.1 (q), 27.7 (t), 30.6 (t), 35.3 (t), 37.5 (s), 51.8 (q), 52.0 (q), 126.1 (s), 129.4 (s), 138.4 (s), 148.5 (s), 166.8 (s), 169.7 (s). – MS (70 eV): *m/z* (%) = 264 (5) [M^+], 249 (17), 233 (20), 217 (100).

$C_{15}H_{20}O_4$ (264.3) Calcd. C 68.16 H 7.63
Found C 68.32 H 7.95

Methyl 4,4-Dimethyl-4,7-dihydroindan-5-carboxylate (**24a**) *and Methyl 4,4-Dimethyl-4,7-dihydroindan-6-carboxylate* (**24b**): 2.00 g (16.0 mmol) of **5** in 10 ml of THF were treated with 1.38 g (16 mmol) of methyl propiolate for 22 d at 65°C. After removal of the solvent the product was taken up in 15 ml of pentane and filtered to remove some polymeric material. After addition of 15 ml of diethyl ether the solution was filtered over 5 cm of silica gel (diameter 15 mm) and the silica gel washed with 100 ml of pentane/diethyl-ether (1 : 1). The residue was bulb-to-bulb-distilled at 20 Pa yielding 2.64 g (78%) of colorless product, mp 20°C. The mixture of isomers was not separated. – IR (film): $\tilde{\nu}$ = 1715 cm^{-1} (C=O), 1630 (C=C). – ^1H NMR ($CDCl_3$) (major isomer): δ = 1.33 (s, 6H), 1.85 (quint, *J* = 7 Hz, 2H), 2.3 (m, 4H), 2.76 (m, 2H), 3.73 (s, 3H), 6.97 (t, *J* = 3.7 Hz, 1H). – ^{13}C NMR ($CDCl_3$) (major isomer): δ = 21.9 (t), 25.9 (q), 28.2 (t), 30.6 (t), 35.3 (t), 35.9 (s), 51.0 (q), 127.8 (s), 136.6 (d), 137.0 (s), 141.5 (s), 167.4 (s). – MS (70 eV): *m/z* (%) = 206 (29) [M^+], 191 (100) [$M^+ - CH_3$].

$C_{13}H_{18}O_2$ (206.3) Calcd. C 75.69 H 8.80
Found C 75.74 H 8.95

5,5,6,6-Tetracyano-4,4,7-trimethyl-4,5,6,7-tetrahydroindan: A mixture of **6** and **7** (3.00 g, 22.0 mmol) was treated in THF (7.0 ml) with TCNE (1.56 g, 12.2 mmol). The initially strongly exothermic reaction was analyzed by GC after 20 min. Diene **6** had reacted, and one product had been formed. Removal of all volatile material at 20 Pa gave 3.31 g of a yellow, viscous oil. Crystallization from tetrachloromethane/pentane yielded 2.66 g (83% relative to TCNE) of colorless crystals with mp 88°C. – IR (KBr): $\tilde{\nu}$ = 2250 cm^{-1} (C≡N). – ^1H NMR ($CDCl_3$): δ = 1.54 (s, 3H), 1.56 (d, *J* = 7 Hz, 3H), 1.65 (s, 3H), 1.96 (quint, *J* = 8 Hz, 2H), 2.5 (m, 4H), 3.22 (m, 1H). – ^{13}C NMR ($CDCl_3$): δ = 15.7 (q), 21.4 (t), 24.3 (q), 27.5 (q), 32.4 (t), 33.9 (t), 37.8 (d), 41.5 (s), 44.8 (s), 50.2 (s), 110.3 (s), 110.8 (s), 112.2 (s), 131.6 (s), 138.5 (s). – MS (70 eV): *m/z* (%) = 264 (11) [M^+], 249 (3), 136 (100), 121 (29), 107 (12), 93 (14), 77 (11).

$C_{16}H_{16}N_4$ (264.3) Calcd. C 72.70 H 6.10 N 21.20
Found C 72.49 H 6.05 N 21.20

Dimethyl 4,4,7-Trimethyl-4,7-dihydroindan-5,6-dicarboxylate (**26**): 0.70 g (5.0 mmol) of **6** and 0.73 g (5.0 mmol) of dimethyl acetylenedicarboxylate in 10 ml of THF were heated under reflux for 24 h. Removal of the solvent and bulb-to-bulb distillation (bath temp. 100°C and 10 Pa) gave 1.32 g (92%) of **26**. – IR (film): $\tilde{\nu}$ = 1725 cm^{-1} (C=O), 1630 (C=C). – ^1H NMR ($CDCl_3$): δ = 1.11 (d, *J* = 7 Hz, 3H), 1.13 (s, 3H), 1.36 (s, 3H), 1.88 (quint, *J* = 8 Hz, 2H), 2.1–2.6 (m, 4H), 3.26 (q, *J* = 7 Hz, 1H), 3.76 (s, 3H), 3.78 (s, 3H). – ^{13}C NMR ($CDCl_3$): δ = 19.1 (q), 22.0 (t), 24.8 (q), 28.2 (q), 30.9 (t), 32.5 (d), 33.5 (t), 37.2 (s), 51.7 (q), 51.9 (q), 133.4 (s), 134.8 (s), 138.3 (s), 146.5 (s), 167.5 (s), 169.5 (s). – MS (70 eV): *m/z* (%) = 278 (6) [M^+], 263 (10), 247 (28), 246 (27), 231 (100), 219 (100).

$C_{16}H_{22}O_4$ (278.3) Calcd. C 69.04 H 7.97
Found C 68.83 H 8.04

Methyl 4,4,7-Trimethyl-4,7-dihydroindan-5-carboxylate (**27a**) *and Methyl 4,4,7-Trimethyl-4,7-dihydroindan-6-carboxylate* (**27b**): 0.7 g (5.0 mmol) of **6** and 0.43 g (5.0 mmol) of methyl propiolate were allowed to react in 5 ml THF for 15 d under reflux. After removal of the solvent the oily product was bulb-to-bulb-distilled at a bath temp. of 80°C and 20 Pa; yield 0.86 g (76%) of a colorless oil. The ratio of **27a** : **27b** was determined by ^1H NMR in a separate experiment. The mixture was chromatographed on silica gel with tetrachloromethane as eluent. The first compound obtained was **27a**. **27b** was recovered by subsequent elution with diethyl ether.

$C_{14}H_{20}O_2$ (220.3) (mixture of **27a, b**) Calcd. C 76.33 H 9.15
Found C 76.82 H 8.87

27a: IR (film): $\tilde{\nu}$ = 1720 cm^{-1} (C=O), 1630 (C=C). – ^1H NMR ($CDCl_3$): δ = 1.12 (d, *J* = 7 Hz, 3H), 1.31 (s, 3H), 1.33 (s, 3H), 1.84 (quint, *J* = 7 Hz, 2H), 2.1–2.5 (m, 4H), 2.8 (m, 1H), 3.73 (s, 3H), 6.84 (d, *J* = 3.5 Hz, 1H). – ^{13}C NMR ($CDCl_3$): δ = 19.6 (q), 22.0 (t), 25.6 (q), 26.9 (q), 30.9 (t), 32.6 (q), 33.5 (t), 36.1 (s), 51.2 (q), 133.0 (s), 136.1 (s), 141.2 (s), 142.7 (d), 167.8 (s). – MS (70 eV): *m/z* (%) = 220 (38) [M^+], 205 (91), 161 (100).

27b: IR (film): $\tilde{\nu}$ = 1715 cm^{-1} (C=O), 1635 (C=C). – ^1H NMR ($CDCl_3$): δ = 1.12 (s, 3H), 1.13 (d, *J* = 7 Hz, 3H), 1.13 (s, 3H), 1.86 (quint, *J* = 7 Hz, 2H), 2.0–2.6 (m, 4H), 3.10 (q, *J* = 7 Hz, 1H), 3.76 (s, 3H), 6.74 (d, *J* = 0.7 Hz, 1H). – ^{13}C NMR ($CDCl_3$): δ = 20.2 (q), 22.1 (t), 27.5 (q), 28.1 (q), 30.7 (t), 31.8 (d), 33.6 (t), 35.6 (s), 51.5 (q), 131.7 (s), 136.2 (s), 138.1 (s), 147.5 (d), 168.0 (s). – MS (70 eV): *m/z* (%) = 220 (22) [M^+], 205 (100) [$M^+ - CH_3$].

Kinetic Measurements: 0.5 ml of an exactly 0.1 M solution of the diene, to which octane had been added as standard, and 0.5 ml of an equimolar solution of the diene were mixed and heated at 80.0 ± 0.2°C in sealed ampoules. At least 8 ampoules were prepared for each run, and each measurement was repeated three times. The decrease of the diene was monitored by GLC, and each measurement was followed to at least 85% completion. The rate constants for the Diels-Alder reactions are collected in Table 2.

5-Cyano-4,7-dihydroindan (**14**): 0.47 g (5.0 mmol) of **1** and 0.27 g (5.0 mmol) of acrylonitrile were allowed to react in 10 ml of THF at room temp. for 140 h. Recrystallization of the crude product after removal of the solvent gave 0.62 g (84%) of product. – ^1H NMR ($CDCl_3$): δ = 1.30–2.15 (br. m). – ^{13}C NMR ($CDCl_3$): δ = 21.91 (t, C-1), 25.25 (d, C-2), 26.19 (t), 35.72 (t), 29.25 (t), 122.23 (s, CN), 130.90 (s), 134.11 (s).

5,6-Dicyano-4,7-dihydroindan (**15**): 0.47 g (5.0 mmol) of **1** and 0.39 g (5.0 mmol) of fumaronitrile reacted in 10 ml of THF for 140 h. Removal of solvent and recrystallization from diethyl ether at –80°C gave 0.70 g (88%) of product with mp 98°C. – ^1H NMR ($CDCl_3$): δ = 1.45–1.95 (br. m). – ^{13}C NMR ($CDCl_3$): δ = 21.69 (t, C-1), 27.38 (t, C-4), 35.32 (t, C-2 and C-9), 27.99 (d, C-5 and C-6), 119 (s, CN), 131.09 (s, C-3 and C-8).

5,5,6,6-Tetracyano-4,4-dimethyl-4,5,6,7-tetrahydroindan (**25**): To 1.00 g (8.2 mmol) of **5** was slowly added 1.05 g (8.2 mmol) of tetracyanoethylene, dissolved in 7 ml of THF, at room temp. After 30 min the solvent was removed, and 2.01 g (98%) of adduct with mp 106–108°C was isolated. – ^{1}H NMR (CD_2Cl_2): δ = 1.62 (s, 6H, CH_3), 1.95 (quint, J = 8 Hz, 2H), 2.49 (t, J = 8 Hz, 4H), 3.15 (s, 2H).

$C_{15}H_{14}N_4$ (250.3)	Calcd.	C 71.98	H 5.64	N 22.38
	Found	C 71.53	H 5.75	N 22.29

A separate experiment on an NMR scale in CD_2Cl_2 was carried out at −70°C. After mixing equimolar amounts at −70°C and transferring the tube with the solution to the precooled NMR spectrometer (−70°C) the recorded spectrum corresponded already to that of the final product. No other signals were detected, excluding an intermediate (2 + 2) adduct which might rearrange to the (4 + 2) product.

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1: 20968-70-1 / **2**: 121013-07-8 / **3**: 92013-63-3 / **4**: 121013-08-9 / **5**: 121013-09-0 / **6**: 121013-10-3 / **7**: 121013-11-4 / **9**: 26343-69-1 / **14**: 121013-12-5 / **15**: 121013-13-6 / **16**: 121013-14-7 / **17**: 121013-15-8 / **18**: 121013-16-9 / **19**: 121013-17-0 / **20**: 121013-18-1 / **21**: 121013-19-2 / **22**: 121013-20-5 / **23**: 121013-21-6 / **24a**: 121013-22-7 / **24b**: 121013-25-0 / **25**: 121013-23-8 / **26**: 121013-24-9 / **27a**: 121013-27-2 / **27b**: 121013-28-3 / TCNE: 670-54-2 / acrylonitrile: 107-13-1 / fumaronitrile: 764-42-1 / 2-isopropylidenecyclopentanone: 2758-17-0 / methyl propiolate: 922-67-8 / dimethyl acetylenedicarboxylate: 670-54-2 / 5,5,6,6-tetracyano-4,4,7-trimethyl-4,5,7-tetrahydroindan: 121013-26-1 / cycopentanone: 120-92-3 / 2-(dimethylamino)methylcyclopentanone: 6947-99-5 / trimethyl[(2-methylenecyclopentyl)methyl]ammonium iodide: 121013-29-4

[1] P. D. Bartlett, A. S. Wingrove, R. Owyang, *J. Am. Chem. Soc.* **90** (1968) 6067.
[2] H. D. Scharf, H. Plum, J. Fleischhauer, W. Schieker, *Chem. Ber.* **112** (1979) 862.
[3] R. Sustmann, M. Boehm, J. Sauer, *Chem. Ber.* **112** (1979) 883.
[4] P. V. Alston, R. M. Ottenbrite, *J. Org. Chem.* **41** (1976) 1635.
[5] A. Chollet, C. Mahaim, C. Foetisch, M. Hardy, P. Vogel, *Helv. Chim. Acta* **60** (1977) 59.
[6] M. Strecker, M. Klessinger, K. Wilhelm, *Org. Magn. Reson.* **17** (1981) 153.
[7] H.-U. Pfeffer, M. Klessinger, *Chem. Ber.* **112** (1979) 890.
[8] J. Sauer, R. Sustmann, *Angew. Chem.* **92** (1980) 773; *Angew. Chem. Int. Ed. Engl.* **19** (1980) 779.
[9] W. J. Bailey, W. R. Sorenson, *J. Am. Chem. Soc.* **76** (1954) 5421.
[10] C. L. Kirkemo, J. D. White, *J. Org. Chem.* **50** (1985) 1316.
[11] A. T. Blomquist, J. Wolinsky, Y. C. Meinwald, D. T. Longone, *J. Am. Chem. Soc.* **78** (1956) 6057.
[12] R. B. Bates, B. Gordon III, T. K. Highsmith, J. J. White, *J. Org. Chem.* **49** (1984) 2981.
[13] J. W. van Straten, J. J. van Norden, T. A. M. van Schaik, G. T. Franke, W. H. de Wolf, F. Bickelhaupt, *Recl. Trav. Chim. Pays-Bas* **97** (1978) 105.
[14] W. A. Nugent, J. C. Calabrese, *J. Am. Chem. Soc.* **106** (6422) 1984.
[15] R. Sauer, *Dissertation*, Universität Essen, 1988.
[16] P. Daute, *Dissertation*, Universität Essen, 1988.
[17] P. Asmus, M. Klessinger, *Tetrahedron* **30** (1974) 2477.
[18] A. Sommer, *Diplomarbeit*, Universität Essen, 1988.
[19] I. Fleming, *Frontier Orbitals and Chemical Reactions*, Wiley & Sons, New York 1976.
[20] C. Rücker, D. Lang, J. Sauer, H. Friege, R. Sustmann, *Chem. Ber.* **113** (1980) 1663.
[21] C. A. Stewart, *J. Am. Chem. Soc.* **84** (1962) 117.
[22] W. S. Trahanovsky, unpublished results.
[23] H. Booth, F. E. King, K. G. Mason, J. Parrick, R. L. S. D. Whitehead, *J. Chem. Soc.* **1959**, 1050.
[24] R. Mayer, *Chem. Ber.* **88** (1955) 1853.
[25] J. T. Sharp, R. H. Findlay, P. Thorogood, *J. Chem. Soc., Perkin Trans. 1*, **1975**, 102.
[26] L. Birkofer, M. K. Sung, H. D. Engels, *Chem. Ber.* **95** (1962) 1495.
[27] R. Cornubert, C. Borrel, *Chem. Abstr.* **25** (1931) 508.
[28] G. Vavon, A. Apchie, *Bull. Soc. Chim. Fr.* **43** (1928) 667.
[29] N. Ono, R. Tamura, T. Nakatsuka, J. Hayami, A. Kaji, *Bull. Chem. Soc. Jpn.* **53** (1980) 3295.

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