Tetraacylethenes as Dienophiles and Hetero Dienes in Two-Step Diels–Alder Reactions

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Oxidation with barium manganate of the enol of tetraacetylethane (**10**) affords tetraacetylethylene (**7a**) in good yield. Treatment of the 1,3-diketones **15a** and **b** with iodosobenzene in the presence of boron trifluoride does *not* result in oxidative coupling yielding **10** and diacetyldibenzoylethane **17**, respectively, as has been reported by Moriarty et al. Instead the known difluoroborylenolates **16** are formed. Oxidative coupling of the sodium enolate of **15b** with iodine affords the *meso*-tetraketone *meso*-**17** and diacetyldibenzoylethylene (*E*)-**7b** besides small amounts of *rac*-**17** and the bisenol **19**. In the presence of 1,4-diazabicyclo[2.2.2]octane, *meso*-**17** and **19** tautomerise yielding identical equilibrium mixtures of *meso*-**17**, *rac*-**17**, and **19** (26:29:45). Dehydrogenation with 5,6-dichloro-2,3-dicyanobenzoquinone of *meso*-**17** yields (*E*)-**7b** and an isomer (77:23) which was assigned structure (*Z*)-**7b** on the basis of spectroscopic evidence. – Tetraacetylethylene (**7a**) reacts with 1,2-dimethylenecyclohexane to afford two different [4+2]cycloadducts, viz. the spirocyclic dihydropyran **25** (30 %) and the tetraacetyloctalin **27**. Whereas the latter is stable, the former isomerises to the latter on heating. Formation of both [4+2]cycloadducts and the isomerisation **25** → **27** are interpreted by invoking the zwitterion **26** as common intermediate. Monoolefines that cannot generate stable carbenium ions don't give [4+2]cycloadducts with **7a**. In contrast, α-methylstyrene yields the oxa Diels–Alder product **30**. The structures of (*E*)-**7b**, **19**, **25**, and **27** are established by X-ray diffraction analyses.

Introduction

Tetra*cyano*ethylene (**1**) is the archetype of strongly electron-deficient ethylenes and undergoes a host of cycloaddition reactions.[1] Other electron-deficient ethylenes, e.g. ethylene tetracarboxylates (**4**), are less prone to cycloadditions,[2] in part because steric strain is developed during these reactions. Much less is known about tetra*acyl*ethylenes. In fact only two compunds of this type have been described. Tetra*acetyl*ethylene (**7a**) has been synthesised by Adembri, Scotton et al.[3][4] Tetra*benzoyl*ethylene has been obtained in several ways from dibenzoylmethane[5] or by oxidative cleavage of 3,4-dibenzoyl-2,5-diphenylfuran with cerium(IV) ammonium nitrate.[6] We became interested in [4+2] cycloaddition reactions of diacetyldiacylethylenes **7**, because the intramolecular aldol reaction of the cycloadducts **8** might provide a novel access to functionalised [4.3.3]propellanes **9**.[7] This approach appeared attractive since the analogous [4+2]cycloadducts **2**[8] and **5**[9] served as precursors to the hetero[4.3.3]propellanes **3** and **6**, respectively, and many examples of intramolecular aldol reactions that yield cyclopentenones are known.[10] Although the final goal could not be reached, the results of the present study merit interest in their own right. We describe here an improved, convenient preparation of tetraacetylethylene and the first synthesis of diacetyldibenzoylethylene (**7b**). Conflicting reports on the long-known oxidative coupling of benzoylacetone (**15b**) are in part clarified. Eventually, **7a** turned out to be a mechanistic chameleon which gave two different Diels−Alder products with 1,2-dimethylenecyclohexane by reacting as an electron-deficient dienophile and as an 1-oxa-1,3-diene as well, probably via a zwitterionic intermediate.

Results and Discussion

The simple synthesis of tetraacetylethylene from the readily available enol of tetraacetylethane (**10**)[11] by oxidation of the thallium enolate **12** with iodine[3][4] has been repeated several times[12][13] although the reaction is rendered very inconvenient by the formation of large amounts of thallium iodide waste arising as a very fine powder that is difficult to remove from the product and the equipment, and, of course, to dispose of. Attempts to avoid this problem by a synthesis from bromoacetylacetone (**13b**) patterned upon the preparation of ethylene tetracarboxylates from bromomalonates,[14] have met with failure.[3] Oxidation, by iodine, of **10**, previously treated with sodium ethoxide, was equally unsuccessful.[3] Only recently, a second method has been reported, i.e. the cerium-mediated electrochemical oxidation

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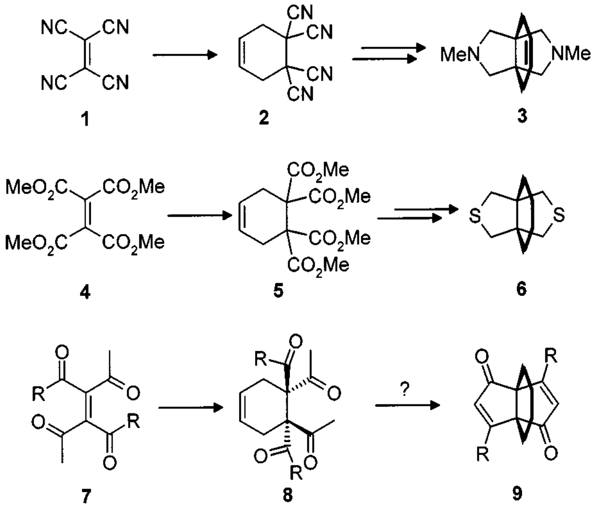
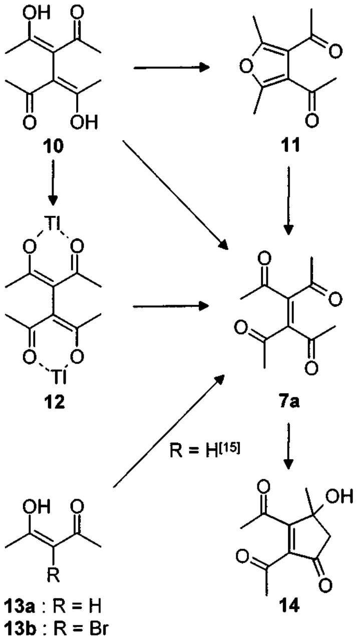


	R
7a – 9a	Me
7b – 9b	Ph



of acetylacetone,[15] which, however, requires special equipment. The difficulties encountered in the chemical oxidation of **10** can be traced back to the sensitivity towards base of both the starting material **10** and the product **7a**. The former undergoes cyclisation to yield 3,4-diacetyl-2,5-dimethylfuran (**11**) in the presence of lithium hydroxide, sodium ethoxide, or potassium carbonate,[16] the latter forms the base-induced cyclic aldol adduct **14**[4] and complex products derived thereof.[17]

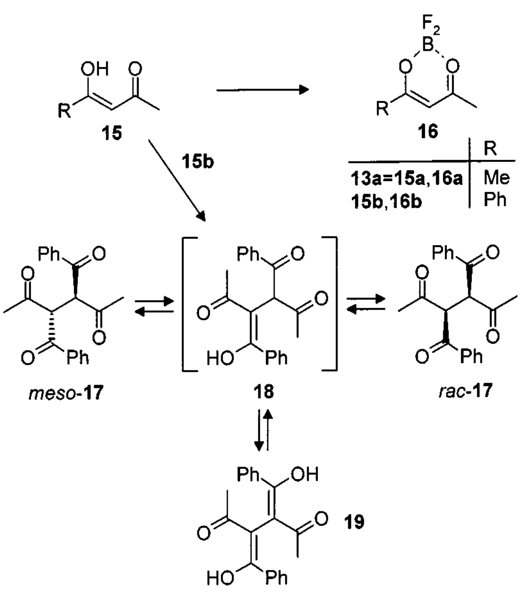
Oxidative cleavage with cerium(IV) ammonium nitrate of a highly substituted furan to yield tetrabenzoylethylene has been reported by Lepage and Lepage.[6] This reagent converted the furan **11** into a mixture of four products (HPLC) from which **7a** could be isolated in 13% yield by recrystallisation. Attempts at the oxidative cleavage of **11** with 3-chloroperbenzoic acid or pyridinium chlorochromate[18] furnished only small amounts of **7a** after extended reaction periods.

A number of reagents were tried for the direct oxidation of **10** to **7a**. Manganese dioxide,[19] lead tetraacetate,[20] ruthenium tetroxide,[21] nickel peroxide,[22] potassium ferrate,[23] and 5,6-dichloro-2,3-dicyanobenzoquinone[24] failed to produce more than tiny amounts of **7a**. By contrast, promising results were obtained with a suspension of barium manganate in dichloromethane as solvent.[25] Monitoring of the conversion with HPLC revealed the initial rise of **7a**, which slowly disappeared with the formation of the cyclic aldol adduct **14**. This problem was avoided by the addition of small amounts of acetic acid, which served to neutralise basic impurities in the barium manganate. Ultrasonic irradiation of the suspension considerably accelerated the oxidation. Thus, a simple and efficient protocol avoiding toxic waste was developed for the direct conversion of **10** into **7a**, which could be obtained in 69% yield after recrystallisation from ethyl acetate.

Whereas the coupling product of acetylacetone (**15a**) exclusively exists as bisenol **10** in the solid state,[26] conflicting reports have been published on the oxidative coupling of the enol derived from benzoylacetone (**15b**), carried out for the first time by Fischer and Bülow more than a century ago.[27] Coupling has been performed by oxidation of the sodium enolate with iodine[27–30] or anodic oxidation of the potassium enolate,[31] anodic oxidation of **15b**,[32], and oxidation of **15b** with dibenzoylperoxide[33] or iodosobenzene in the presence of boron trifluoride.[34] The coupling product was also obtained by the reaction of the sodium enolate of **15b** with 2-bromo-1-phenyl-1,3-butanedione.[35] An unusual number of different melting points have been reported in the literature for the coupling product of **15b**. The highest melting point (197.5−199.5°C) belongs to the tetraketone *meso*-**17** whose structure has been established unequivocally by an X-ray diffraction analysis.[29] The lower melting points are apparently indicative of different structures.

A much lower melting point (155°C) was reported by Moriarty and coworkers for a product, claimed to be **17** (without assignment of configuration), which they had obtained from benzoylacetone by a novel method of oxidative coupling involving treatment with iodosobenzene in the presence of boron trifluoride−diethyl ether.[34] Unfortunately, their alleged coupling product turned out to be the long-known product **16b** of benzoylacetone and boron trifluoride (m.p. 157°C).[36] This became now evident by a comparison of the compound that was obtained according to Moriarty's procedure with an authentic sample of **16b**. Likewise, acetylacetone did *not* undergo oxidative coupling with iodosobenzene in the presence of boron trifluoride−diethyl ether to afford **10** as claimed[34] but yielded the known difluoroboryloxypentenone **16a**.[36]

Lacán et al. reported melting points of 178−180°C for a tetraketone presumed to be the *meso* diastereomer *meso*-**17** and of 144−146°C for golden-yellow needles considered as bis-enol **19**. The structures were assigned on the basis of proton, IR, and UV/Vis spectra.[31] Oxidation with iodine of the sodium enolate of benzoylacetone suspended in di-



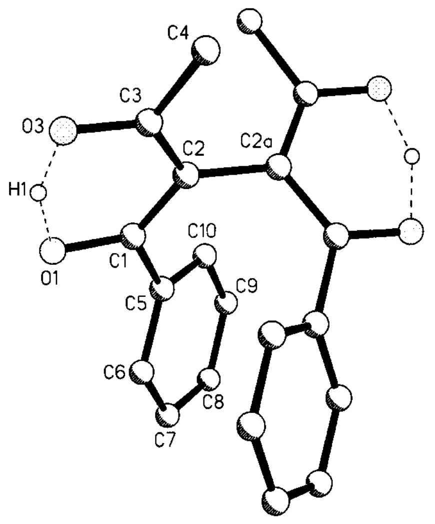


Figure 1. Stereographic projection of the bis-enol **19** with the numbering of the atoms

ethyl ether according to Fischer and Bülow[27][29] gave a precipitate in modest yield (21%) which contained *meso*-**17** and, surprisingly, (*E*)-**7b** (7:3 to 8:2, ^{1}H NMR). Recrystallisation from ethyl acetate furnished pure *meso*-**17** (m.p. 196−198 °C, 11%), which does not react with iron(III) chloride and does not undergo H/D exchange on treatment with deuterium oxide.[29] Surprisingly, repeated recrystallisation of the crude product from *ethanol*, as described by Fischer and Bülow,[27] did not remove but enriched (*E*)-**7b** to yield a colourless powder with a melting range 168−180 °C that consisted of *meso*-**17** and (*E*)-**7b** in the ratio 3:2.

Slow evaporation of the solvent from the reaction mixture after removal of the solid material yielded a brown, viscous, oily precipitate containing predominantly benzoylacetone and *rac*-**17** (3:2) besides small amounts of (*E*)-**7b**, *meso*-**17** and several unidentified minor products (^{1}H NMR, HPLC). A small amount (1%) of pale yellow, coarse crystals formed slowly, which melted at 170−175 °C. The NMR spectra of this minor by-product indicated a structure of twofold symmetry and the characteristics of a bis-enol. It gave an intense violet colour with iron(III) chloride.

The bis-enol structure **19** was confirmed by an X-ray diffraction analysis (Figure 1). Both halves of **19** are substantially planar and strongly twisted around the central carbon−carbon bond, and may be superimposed by the operation of a glide reflection plane. In the solid state, bis-enol **19** closely resembles bis-enol **10** which has been studied by X-ray crystallography and neutron diffraction.[26]

In the absence of base, solutions of both tautomers *meso*-**17** and **19** in inert solvents are stable for hours. The availability and unequivocal characterisation of *meso*-**17** and **19** offered the opportunity to investigate the base-catalysed equilibration by approach from both sides. Toward this end, high-field proton and ^{13}C spectra were recorded for solutions of *meso*-**17** and **19** in [D]trichloromethane in the presence of 1,4-diazabicyclo[2.2.2]octane (Figure 2). From both tautomers, identical mixtures were obtained consisting of *meso*-**17**, **19**, and a third tautomer (26:45:29), which could be characterised spectroscopically in this way. Its proton and ^{13}C spectra showed that the molecule − like *meso*-**17** − consisted of two structurally identical halves which closely resembled those of *meso*-**17**. Therefore, the third tautomer was assigned the structure of the diastereomer *rac*-**17**. Surprisingly, the half-enolised tautomer **18**, which must be an intermediate in the equilibration, could not be detected by high-field proton or ^{13}C spectroscopy. The nature of the various compounds that melt more or less sharply in the temperature range between 170 and 180 °C[27,28,31,33,35] remains enigmatic.

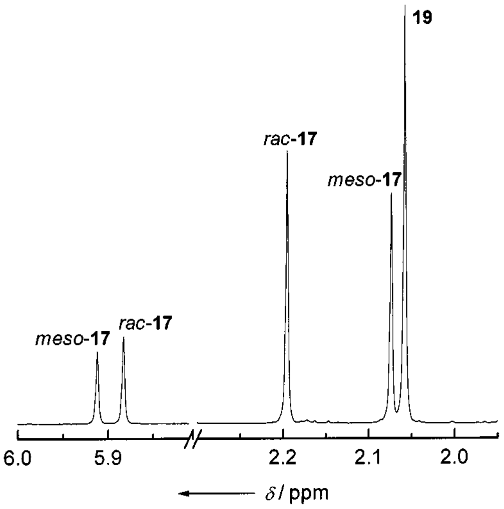


Figure 2. Proton spectra recorded for solutions of *meso*-**17** and **19** in [D]trichloromethane in the presence of 1,4-diazabicyclo[2.2.2]octane; the signals of the phenyl groups and of the hydroxy protons of **19** are not shown

A number of reagents were tried for the oxidation of tetraketone *meso*-**17** to the tetraacylethylene **7b**. Manganese dioxide and barium manganate did not react. Bromination with *N*-bromosuccinimide followed by dehydrobromination was equally unsuccessful. Eventually, oxidation was achieved by treatment of *meso*-**17** with 5,6-dichloro-2,3-dicyanobenzoquinone for extended periods of time at elevated temperatures.[24c] Flash chromatography separated the resulting mixture yielding two crystalline diastereomers. The major product, obtained in 68% yield, was assigned structure (*E*)-**7b** on the basis of spectroscopic evidence. Unequivocal proof was provided by an X-ray diffraction analysis (Figure 3). Like tetraacetylethylene (**7a**),[12] the molecule adopts a centrosymmetric conformation in the solid state in which steric and dipole-dipole repulsion between the carbonyl groups are minimised. The 3-pentene-2,5-dione moiety is planar while the benzoyl groups are strongly twisted from the central plane.

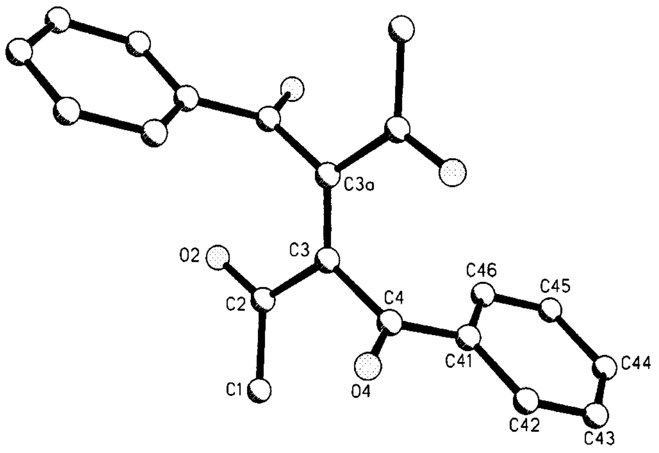
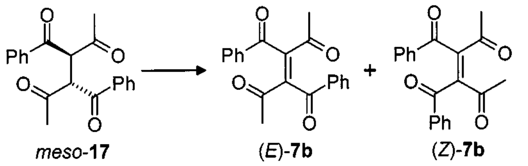
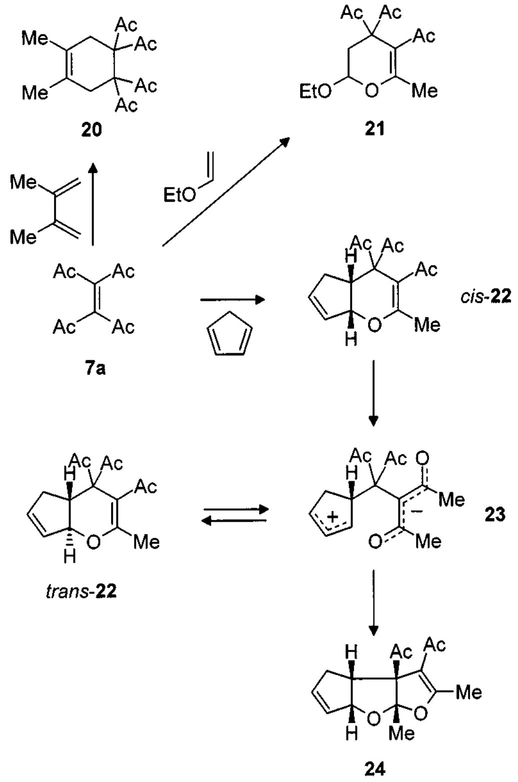


Figure 3. Stereographic projection of the tetraacylethylene (*E*)-**7b** with the numbering of the atoms

The minor diastereomer [(*Z*)-**7b**] was isolated in 20% yield. Its proton and ^{13}C spectra closely resemble those of (*E*)-**7b** and attest to the equivalence of the two acetyl and benzoyl groups. Surprisingly however, the two carbon atoms of the double bond give *two different* signals. We explain this puzzling feature in terms of one or more asymmetrical structures with the double bond in the (*Z*) configuration and different conformations for the acetyl and benzoyl groups, whose apparent equivalence is hence a matter of the NMR time scales. Rotation around the bond between a single carbonyl group and a central carbon atom is probably fast but exchange of the two central carbon atoms requires geared rotation of all four groups, a process which apparently occurs only slowly.



The Diels–Alder chemistry of tetraacetylethylene is far from being completely understood. Obviously, it is strongly electron-deficient and hence may be anticipated to react as 1-oxa-1,3-butadiene with electron-rich alkenes in hetero Diels–Alder reactions with inverse electron demand[37] or as dienophile in normal Diels–Alder reactions. The only example of the latter is provided by the reaction with 2,3-dimethyl-1,3-butadiene yielding **20**.[3][38] Other common dienes, viz. 1,3-butadiene itself, anthracene, hexachlorocyclopentadiene, and diphenylfulvene, reacted only slowly or not at all. On the other hand, ethyl vinyl ether afforded the expected dihydropyran **21**.[39] Cyclopentadiene also yielded a dihydropyran (*cis*-**22**). This result was interpreted in terms of unfavourable interactions between the acetyl groups that would render the hypothetical alternative Diels–Alder adduct tetraacetylnorbornadiene unstable.[40] Under a variety of reaction conditions, *cis*-**22** undergoes rearrangements to *trans*-**22** and the tricyclic isomer **24**, presumably via the zwitterionic intermediate **23**.[40][41]



We employed the readily available 1,2-dimethylenecyclohexane[42] because of its permanently cisoid geometry.[43] The reaction with tetraacetylethylene (**7a**) in acetonitrile solution at 65°C was monitored by HPLC and was complete in two days. Two cycloadducts were obtained as colourless crystals, m.p. 125–127°C (50%) and m.p. 104–106°C (30%), after separation by flash chromatography, besides small amounts (18%) of the known intramolecular aldol adduct **14**.[4] The structures **27** for the higher melting cycloadduct and **25** for the lower melting one were based on spectroscopic evidence and eventually established by X-ray diffraction analyses (Figures 4 and 5).

The formation of the two cycloadducts demonstrates that **7a**, with the same reagent and under the same conditions, formally reacts as both, dienophile *and* hetero diene. The clue to a rationalisation of this mechanistic bifurcation was provided by thermal equilibration experiments which were monitored by HPLC and proton spectroscopy. The octalin **27** survived heating in [D$_3$]acetonitrile solution for two days without any change. In contrast, the spirocyclic dihydropy-

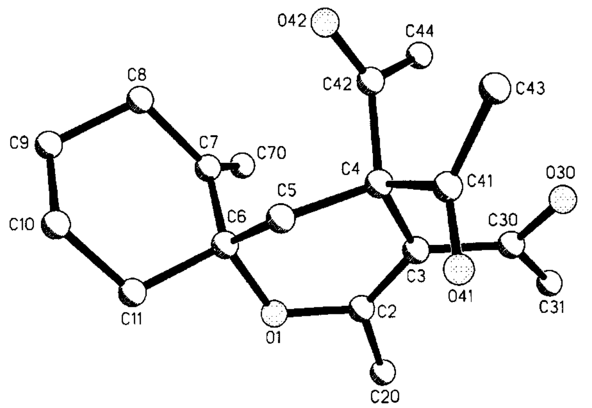


Figure 4. Stereographic projection of the spirocyclic dihydropyran **25** with the numbering of the atoms

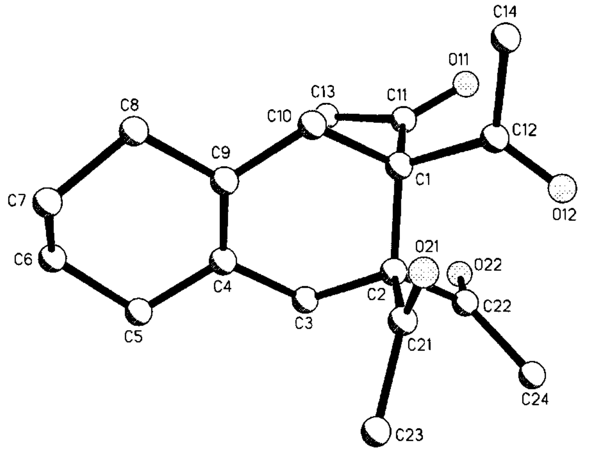
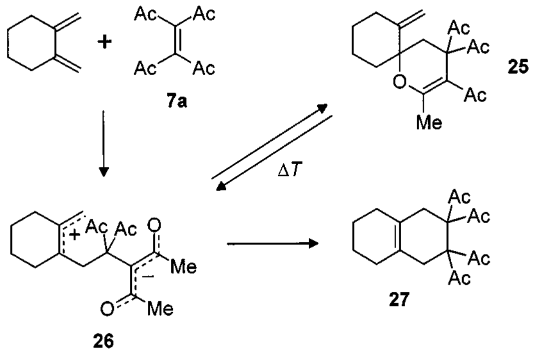
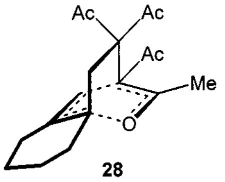


Figure 5. Stereographic projection of the tetraacetyloctalin **27** with the numbering of the atoms





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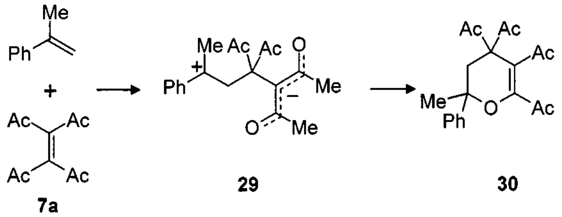
ran **25** quantitatively rearranged to **27** under these conditions. The retro Diels−Alder products 1,2-dimethylenecyclohexane and **7a** were not observed. This isomerisation represents a [3,3]sigmatropic rearrangement, more precisely, an oxa Cope rearrangement. It cannot be concerted, however, because a concerted mechanism would have to involve the highly strained, tricyclic boat transition state **28**. Therefore, we assume that the reaction occurs in two steps via the zwitterionic intermediate **26**. Zwitterions of this type offer themselves as the crucial intermediates for an explanation of the ambiguity in the Diels−Alder reaction between **7a** and 1,2-dimethylenecyclohexane, and also for the reactivity of **7a** towards other dienes[3][40] and dienophiles.[39] Similar zwitterions have been invoked as intermediates in Diels−Alder reactions of substituted 1,3-butadienes with other highly electron-deficient dienophiles, viz. tetracyanoethylene[44] and 4-phenyl-1,2,4-triazoline-3,5-dione,[45] and in Diels−Alder reactions with inverse electron demand between 1,3-dimethyl-2-alkylidenimidazolines and electron-deficient dienes.[46]

We performed a few experiments, the results of which support the mechanistic hypothesis. Obviously, the reactivity of alkenes towards **7a** should be related with stability of the cationic moiety of the zwitterions. Accordingly, the potential dienophiles methylenecyclohexane and norbornene did *not* react with **7a** when the components were heated in [D$_3$]acetonitrile solution for several days at 85°C. Only slow, undefined decomposition was observed by proton spectroscopy. In contrast, α-methylstyrene, which should give rise to the formation of a tertiary benzyl carbenium ion as the cationic moiety of the intermediate zwitterion, smoothly afforded the hetero Diels−Alder adduct **30**.



Whereas a host of examples exist for intramolecular aldol reactions yielding cyclopentenones,[10] and a compound similar to **27**, viz. 1,1,2,2-tetraacetylcyclopropane, could be cyclised in this way,[47] numerous attempts to achieve an intramolecular aldol reaction with **27** under a variety of conditions met with failure. Only a dark brown oil, which consisted of many unidentified products, resulted.

Experimental Section

General Remarks: ^{1}H NMR: Table 1. − ^{13}C NMR Table 2. − Molecular formulae and masses, and elemental analyses: Table 3. − Melting points: Kofler apparatus from Reichert, Vienna, Austria. − IR: Perkin−Elmer 1420. − ^{1}H and ^{13}C NMR: Bruker AC250. The signals of **22** were assigned by means of ^{1}H,^{1}H- and ^{13}C,^{1}H-COSY experiments. − MS (70 eV): Finnigan MAT 8200. The exact mass of **30** was determined by means of a Finnigan MAT 90 high-resolution mass spectrometer and perfluorokerosene calibration. − Flash chromatography: UV detector Knauer 87.00 (λ = 254 nm) (40 × 4)cm or (35 × 2.5)cm glass column packed with silica gel 32−63 μm (ICN Biomedicals), petroleum ether (boiling range 50−70°C) (PE)/ethyl acetate (EA), 1.8 bar N$_2$. − HPLC: Waters

M-6000A equipped with UV detector 440 (λ = 254 nm) and differential refractometer R401, (250 × 4.6)mm stainless steel column packed with silica gel LiChrosorb Si60, 5 µm (Knauer); 1.5 mL/min PE/EA (50:50), retention time (t_R) [min] = 3.0 (**10**), 5.0 (**7a**), 6.2 (**27**), 6.8 (1,2-dimethylenecyclohexane), 7.5 (**14**); 1.5 mL/min PE/EA (70:30) t_R = 3.6 (**19**), 5.0 (*meso*-**17**), 5.2 [(*E*)-**7b** and **10**], 5.4 (**16b**), 6.0 [(*Z*)-**7b**], 11.2 (**11**), 12.3 (**7a**). – Solvents were distilled under purified N_2 or Ar: Diethyl ether from NaH, toluene and dimethyl sulphoxide (15 Torr) from CaH_2, PE, dichloromethane, EA, and acetonitrile from P_2O_5. Dry acetonitrile was stored over molecular sieves (3 Å). PE and EA were eventually distilled through a 2.5-m column with stainless steel helices. – Known starting materials, reference compounds, and reagents were prepared according to literature procedures: **10**:[11] colourless crystals, m.p. 193–194°C (after repeated sublimation at 80–90°C/10^{-2} Torr). – **11**:[23b] colourless crystals, m.p. 62–63°C (from water); ^{1}H NMR: ref.[16c]; IR (KBr): $\tilde{\nu}$ = 1670 (C=O), 1602 cm^{-1} (C=C). – **16a**:[36] colourless crystals, m.p. 42–43°C (from diethyl ether); ^{1}H NMR: ref.[36]; IR (KBr): $\tilde{\nu}$ = 1550 (C=O), 1390 (B–O), 1170–1020 cm^{-1} (B–O and B–F); MS: *m/z* (%) = 148 (14) [M$^+$], 133 (26) [M$^+$ – CH_3], 129 (14) [M$^+$ – F], 128 (5), 43 (100). – **16b**:[36] colourless crystals, m.p. 156–158°C (from EA); ^{1}H NMR: ref.[36]; IR (KBr): $\tilde{\nu}$ = 1550 (C=O), 1370 (B–O), 1170–1020 cm^{-1} (B–O and B–F); MS: *m/z* (%) = 210 (66) [M$^+$], 209 (86) [M$^+$ – H], 195 (24) [M$^+$ – CH_3], 191 (13) [M$^+$ – F], 105 (100), 77 (29), 51 (12), 43 (40). – 1,2-Dimethylenecyclohexane:[42] colourless liquid, b.p. 70–72°C/135 Torr [distillation through a 30-cm Spaltrohr column (Fischer, D-53340 Meckenheim)]; ^{1}H NMR: ref.[42]; ^{13}C NMR ($CDCl_3$): δ = 26.8 (C-4, C-5), 35.3 (C-3, C-6), 107.8, 149.7 (H_2C=C); IR (neat liquid): $\tilde{\nu}$ = 1645 cm^{-1} (C=C). – Iodosobenzene.[48] – Barium manganate.[25]

Table 1. Chemical shifts (δ values) in proton spectra recorded for solutions in [D]trichloromethane

Cpd.	CH_3	CH	Ph	OH
7a	2.349			
(*E*)-**7b**	2.142		7.5 – 8.1	
(*Z*)-**7b**	2.318		7.5 – 8.1	
10	2.015			14.87
meso-**17**	2.076	5.917	7.5 – 8.2	
rac-**17**	2.196	5.883	7.3 – 8.2	
19	2.057		7.3 – 7.4	17.45

3,4-Diacetylhex-3-ene-2,5-dione (7a): Barium manganate (20.1 g, 80 mmol) was added to a solution of **10** (3.96 g, 20 mmol) and acetic acid (1.20 g, 20 mmol) in dichloromethane (250 mL). The suspension was heated under ultrasonic irradiation [Sonorex RK102 (120 W, 50 kHz), Bandelin Electronic, Berlin] and reflux for 6 h. The solid material was removed with the help of a centrifuge to give a clear blue solution. Activated carbon (7 g) was added, and the suspension was stirred until the solution turned pale yellow (ca. 1 h). The solid was removed by filtration. Distillation of the solvent i. vac. and recrystallisation from EA at –20°C afforded pale yellow needles (2.70 g, 69%), m.p. 139–140°C (ref.[3][4]: 139–140°C). – MS: *m/z* (%) = 196 (3) [M$^+$], 154 (13), 127 (9), 112 (26), 67 (15), 43 (100). – IR (KBr): $\tilde{\nu}$ = 1695, 1685 (C=O), 1645 cm^{-1} (C=C).

Oxidative Coupling of the Sodium Salt of 15b: a) A suspension of the sodium salt of **15b** (10.1 g, 58.5 mmol) in diethyl ether (200 mL) was heated under reflux for 2 h beneath iodine (7.62 g, 30 mmol), which was placed into a Soxhlet thimble, so that the iodine was leached gradually into the reaction mixture.[29] After cooling, the precipitate was isolated by filtration and suspended in water (100 mL). The suspension was stirred for 0.5 h. The solid material was isolated by filtration and dried to afford a pale yellow powder (1.15 g) consisting of (*E*)-**7b** and *meso*-**17** (2:5, ^{1}H NMR). Repeated recrystallisation from ethanol afforded a colourless powder (0.45 g, m. range 168–180°C), consisting of (*E*)-**7b** and *meso*-**17** (2:3). – Distillation of the solvent from the diethyl ether mother liquor gave a dark brown oil, consisting of **15b** and *rac*-**17** (3:2), besides small amounts of (*E*)-**7b**, *meso*-**17**, and several unidentified products.

b) The pale yellow precipitate obtained according to a) was dissolved in a mixture of EA and water (1:1, 200 mL). The org. layer was separated and dried with $MgSO_4$. Distillation of the solvent i. vac. yielded a brown solid residue (1.89 g, 21%) consisting of (*E*)-**7b** and *meso*-**17** (1:3, ^{1}H NMR). Recrystallisation from EA at 4°C afforded pale yellow crystals of *meso*-**17** (1.04 g, 11%), m.p. 196–198°C (ref.[29]: 197.5–199.5°C). – IR (KBr): $\tilde{\nu}$ = 1710, 1665

Table 2. Chemical shifts (δ values) in ^{13}C spectra recorded for solutions in [D]trichloromethane

Cpd.	CH_3	CH		C=C	C=O	*i*-C	*o*, *m*-C	*p*-C
7a	29.7			145.9	198.3			
(*E*)-**7b**	29.23			146.92	194.0 195.3	135.59	128.71 129.23	134.40
(*Z*)-**7b**	30.56			146.47 150.2	192.0 197.6	135.03	128.87 129.98	134.60
10	23.6			108.1	192.7			
11	13.6 30.6			123.3 153.9	195.7			
16a	24.1	101.9			192.5			
16b	24.7	97.5			182.9 192.7	131.2	129.02 129.21	135.5
meso-**17**	30.52	62.49			194.74 200.04	136.67	129.03 129.20	134.01
rac-**17**	30.33	62.39			194.39 199.94	136.35	128.90 128.96	133.93
19	25.04			107.97 184.15	198.00	135.93	128.03 128.18	130.89
		CH_2	quat. C					
14	26.7 30.2 31.1	52.3	75.3	136.9 177.4	195.5 200.9 203.0			
20	18.9 28.5	37.1		124.5	206.3			
25	22.6 27.9 28.8 31.7	23.1 27.6 33.0 36.4 40.5	64.0 80.9	109.1 148.9 116.1 166.6	198.3 205.2 207.5			
27	28.5	22.7 29.8 35.9	70.8	126.9	206.2			
30	22.4 27.1 28.4 29.3 31.3	41.3	65.2 79.1	116.7 164.8	199.3 206.3 207.5	142.8	125.0 128.5	127.7

cm^{-1} (C=O). − MS: *m*/*z* (%) = 322 (0.2) [M$^+$], 105 (100), 77 (37), 51 (7), 43 (14). − Slow evaporation of the solvent from the diethyl ether mother liquor obtained according to a) afforded small amounts of pale yellow, coarse crystals and a brown oily residue. Recrystallisation from diethyl ether afforded pale yellow crystals of **19** (0.09 g, 1%), m.p. 170−175°C. − MS: *m*/*z* (%) = 322 (3) [M$^+$], 304 (44) [M$^+$ − H$_2$O], 303 (52), 105 (100), 77 (54), 51 (8), 43 (28).

3,4-Bis(hydroxyphenylmethylene)hexane-2,5-dione (19): Pure *meso*-**17** (0.54 g, 1.7 mmol) was added to a stirred solution of sodium hydroxide (0.13 g, 3.4 mmol) in methanol (10 mL).[31] Stirring was continued for 20 min, and the yellow solution was poured into ice−water (100 mL). The pH value was adjusted to 4 with aq. HCl (2 M). The precipitate was isolated by filtration and dried i. vac. to afford a colourless powder [0.47 g, 87%, purity > 95% (^{1}H NMR)], m. range 146−156°C. Repeated recrystallisation from ethanol afforded a colourless powder, m. range 150−158°C, which was pure according to ^{1}H and ^{13}C NMR (ref.[31]: golden-yellow needles, m.p. 144−146°C, dec., from benzene).

4,4,5,5-Tetraacetyl-1,2-dimethylcyclohex-1-ene (20): A solution of **7a** (3.00 g, 15.1 mmol) and 2,3-dimethyl-1,3-butadiene (1.72 g, 20.4 mmol) in acetonitrile (20 mL) was stirred at 65°C for 2 d in a closed 100-mL Schlenk tube. The solution was kept overnight at −4°C to yield pale yellow crystals. Recrystallisation from PE afforded colourless crystals (1.20 g, 28%), m.p. 106−108°C (ref.[3]: 106−108°C). − ^{1}H NMR: ref.[3] − IR (KBr): ṽ = 1700 (C=O), 1650 cm^{-1} (C=C). − MS: *m*/*z* (%) = 278 (0.1) [M$^+$], 235 (5) [M$^+$ − CH$_3$CO], 175 (10), 154 (17), 112 (30), 43 (100).

3,4-Dibenzoyl-3-hexene-2,5-dione [(*E*)- and (*Z*)-7b]: A solution of *meso*-**17** (0.50 g, 1.6 mmol) and 5,6-dichloro-2,3-dicyanobenzoquinone (0.6 g, 2.6 mmol) in toluene (50 mL) was heated at 90°C for 2 d. The precipitate was isolated by filtration. The solvent was distilled i. vac. to afford a yellow solid. Flash chromatography with PE/EA (70:30) gave as first fraction a yellow solid [(*E*)-**7b**, 0.35 g, 68%]. Recrystallisation from EA afforded rodlike yellow crystals, m.p. 139−141°C. − MS: *m*/*z* (%) = 320 (3) [M$^+$], 278 (7), 236 (9), 227 (8), 105 (100), 77 (37), 51 (9), 43 (12). − IR (KBr): ṽ = 1690, 1665 cm^{-1} (C=O).

The second fraction yielded pale brown crystals [(*Z*)-**7b**, 0.10 g, 20%]. Recrystallisation from EA/hexane (1:1) afforded colourless crystals, m.p. 101−102°C. − MS: *m*/*z* (%) = 320 (2) [M$^+$], 278 (9), 236 (1), 227 (4), 105 (100), 77 (37), 51 (8), 43 (12). − IR (KBr): ṽ = 1670, 1650 (C=O), 1635 cm^{-1} (sh., C=C).

Table 3. Molecular formulae and masses, and elemental analyses

Cpd.		Molecular mass		Elemental analyses C	H
(*E*)-**7b**	$C_{20}H_{16}O_4$	320.3	calcd.	74.99	5.04
			found	74.73	5.25
(*Z*)-**7b**			found	74.75	5.05
19	$C_{20}H_{18}O_4$	322.4	calcd.	74.52	5.63
			found	74.24	5.60
25	$C_{18}H_{24}O_4$	304.4	calcd.	71.03	7.95
			found	70.57	8.34
27			found	70.80	8.12
				Exact mass	
30	$C_{19}H_{22}O_4$	314.4	calcd.	314.1518	
			found	314.1526	

[4+2]Cycloadditions of 7a and 1,2-Dimethylenecyclohexane: A solution of **7a** (0.98 g, 5.0 mmol) and 1,2-dimethylenecyclohexane (1.08 g, 10 mmol) in acetonitrile (14 mL) was heated at 65°C for 2 d in a closed 100-mL Schlenk tube. The solvent was distilled i. vac. to afford a dark brown oil. Flash chromatography of the residue with PE/EA (70:30) gave three fractions:

3,3,4,4-Tetraacetylbicyclo[4.4.0]dec-1(6)-ene (27) as pale yellow solid. Recrystallisation from PE afforded colourless crystals (0.77 g, 51%), m.p. 125−127°C. − ^{1}H NMR (CDCl$_3$): δ = 1.55−1.65 (m, 8-H$_2$, 9-H$_2$), 1.85−1.95 (m, 7-H$_2$, 10-H$_2$), 2.25 (4 CH$_3$), 2.39−2.47 (m, 2-H$_2$, 5-H$_2$). − MS: *m*/*z* (%) = 304 (0.2) [M$^+$], 261 (32) [M$^+$ − CH$_3$CO], 243 (33), 177 (15), 159 (19), 91 (11), 43 (100). − IR (KBr): ṽ = 1710, 1690 (C=O), 1655 cm^{-1} (C=C).

4′,4′,5′-Triacetyl-6′-methyl-2-methylenespiro[cyclohexan-1,2′-(3′,4′-dihydro-2*H*-pyran)] (25) as yellow oil, which was dissolved in a small amount of EA. Addition of the same volume of pentane and crystallisation from this mixture at −20°C afforded colourless crystals (0.45 g, 30%), m.p. 104−106°C. − ^{1}H NMR (CDCl$_3$): δ = 1.58−1.82 (m, 4-H$_2$, 5-H$_2$, 6-H$_2$), 1.72, 3.08 (2 d, ^2J = 13.5 Hz, 3′-H$_2$), 2.00 (6′-CH$_3$), 2.08−2.30 (m, 3-H$_2$), 2.15 (CH$_3$CO), 2.47 (2 CH$_3$CO), 4.55, 4.75 (H$_2$C=C). − MS: *m*/*z* (%) = 304 (0.8), 261 (0.5), 154 (22), 112 (36) 69 (7), 43 (100). − IR (KBr): ṽ = 1740, 1710, 1695 (C=O), 1645 cm^{-1} (C=C).

2,3-Diacetyl-4-hydroxy-4-methylcyclopent-2-en-1-on (14) as pale yellow oil (0.17 g, 18%), which crystallised slowly at 4°C. Recrystallisation from PE afforded colourless crystals, m.p. 52−54°C (ref.[4]: 53−55°C). − ^{1}H NMR (CDCl$_3$): ref.[4]

Rearrangement of 25 to 27: A solution of **25** (30 mg, 0.1 mmol) in [D$_3$]acetonitrile (0.7 mL), contained in an evacuated, flame-sealed NMR sample tube, was heated at 85−90°C. The conversion was monitored by ^{1}H-NMR spectroscopy, until **25** had disappeared (6 d). Thereupon the proton spectra indicated the presence of only **27**. Signals of the retro Diels−Alder products 1,2-dimethylenecyclohexane and **7a** could not be detected at any time.

4,4,5-Triacetyl-2,6-dimethyl-2-phenyl-3,4-dihydro-2*H*-pyran (30): a) A solution of α-methylstyrene (177 mg, 1.5 mmol) and **7a** (59 mg, 0.3 mmol) in [D$_3$]acetonitrile (0.7 mL) was heated at 80°C. The conversion was monitored by ^{1}H-NMR spectroscopy, until **7a** had disappeared (4 d). Thereupon the proton spectrum indicated the presence of **30** besides small amounts of unidentified products.

b) A solution of of α-methylstyrene (1.77 g, 15 mmol) and **7a** (0.59 g, 3 mmol) in dry acetonitrile (10 mL) was heated under reflux for 4 d. Flash chromatography of the reaction mixture with PE/EA (1:1) and distillation of the solvent i. vac. yielded a dark yellow oil (0.63 g, 67%), which was purified by repeated flash chromatography with PE/EA (7:3) to afford a pale yellow oil (0.37 g, 39%). − ^{1}H NMR (CDCl$_3$): δ = 1.51, 1.54, 2.21, 2.46, 2.52 (5 CH$_3$), 2.41 (d, 1 H), 2.74 (d, 1 H, ^2J = 14.1 Hz), 7.1−7.4 (Ph). − MS: *m*/*z* (%) = 314 (1) [M$^+$], 255 (6), 254 (12), 169 (6), 121 (13), 105 (16).

X-ray Diffraction Analyses were performed on transparent, yellow [(*E*)-**7b**], pale yellow (**19**), and colourless crystals (**25**, **27**). The cell parameters were determined on the basis of 70 reflections. The number of reflections reported in Table 4 were obtained with Mo-K_α radiation and 2 Θ_{max} = 55° (graphite monochromator, ω-scan). Measurements were carried out with a system Siemens P4. The programme SHELXTL PLUS[49] was employed. The structure was solved by direct methods and refined anisotropically by the least-squares method. The weighting scheme for R_w is $1/\sigma^2$. The positions of the hydrogen atoms were calculated by the riding model and included with isotropic descriptions.[50]

Table 4. Experimental details and results of the X-ray diffraction analyses

Cpd.		(*E*)-**7b**	**19**	**25**	**27**
Molecular formula		$C_{20}H_{16}O_4$	$C_{20}H_{18}O_4$	$C_{18}H_{24}O_4$	$C_{18}H_{24}O_4$
Molecular mass		320.36	322.36	304.42	304.42
Crystal system		monoclinic	orthorhombic	monoclinic	monoclinic
Space group		$P2_1/n$	$Pbcn$	$P2_1/c$	$P2_1/a$
a [pm]		544.7(1)	1196.6(1)	1530.5(2)	1068.6(2)
b [pm]		751.3(1)	1005.1(1)	1398.0(2)	1419.0(4)
c [pm]		2071.9(2)	1376.5(2)	771.8(2)	1091.1(3)
β [°]		94.018(9)		95.20(1)	95.68(3)
V [$10^{-6}\cdot$pm^3]		845.9(1)	1655.6(4)	1644.6(6)	1646.4(5)
Z		2	4	4	4
d(calcd.) [g cm^{-3}]		1.258	1.293	1.220	1.228
Size of crystal [mm]		0.25 × 0.25 × 0.3	0.45 × 0.35 × 0.85	0.35 × 0.45 × 0.55	0.3 × 0.35 × 0.1
Range	h	$0 \rightarrow 7$	$-1 \rightarrow 13$	$-19 \rightarrow 19$	$-13 \rightarrow 13$
	k	$0 \rightarrow 9$	$-1 \rightarrow 15$	$0 \rightarrow 18$	$0 \rightarrow 18$
	l	$-26 \rightarrow 26$	$-1 \rightarrow 17$	$0 \rightarrow 10$	$0 \rightarrow 14$
No. of measured reflections		2303	2839	4206	3922
symmetry-independent refl.		1936	1901	3759	3772
Observed refl. $F > 3\sigma(F)$		1338	1606	2442	1402
Lin. absorpt. coeff. [mm^{-1}]		0.09	0.09	0.09	0.09
Absorption correction		ψ-scan	ψ-scan	ψ-scan	ψ-scan
Ratio F_{obs}/parameters		12.16	14.09	12.27	7.01
R		0.076	0.052	0.89	0.062
R_W		0.075	0.060	0.89	0.038
Diff. Four.	$\Delta\rho_{max}$[a] [eÅ^{-3}]	0.31	0.28	0.32	0.39
	$\Delta\rho_{min}$[b]	0.34	0.23	0.35	0.36

[a] Maximum and [b] minimum of the remaining electron density in the final differential Fourier synthesis.

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[50] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-125740 (**27**), -125741 (**25**), -125742 (**19**), -125743 [(*E*)-**7b**]. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: internat. code + 44-1223/336-033, E-mail: deposit@ccdc.cam.ac.uk].

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