The cheletropic ene-reaction and its reversal; additions to 1,2,3,4-tetrachloro-5-methylenecyclohexa-1,3-diene

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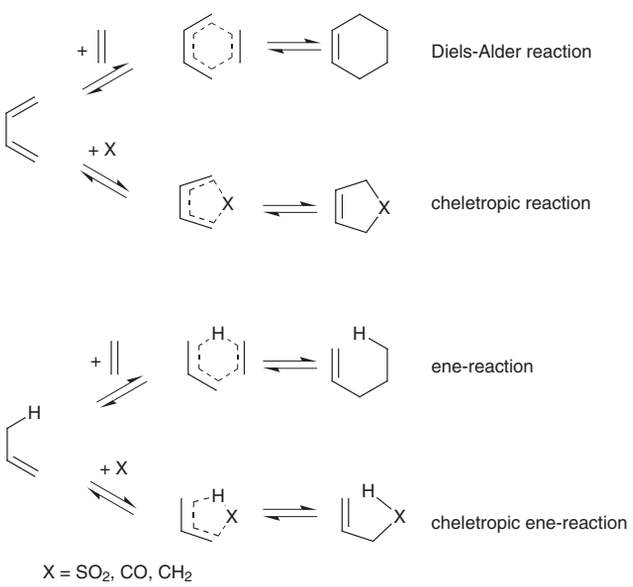
The cheletropic ene-reaction is presented as an extension of the known pericyclic additions. No example of this process is known but some decarbonylations have been discussed as its reverse. The scope of these reactions is extended by the facile decarbonylation of the alicyclic trienal **11** to give *o*-xylene. The dramatic lowering of the activation energy when an arene is formed and the finding that in this system phenyl isocyanide can also act as a chelefuge underline the pericyclic character of this reaction. In quest of a cheletropic addition to an ene 1,2,3,4-tetrachloro-5-methylenecyclohexa-1,3-diene was reacted with CO under pressure but to no avail. The reactive ene however readily adds an electron deficient ketone and molecular oxygen.

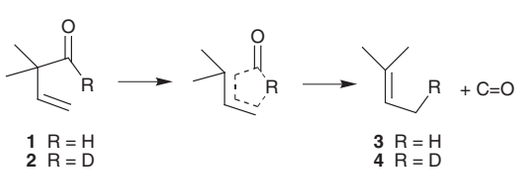
Three pericyclic addition reactions, *i.e.* the Diels–Alder reaction[1] including its 1,3-dipolar extension,[2] the cheletropic reaction[3] and the ene-reaction[4] are well recognized and broadly used in their forward and reverse sense. A fourth reaction can be envisioned to complete this set, namely the addition of a cheletropic reagent X to an ene (Scheme 1). No example of this



Scheme 1

cheletropic ene-reaction is known to the best of our knowledge but there are fragmentations that can be interpreted as the reverse of this reaction. The thermal decarbonylation of β-ketoaldehydes[5] and of β,γ-unsaturated aldehydes[6] fall into this category.

A well studied example of the latter reaction is the fragmentation of 2,2-dimethylbut-3-enal **1** into 2-methylbut-2-ene **3** and CO (Scheme 2).[7] First order kinetics, a 1,4-deuterium migration to the unsaturated terminus, a primary isotope effect and a negative crossover experiment with the 1,4,4-trideuterio derivative strongly argue for a concerted process as depicted above for the cheletropic *retro* ene-reaction.



Scheme 2

Being unaware of this study in the early stage of our work, we repeated the kinetic measurement of the decarbonylation of **1** and **2** in the gas phase from 250–330 °C and obtained parameters that exceed the limits of error of the earlier work [eqns. (1)–(3)].

$$\log k_{\mathrm{H}} = (12.38 \pm 0.07) - (41.25 \pm 0.17)/2.303\ RT \quad (1)$$

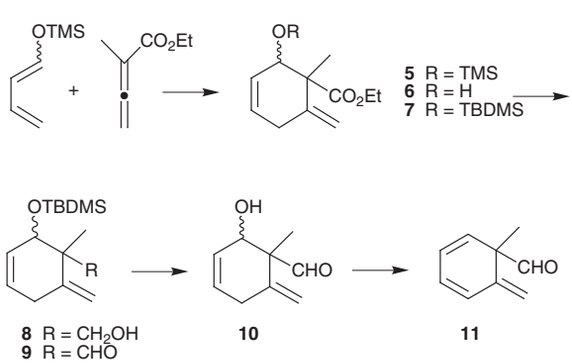
$$\log k_{\mathrm{D}} = (12.49 \pm 0.02) - (42.87 \pm 0.04)/2.303\ RT \quad (2)$$

$$k_{\mathrm{H}}/k_{\mathrm{D}} = (0.78 \pm 0.13)\exp[(1.62 \pm 0.18)/RT];$$
$$R = 1.987\ 10^{-3}\ \mathrm{kcal\ mol^{-1}\ K^{-1}} \quad (3)$$

At 300 °C $k_{\mathrm{H}}/k_{\mathrm{D}} = 3.0$ (see Experimental) which is consistent with a primary isotope effect and is similar to that found for the sigmatropic 1,5-hydrogen shift in (*Z*)-penta-1,3-diene.[8]

In pericyclic reactions the formation or translocation of a double bond occurs in the transition state whose energy is considerably lowered if the new double bond completes an aromatic system. We have applied this often used criterion for concert[9] to the cheletropic *retro* ene-reaction by studying the decarbonylation of 1-methyl-6-methylenecyclohexa-2,4-diene-1-carbaldehyde **11**.

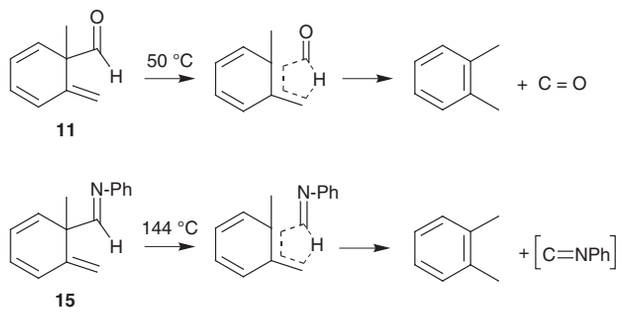
Two steps in the synthesis of **11** (Scheme 3) that starts with



Scheme 3

the cycloaddition of 1-(trimethylsilyloxy)buta-1,3-diene to ethyl 2-methylbuta-2,3-dienoate deserve a comment. i) The exchange of the protecting group for the alcohol (**5**→**7**) is necessary because the trimethylsilyl group is cleaved off under the conditions of the Swern oxidation. ii) The final dehydration (**10**→**11**) must be conducted at ambient temperature and in the absence of base due to the sensitivity of **11**. Both conditions are met by the reagent 2,4-dinitrobenzenesulfenyl chloride.[10]

In a NMR experiment the aldehyde **11** was cleanly decarbonylated to *o*-xylene at 50 °C (Scheme 4). Monitoring the



Scheme 4

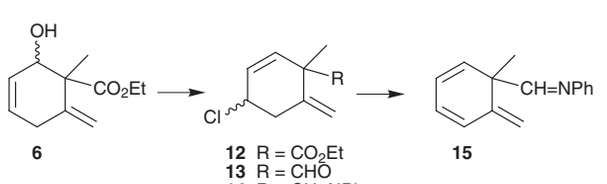
reaction in the temperature range of 64–84 °C established first order kinetics that follow the Arrhenius equation [eqn. (4)].

$$\log k = (11.2 \pm 0.33) - (22.41 \pm 0.52)/2.303\ RT; \qquad R = 1.987\ 10^{-3}\ \text{kcal mol}^{-1}\ \text{K}^{-1} \quad (4)$$

As demanded by a pericyclic transition state, the formation of an arene instead of an olefin increases the rate dramatically. The observed lowering of the activation energy by 18.9 kcal mol^{-1} falls into the range of 19–16 kcal mol^{-1} that is found for (4+2)-cycloreversions[11] and dyotropic hydrogen migrations[12] if an arene is formed instead of an olefin. This analogy with other well established pericyclic reactions is a strong argument for the concertedness of the *retro* cheletropic ene-reaction but the resonance stabilization of the cyclohexadienyl radical formed from **11** by a stepwise process should also effect a rate enhancement. The radical process, however, does not agree with the negative result of the crossover experiment with **1** and its 1,4,4-trideuterio derivative. Interestingly, in pericyclic reactions that occur with the cleavage of only one σ-bond (sigmatropic rearrangments or electrocyclic ring openings), the formation of a benzene ring lowers the activation energy by only about 10 kcal mol^{-1}.[13]

A force field calculation[14] showed the decarbonylation of the triene aldehyde **11** to be exothermic by −26.5 kcal mol^{-1}. This high driving force raises the question of whether another divalent species can act as a chelefuge in this system also. An isocyanide appeared a possible candidate as its extrusion would be accompanied by a loss of −16 kcal mol^{-1}. Accordingly, we have prepared the *N*-phenylimine **15** of the triene aldehyde **11** and studied its thermolysis.

As the direct coupling of the labile aldehyde **11** with aniline is not possible, this step was performed at an earlier stage of the synthesis (Scheme 5). Starting with the free alcohol **6,**

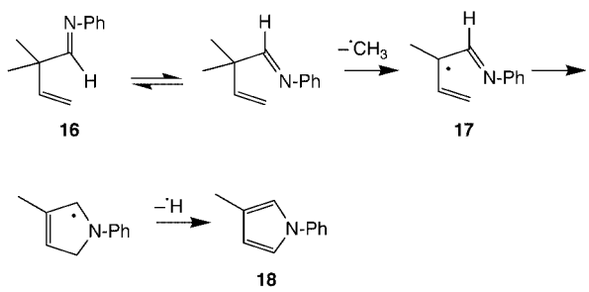


Scheme 5

chlorination with thionyl chloride occurred predominantly with allylic migration of the double bond. Reduction of the ester group in chloride **12** with DIBAL-H resulted in the aldehyde **13** which was coupled with aniline to the phenylimine **14**. The final dehydrochlorination could be performed with Schwesinger's phosphazene base[15] as the resulting triene imine **15** is less sensitive towards base than the parent aldehyde.

In an NMR experiment the imine **15** gave *o*-xylene in a clean reaction at 144 °C (Scheme 4). No other product could be detected but a colorless film formed on the wall of the NMR tube. We assume it to be a polymer of the unstable phenyl isocyanide[16] which does not isomerize to benzonitrile under the reaction conditions.[17] The fragmentation of the imine (Scheme 4) occurs with first order kinetics and the rate constant $k = 3.5\ 10^{-4}\ s^{-1}$ was derived; it is 650 times smaller than that extrapolated for the decarbonylation of the parent aldehyde.

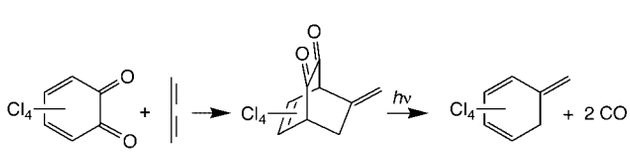
The successful exchange of CO by phenyl isocyanide in this exothermic cheletropic *retro* ene-reaction led us to examine also the thermolysis of the phenylimine **16** of the parent 2,2-dimethylbut-3-enal **1**. This reaction is endothermic by +9 kcal mol^{-1} [14] but the gain in entropy should favor the fragmentation. The imine **16** was prepared by the conventional method and submitted to a vacuum flash pyrolysis. At 500 °C a clean demethylation and cyclization to 3-methyl-*N*-phenylpyrrole **18** occured, accompanied by traces of benzonitrile, the expected rearrangement product of any extruded phenyl isocyanide (Scheme 6). Apparently, the breaking of a methyl bond to



Scheme 6

form the (*Z*)-azapentadienyl radical **17** is favored over the cheletropic *retro* ene-reaction. The radical undergoes an electrocyclization and loses a hydrogen atom to give the observed pyrrole.

The low activation barrier of cheletropic *retro* ene-reactions that form an aromatic system should also be observed for the forward reaction if aromaticity is gained. *o*-Isotoluene (5-methylenecyclohexa-1,3-diene) appears a promising ene in this respect as the addition of CO would form phenylacetaldehyde. A force field calculation[14] predicted this process to be exothermic by −29 kcal mol^{-1} and we decided to test it. As the syntheses of the parent *o*-isotoluene[18] are rather tedious, we switched to 1,2,3,4-tetrachloro-5-methylenecyclohexa-1,3-diene **20**, for which a short synthesis was developed (see Scheme 7).

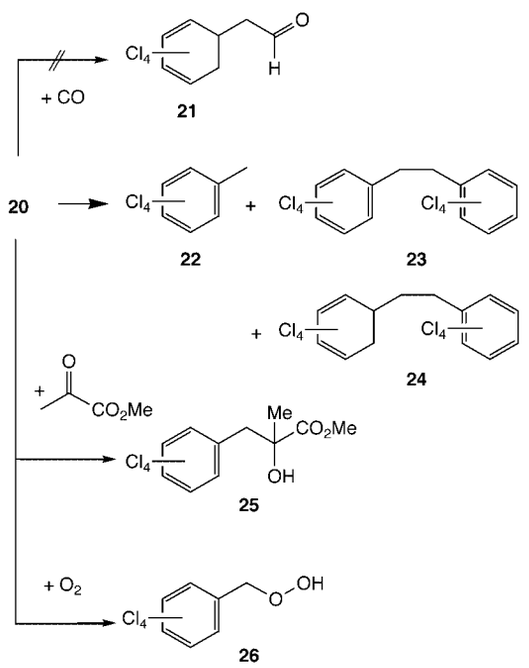


Scheme 7

Cycloaddition of allene to *o*-chloranil (tetrachloro-1,2-benzoquinone) at 75 °C gave 7-methylenetetrachlorobicyclo[2.2.2]oct-5-ene-2,3-dione **19** in satisfactory yield. Irradiation of the α-diketone **19** with a projector lamp at 0 °C resulted in quantitative didecarbonylation to tetrachloro-*o*-isotoluene **20**. In an NMR experiment **20** proved rather stable in

$CDCl_3$ at room temperature, rearranging slowly to its aromatic tautomer **22** in the course of two days.

In order to generate the isotoluene **20** in the presence of CO, a diethyl ether solution of the α-diketone **19** was deaerated and was set under a 5 bar pressure of CO. The solution was irradiated at 0 °C for 20 min during which the yellow color changed to magenta and then disappeared. After standing for 20 h under CO at room temperature (rt) the reaction mixture showed no trace of the expected tetrachlorophenylacetaldehyde **21**, instead tetrachlorotoluene **22**, octachlorobibenzyl **23** and its dihydro derivative **24** were isolated (Scheme 8). These products probably



Scheme 8

arise *via* radical chain reactions since tetrachloroisotoluene proved unreactive as an ene. Thus it did not add to the enophile norbornadiene even if the latter is used as the solvent. However it readily added to the carbonyl group of methyl pyruvate by an oxo-ene-reaction yielding the 3-(tetrachlorophenyl)-2-hydroxy-2-methylpropionate ester **25**. The propensity of isotoluene **20** towards radical attack was further shown by the facile addition of molecular oxygen.[19] When a diethyl ether solution of **20** was percolated with oxygen for 3 h tetrachlorobenzyl hydroperoxide **26** resulted in good yield.

Conclusion

For the extrusion of CO from β,γ-unsaturated aldehydes a pericyclic transition state is indicated as, in analogy to other concerted processes, a large rate acceleration is observed if the product is an arene instead of an olefin. Accordingly, the reaction can be categorized as the reverse of the unknown cheletropic ene-reaction. Phenyl isocyanide undergoes the same extrusion if the reaction is driven by the formation of an arene. The cheletropic ene-reaction itself could not be realized with the ene tetrachloro-*o*-isotoluene, for which an efficient synthesis was developed. When this isotoluene is treated with CO under a pressure of 5 bar no addition of CO occurs to form tetrachlorophenylacetaldehyde. Instead, the triene stabilizes itself *via* tautomerization and dimerization. Tetrachloro-*o*-isotoluene also proved unreactive as an ene in the ene-reaction with norbornadiene but readily undergoes the oxo-ene-reaction with an electron deficient ketone.The addition of molecular oxygen occurs by a radical chain process in analogy to the parent compound.

Experimental

NMR spectra were recorded on a Bruker AM 300 spectrometer at 300 MHz (^{1}H) and 75.5 MHz (^{13}C) in $CDCl_3$. Chemical shifts are in ppm relative to internal TMS. Signals were assigned by C–H COSY and NOE methods. Signal patterns and nuclei are abbreviated as follows: AB (AB system), Δν (shift difference of nuclei A, B in Hz), J (coupling constant in Hz), s (singlet), d (doublet), t (triplet), q (quartet), Cq (quaternary carbon atom). UV spectra were obtained using a Perkin-Elmer Lambda 7 spectrometer, IR spectra were recorded on a Perkin-Elmer 1600 FTIR spectrometer, mass spectra on a Finnigan MAT INCOS 50 spectrometer. GLC was performed with a Perkin-Elmer 8320 chromatograph (25 m capillary, OV-1 permaphase) for analyses and with a Varian Aerograph P 90 for preparations. Reactions under pressure were performed in a 50 ml steel autoclave fitted with a removable glass liner. The screwed on lid was equipped with a safety disk (200 bar). For irradiations a halogen lamp (Osram Xenophot, 36 V, 400 W) was used that was installed in a water cooled Pyrex immersion well. Melting points were determined in open capillaries with a Tottoli apparatus (Büchi, Flawil). For flash chromatography Silitech 32-64 60A (ICN, Eschwege) was used in a column (50 × 3 cm) filled to a third of its height.

2,2-Dimethylbut-3-enal 1

The aldehyde **1** was prepared as published[20] *via* Reformatsky reaction of α-bromoisobutyric acid ethyl ester with acetaldehyde, dehydration of the resulting 3-hydroxy-2,2-dimethylbutyric acid ethyl ester to 2,2-dimethylbut-3-enoic acid ethyl ester and transformation of the ester into the aldehyde function by reduction with LAH followed by Swern oxidation.

1-Deuterio-2,2-dimethylbut-3-enal 2

The labeled aldehyde was obtained as the parent compound above, using LAD instead of the protio reagent. The deuterium incorporation amounted to 95% at least, as judged from the ^{1}H, ^{13}C and IR spectrum. **2**; ν_{max} (film)/cm^{-1} 2142, 2052 (CDO); δ_H 1.16 (6 H, s, CH_3), 5.0–5.3 (2 H, m, 4-H), 5.81 (1 H, dd, $^{1,3}J$ 10.2, 3-H); δ_C 20.97 (CH_3), 49.05 (t, J 3, C-2), 115.80 (C-4), 139.71 (C-3), 202.14 (t, J 26.5, C-1).

Thermolysis of 2,2-dimethylbut-3-enals 1, 2[21]

The decarbonylation of **1** and **2** was performed in the gas phase by injection of a 2% solution of either aldehyde in *n*-hexane (0.3 ml), containing 2% of *n*-heptane as a standard, into a thermostated and evacuated glass flask (100 l). The resulting pressure in the reaction vessel amounted to 4 Torr. The progress of the decarbonylation was monitored by GC analysis of gaseous samples that were drawn directly into the connected chromatograph (50 m HP1 column, 45 °C, retention time of **3** (**4**), **1** (**2**) and *n*-heptane: 5.02, 7.70, 8.70 min). For results, see Tables 1 and 2.

Table 1 Experimental first order rate constants for the decarbonylation of **1**

T/°C	251.8	262.05	271.2	281.25	291.05	300.25	311.25	320.75	331.3
k/10^{-4} s^{-1}	0.1612	0.3441	0.6535	1.3179	2.5115	4.6282	9.0041	15.711	29.36

Table 2 Experimental first order rate constants for the decarbonylation of **2**

T/°C	281.43	291.69	301.75	312.31	322.56	332.56	343.18	352.89	363.4
$k/10^{-4}$ s^{-1}	0.3875	0.7785	1.5334	2.9853	5.6595	10.363	18.977	32.843	57.98

syn, *anti*-1-Methyl-6-methylene-2-(trimethylsilyloxy)cyclohex-3-ene-1-carboxylic acid ethyl ester 5

2-Methylbuta-2,3-dienoic acid ethyl ester[22] (9.345 g, 74 mmol) and 1-trimethylsilyloxybuta-1,3-diene[23] (16.02 g, 112.5 mmol) were heated in a sealed tube together with a few crystals of 4-*tert*-butylcatechol in toluene (37.5 ml) to 180 °C for 8 h. The reaction mixture was concentrated and the residue was distilled over a Zincke apparatus to yield a mixture of *syn*- and *anti*-**5** (13.7 g, 88.7% pure, 61.2%); bp 82–87 °C/0.4 Torr. The ratio and the configuration of the products were determined after hydrolysis to the alcohols.

syn- and *anti*-2-Hydroxy-1-methyl-6-methylenecyclohex-3-ene-1-carboxylic acid ethyl ester 6

The solution of the raw mixture of **5** in ethanol (100 ml) was treated with trimethylsilyl chloride (1 ml) and left at rt for 15 h. After concentration in a rotary evaporator the product was distilled over a short Vigreux column (5 cm) to yield the epimeric alcohols **6** (7.87 g, 93% pure, 85%); bp 72.5–80 °C, 0.26 Torr. For spectral analyses the pure alcohols were separated by GLC (0.5 m, 15% SE 30 on silica gel, 110 °C), the major component (65%) eluting first. The IR spectra of both alcohols in 10% CCl_4 solution showed a broad absorption at 3300–3600 cm^{-1} of the hydrogen bonded OH group. In 1% solution the major product retained this absorption, the minor product, however, displayed a sharp band at 3600 cm^{-1} for the free OH group. Both the retention time and the IR spectrum indicate that the *syn*-configuration for the major alcohol is able to form an intramolecular hydrogen bond.

***syn*-6.** δ_H 1.23 (3 H, t, CH_3 ester), 1.53 (3 H, s, CH_3), 2.84 (2 H, AB, $\Delta\nu$ 27.3, J 19.5, 5-H), 4.02 (2 H, AB, $\Delta\nu$ 49, J 10.6, 2-H, OH), 4.15 (2 H, q, CH_2 ester), 5.03 (2 H, m, $=CH_2$), 5.70 (2 H, AB, $\Delta\nu$ 16.6, J 10.7, 3-H, 4-H); δ_C 14.02 (CH_3), 19.03 (CH_3 ester), 33.51 (C-5), 52.82 (C-1), 61.04 (CH_2 ester), 75.63 (C-2), 111.01 ($=CH_2$), 125.98 (C-4), 131.96 (C-3), 144.59 (C-6), 176.4 (CO).

***anti*-6.** δ_H 1.25 (3 H, t, CH_3 ester), 1.39 (3 H, s, CH_3), 2.89 (2 H, AB, $\Delta\nu$ 28.2, J 19, 5-H), 4.18 (2 H, q, CH_2 ester), 4.52 (1 H, d, J 4, 2-H), 4.93 (1 H, s, $=CH_2$ (Z)), 5.09 (1 H, s, $=CH_2$ (E)), 5.80 (2 H, AB, $\Delta\nu$ 18.3, J 8, 3-H, 4-H); δ_C 14.08 (CH_3), 17.65 (CH_3 ester), 33.45 (C-5), 53.8 (C-1), 60.83 (CH_2 ester), 70.68 (C-2), 111.98 ($=CH_2$), 128.87 (C-4), 129.0 (C-3), 143.37 (C-6), 174.67 (CO).

2-(*tert*-Butyldimethylsilyloxy)-1-methyl-6-methylenecyclohex-3-ene-1-carboxylic acid ethyl ester 7

The stirred solution of the alcohol **6** (7.5 g, 93% pure, 38.7 mmol) in methylene chloride (45 ml) was treated at 0 °C first with 2,6-lutidine (2,6-dimethylpyridine) (11.2 g, 104.1 mmol), then with *tert*-butyldimethylsilyl triflate (10.5 ml, 45.8 mmol). After 10 min at 0 °C and 15 h at rt the reaction mixture was washed with 5% aqueous $NaHSO_4$ and with brine and dried over $MgSO_4$. Concentration in a rotary evaporator at 0 °C left an oil that was distilled under vacuum in a Zincke apparatus to yield **7** (12.1 g, 91% pure, 91.5%), bp 87–93 °C at 0.03 Torr; δ_H 0.04, 0.07 (6 H, 2 s, Si-CH_3), 0.84, 0.89 (9 H, 2 s, *tert*-Bu), 1.20, 1.26 (3 H, 2 t, CH_3 ester), 1.31, 1.44 (3 H, 2 s, CH_3), 2.83, 2.93 (2 H, 2 AB, $\Delta\nu$ 27, J 19, $\Delta\nu$ 137, J 18, 5-H), 4.0–4.1 (1 H, 2 m, 2-H), 4.15, 4.19 (2 H, 2 q, CH_2 ester), 4.72, 4.92, 5.00, 5.03 (2 H, 4 s, $=CH_2$), 5.5–5.8 (2 H, m, 3-H, 4-H).

2-(*tert*-Butyldimethylsilyloxy)-1-methyl-6-methylenecyclohex-3-ene-1-carbaldehyde 9

In a flame dried flask the stirred solution of ester **7** (3.1 g, 10 mmol) in *n*-hexane (30 ml) was cooled to −78 °C in an argon atmosphere and treated dropwise with 1 M DIBAL-H in *n*-hexane (22 ml, 22 mmol). After 1 h the reaction mixture was quenched with methanol (2.7 ml) and brought to rt. The gelatinous mixture was diluted with diethyl ether (30 ml) and washed with 20% aqueous sodium potassium tartrate until two clear phases resulted. The organic layer was washed with water and brine, dried over $MgSO_4$ and concentrated. The oily residue on distillation under vacuum yielded the alcohol **8** containing 7% of the aldehyde **9** (2.6 g, 9.7 mmol, 97%), bp 91–92 °C at 0.14 Torr. The raw product was converted in the next step to the aldehyde **9**. To the stirred solution of oxalyl chloride (0.91 ml, 10.5 mmol) in methylene chloride (24 ml) was added dropwise at −60 °C DMSO (1.5 ml, 21 mmol) in methylene chloride (5 ml). After 5 min the solution of the raw alcohol **8** (2.6 g, 9.1 mmol) in methylene chloride (9.5 ml) was dropped into the reaction mixture, keeping the temperature at −60 °C. Without cooling the mixture reached −15 °C after 15 min when triethylamine (6.66 ml, 47.7 mmol) was added. After a further 15 min at −15 °C the product was brought to rt and partitioned between water (50 ml) and methylene chloride (50 ml). The organic phase was washed with 5% aqueous $NaHSO_4$, water, and brine, dried over $MgSO_4$ and concentrated under vacuum. The oily residue yielded after distillation in a Zincke apparatus the aldehyde **9** (2.46 g, 95%) bp 85–90 °C at 0.3 Torr; δ_H 0.02, 0.05, 0.07, 0.08 (6 H, 4 s, Si-CH_3), 0.84, 0.88 (9 H, 2 s, *tert*-Bu), 1.23, 1.28 (3 H, 2 s, CH_3), 2.83 (2 H, AB, $\Delta\nu$ 43, J 21, 5-H,), 4.16, 4.60 (1 H, 2 m, 2-H), 4.71, 4.95, 4.98, 5.04 (2 H, 4 s, $=CH_2$), 5.6–5.7 (2 H, m, 3-H, 4-H), 9.56, 9.87 (1 H, 2 s, CHO).

2-Hydroxy-1-methyl-6-methylenecyclohex-3-ene-1-carbaldehyde 10

The solution of the protected aldehyde **9** (1.20 g, 4.5 mmol) in 85% acetic acid (20 ml) was stirred in an argon atmosphere for 30 h at 60 °C. After concentration in a rotary evaporator at 60 °C and 50 Torr the residue was partitioned between 3 times its volume of water and methylene chloride (40 ml). The organic phase was washed with saturated aqueous $NaHCO_3$, water and brine and dried over $MgSO_4$. Evaporation of the solvent under vacuum at 0 °C left an oil that was distilled in a Zincke apparatus. Flash chromatography of the distillate with *n*-hexane–ethyl acetate 1 : 1 yielded **10** (478 mg, 70%); bp 63–65 °C at 0.1 Torr; δ_H 1.26, 1.35 (3 H, 2 s CH_3), 1.50, 2.76 (1 H, 2 d, OH), 2.88 (2 H, AB, $\Delta\nu$ 30, J 17, 5-H,), 4.05, 4.41 (1 H, 2 m, 2-H), 4.92–5.16 (2 H, 4 s, $=CH_2$), 5.70–5.87 (2 H, m, 3-H, 4-H), 9.53, 9.55 (1 H, 2 s, CHO).

1-Methyl-6-methylenecyclohexa-2,4-diene-1-carbaldehyde 11

To the solution of the aldol **10** (99 mg, 0.65 mmol) in methylene chloride (1.5 ml) was added dry triethylamine (190 µl, 1.37 mmol), that had been freed of secondary and primary by-products. With stirring freshly recrystallized 2,4-dinitrobenzenesulfenyl chloride (160.3 mg, 0.683 mmol) in methylene chloride (2 ml) was dropped in. The reaction mixture turned dark over 5 h at rt and was diluted with pentane (11 ml). A brown precipitate formed, that was removed by filtration through a silica gel column (1 cm, id 1 cm) and washed with pentane until a yellow zone started to move. Concentration of

Table 3 Experimental first order rate constants for the decarbonylation of **11**

T/°C	64.56	67.14	69.63	72.14	74.44	76.84	79.24	81.65	83.25
$k/10^{-3}$ s^{-1}	0.4002	0.5271	0.6469	0.8399	1.0405	1.3999	1.7059	2.0074	2.201

the filtrate at 0 °C under vacuum down to a pressure of 15 Torr left the oily triene **11** containing 17% of its decarbonylation product *o*-xylene. **11** (21.2 mg, 24.3%), λ_{max} (hexane)/nm 222 (ε/dm^3 mol^{-1} cm^{-1} 2900) 289 (3950), 299 (4020); δ_H 1.38 (3 H, s, CH_3), 4.94 (1 H, s, $=CH_2$ (*Z*)), 5.28 (1 H, s, CH_2 (*E*)), 5.48 (1 H, m, 2-H), 5.88 (1 H, m, 4-H), 6.11 (1 H, m, 3-H), 6.17 (1 H, m, 5-H), 9.30 (1 H, s, CHO); δ_C 23.67 (CH_3), 54. 77 (C-1), 117.27 (CH_2), 122.95 (C-4), 124.95 (C-3), 128.50 (C-5), 128.67 (C-2), 143.52 (C-6), 197.21 (CHO).

Kinetic measurement of decarbonylation of 11

The reaction was performed in a double walled cuvette (2.5 ml, 5 cm) placed in a digital spectral fluorometer (PMQ3, Zeiss). The cell was filled with *n*-dodecane (Spectrograde, Aldrich) and heated with circulating water from a thermostat (U6, Lauda). The temperature in the cell was measured with a thermistor (L-LTN-B-3, Linseis), it was constant within ±0.05 K. A 0.001 M solution of **11** in $CDCl_3$ (10 µl) was injected into the heated cell and homogenization was achieved by short shaking. The decrease of the extinction *E* at 305 nm was registered from *ca.* 0.4 to 0.02 *vs*. time and the rate constant was obtained by fitting the trace of *E* to the first order rate equation (for results see Table 3).

4-Chloro-1-methyl-6-methylenecyclohex-2-ene-1-carboxylic acid ethyl ester 12

Alcohol **6** (3.92 g, 20 mmol) in diethyl ether (26 ml) was treated at 0 °C with freshly distilled thionyl chloride (1.72 ml, 23 mmol). The reaction mixture was stirred for 10 min without the ice bath and concentrated under a vacuum reaching 15 Torr. Distillation of the residue yielded impure **12**. The NMR spectrum showed three singlets for the methyl group and a broad absorption extending above 3.0 ppm for the methylene group in the ring. This low field absorption is characteristic for the 6-methylenecyclohex-4-ene system. A GLC analysis showed three components, the minor ones amounting to *ca.* 25% each. From these results the formation of *ca.* 25% of the unrearranged chloride was deduced. **12** (3.50 g, 81.5%), bp 63–67 °C at 0.08 Torr; *m*/*z* 214 (M^+, 1%), 179 (5, $M^+ - Cl$), 141 (37, $M^+ - CO_2Et$), 105 (100, $C_7H_6CH_3^+$).

4-Chloro-1-methyl-6-methylenecyclohex-2-ene-1-carbaldehyde 13

To the stirred solution of the chloroester **12** (3.38 g, 15.7 mmol) in *n*-hexane (190 ml) was added dropwise at −78 °C a 1 M solution of DIBAL-H in hexane (38.2 ml, 38.2 mmol). After 45 min the reaction mixture was quenched with methanol (4.64 ml, 114.6 mmol), brought to rt and extracted with 15% aqueous sodium potassium tartrate (160 ml). The clear phases were separated and the organic one was washed with water and brine and dried over $MgSO_4$. Concentration in a rotary evaporator left a wax that was flash chromatographed with hexane–ethyl acetate 2:1. **13** (1.26 g, 46.5%), δ_H 1.29, 1.37 (3 H, 2 s, CH_3), 2.68 (2 H, AB, $\Delta\nu$ 42.5, *J* 15, 5-H), 4.62 (1 H, m, 4-H), 4.89, 5.05, 5.25, 5.28 (2 H, 4 s, $=CH_2$), 5.81, 5.82 (2 H, 2 AB, $\Delta\nu$ 217, *J* 10.2, $\Delta\nu$ 170, *J* 10.2, 2-H, 3-H), 9.23, 9.29 (1 H, 2 s, CHO); δ_C 20.01, 20.52 (CH_3), 39.80 (C-5), 53.69, 53.93 (C-4), 54.20, 54.48 (C-1), 115.62, 115.82 ($=CH_2$), 130.66, 131.43, 132.11 (C-2, C-3), 139.92, 141.53 (C-6), 197.93, 198.22 (CHO). A second fraction was characterized as the corresponding alcohol (0.32 g, 11.6%), resulting from over-reduction of **12**; it could be transformed into **13** by Swern oxidation.

N-Phenyl-4-chloro-1-methyl-6-methylenecyclohex-2-enyl-methanimine 14

Choroaldehyde **13** (50 mg, 0.29 mmol) in benzene (0.5 ml) was reacted with aniline (28 µl, 0.31 mmol) in the presence of 4 Å molecular sieves (0.3 g) for 15 h at rt.The sieves were removed by filtration and washed with benzene (10 ml); evaporation of the filtrate left the semi-crystalline anil (where anil is an *N*-phenyl imine) **14** (53 mg, 73.7%); δ_H 1.43, 1.48 (3 H, 2 s, CH_3), 3.29 (2 H, AB, $\Delta\nu$ 76, *J* 12, 5-H), 4.65 (1 H, m, 4-H), 4.99, 5.11, 5.13, 5.18 (2 H, 4 s, $=CH_2$), 5.84, 5.91 (2 H, 2 AB, $\Delta\nu$ 125, *J* 10, $\Delta\nu$ 104, *J* 9, 2-H, 3-H), 7.0–7.4 (5 H, 3 m, Ar-H), 7.52, 7.62 (1 H, 2 s, CH=N-); δ_C 22.95, 23.12 (CH_3), 39.76, 40.00 (C-5) 47.34, 47.52 (C-1), 54.75, 55.00 (C-4), 113.94 (C-7), 143.49 (C-6), 167.03, 167.46 (CH=N), 120.60, 124.83, 128.97, 151.80 (*o*-, *p*-, *m*-, Cq); *m*/*z* 245 (M^+, 10%), 230 (18, $M^+ - CH_3$), 210 (21, $M^+ - Cl$), 194 (20, $M^+ - CH_3 - HCl$), 104 (100, $PhNCH^+$).

N-Phenyl-1-methyl-6-methylenecyclohexa-2,4-dienyl-methanimine 15

To **14** (40 mg, 0.163 mmol) in benzene (0.4 ml) was added at 10 °C a 1 M solution of phosphazene base P_4Bu^t [24,25] in hexane (171 µl, 0.171 mmol). The solution turned dark after 10 min and was diluted with diethyl ether–pentane 1:1 (4 ml). The resulting brown precipitate was removed by filtration through a column of neutral alumina (1 cm, id 1 cm) and washed with diethyl ether–pentane (6 ml). The combined filtrates were concentrated at 10 °C under vacuum leaving the desired triene anil together with *o*-xylene in a ratio of 3:1. **13** (14.9 mg, 43.6%); δ_H 1.59 (3 H, s, CH_3), 4.93 (1 H, s, $=CH_2$ (*Z*)), 5.03 (1 H, s, $=CH_2$ (*E*)), 5.60 (1 H, d, *J* 9.8, 2-H), 5.65 (1 H, m, 4-H), 5.80 (1 H, m, 3-H), 6.02 (1 H, d, *J* 9.8, 5-H), 7.0–7.2 (5 H, m, Ar-H), 7.62 (1 H, s, CH=N-); δ_C 27.7 (CH_3), 48.2 (C-1), 116.6 ($=CH_2$), 122.7 (C-3), 122.9 (C-4), 133.9 (C-2), 148.2 (C-6), 166.4 (CH=N-), 121.1, 125.8, 129.5, 152.5 (*o*-, *p*-, *m*-, Cq); *m*/*z* 209 (M^+, 50%), 105 (42, $C_7H_6CH_3^+$), 104 (66, $PhN{=}CH^+$), 77 (100, $C_6H_5^+$).

Thermolysis of *N*-phenyl-1-methyl-6-methylenecyclohexa-2,4-dienylmethanimine 15

A NMR probe of **15** in C_6D_6 was deaerated by two freeze–thaw cycles, sealed under vacuum and was heated to 144 °C in the vapor phase of refluxing *o*-xylene. In the course of 1.5 h the relative concentrations of starting material and of formed *o*-xylene were analyzed by NMR at four times. No other product could be detected but a white solid formed at the inner wall of the NMR tube. The decrease of the methanimine **15** followed the first order rate equation with the rate constant $k = 3.5\ 10^{-4}$ s^{-1}.

N-Phenyl-2,2-Dimethylbut-3-enimine 16

Aldehyde **1** (0.27 g, 2.75 mmol) in benzene (2 ml) was reacted with aniline (0.3 ml, 3.3 mmol) in the presence of 4 Å molecular sieves (2 g). After 20 h at room temperature the sieves were filtered off and washed with benzene (10 ml). The filtrate was concentrated at 20 °C under vacuum, leaving a yellow oil that was purified by bulb to bulb distillation. **16** (465 mg, 97.5%); δ_H 1.30 (6 H,s, CH_3), 5.10 (2 H, m, 4-H), 5.96 (1 H, m, 3-H), 7.0–7.3 (5 H, 3 m, Ar-H), 7.64 (1 H, s, 1-H); δ_C 24.23 (CH_3), 42.98 (C-2), 113.18 (C-4), 143.69 (C-3), 170.53 (C-1), 120.56, 125.27, 128.91, 152.43 (*o*-, *p*-, *m*-, Cq).

3-Methyl-*N*-phenylpyrrole 18

The anil **16** (46 mg, 0.27 mmol) was distilled though a tube (30 cm, id 0.3 cm) that was heated to 500 °C in an electric oven. No gas was used for flashing and the distillation took 0.5 h at 10 Torr, *i.e*. the educt was in contact with the hot zone for approximately 20 s. The distillate, containing 25% of the educt, was separated by flash chromatography with hexane–ethyl acetate 9 : 1 and the product sublimed at 50 °C and 15 Torr. **18** (23.7 mg, 56%), mp 70–71 °C; δ_H 2.17 (3 H, s, CH_3), 6.15 (1 H, m, 4-H), 6.85 (1 H, m, 2-H), 6.95 (1 H, m, 5-H), 7.1–7.4 (5 H, Ar-H); *m*/*z* 157 (M^+, 67%), 156 (100, $M^+ - H$), 142 (2, $M^+ - CH_3$), 128 (11, $M^+ - C_2H_5$), 115 (8, $M^+ - C_3H_6$), 80 (11, $C_5H_5N^+$), 77 (37 $C_6H_5^+$), 51 (34, $C_4H_3^+$). Mp and δ_H are in accord with published data.[26]

1,4,5,6-Tetrachloro-7-methylenebicyclo[2.2.2]oct-5-ene-2,3-dione 19

o-Chloranil (9.83 g, 40 mmol) together with a few crystals of 4-*tert*-butylcatechol was placed into a glass lined steel autoclave (50 ml). The vessel was cooled to −78 °C and allene (24 ml, 0.43 mol) of the same temperature was poured in. The autoclave was heated to 75 °C for 24 h whereafter it was cooled again to −78 °C and was opened. The liquid in the glass liner was decanted from the crystalline orange product into a trap cooled with dry ice. The excess of allene was condensed from the trap into a second one at room temparature and the oily residue was discarded. The product was recrystallized from diethyl ether, keeping the solution in the dark and completing the crystallization at −18 °C. **19** (5.77 g, 50.4%), mp 145 °C; λ_{max} (*n*-hexane)/nm 434 (ε/dm^3 mol^{-1} cm^{-1} 220); ν_{max} (KBr)/cm^{-1} 1761 (CO), 1576 (C=C), 940 (=CH_2); δ_H 3.31 (2 H, AB, Δ*v* 31.8, *J* 16.8, 8-H), 5.44 (1 H, m, =CH_2 (*E*)), 5.89 (1 H, m, =CH_2 (*Z*)); δ_C 40.58 (C-8), 72.40 (C-4), 79.72 (C-1), 116.37 (C-9), 130.08, 130.36 (C-5, C-6), 132.42 (C-7), 174.21, 177.20 (C-2, C-3); *m*/*z* 230 (10%, $M^+ - 2$ CO), 221 (12, $M^+ - CO - Cl$), 193 (100, $M^+ - 2CO - Cl$).

1,2,3,4-Tetrachloro-5-methylenecyclohexa-1,3-diene 20

In an NMR tube a 0.02 M solution of diketone **19** in $CDCl_3$ (0.4 ml) was deaerated and sealed under vacuum. The probe was placed in a beaker with ice water and was irradiated with a projector lamp (Osram Xenophot HLX, 36 V, 400 W). After 20 min the yellow color had vanished and the NMR analysis showed complete decarbonylation of **19** with formation of the isotoluene **20** and a trace of 2,3,4,5-tetrachlorotoluene **22**. The tautomerization of **20** to **22** proceeded to 50% after 20 h at 0 °C and was complete after an additional 48 h at room temperature. **20**, δ_H 3.74 (2 H, t, $^{1,4}J$ 3.2, 6-H), 5.19 (1 H, t, $^{1,4}J$ 3.2, =CH_2 (*Z*)), 5.62 (1 H, t, $^{1,4}J$ 3.2, =CH_2 (*E*)); δ_C 40.40 (C-6), 117.91 (C-7), 135.57 (C-5), 123.37, 131.28, 132.41, 132.68 (C-1,2,3,4). **22**, δ_H 2.36 (3 H, s, CH_3), 7.27 (1 H, s, Ar-H), as compared with δ_H 2.35 and 7.22 in the literature.[27]

Attempted reaction of 1,2,3,4-tetrachloro-5-methylenecyclohexa-1,3-diene 20 with CO

A thick walled glass ampoule (20 ml) was filled with the solution of the diketone **19** (100 mg, 0.35 mmol) in diethyl ether (10 ml). The vessel was connected by high pressure PVC tubing to a manifold with outlets to a vacuum pump and to a CO tank. After deaerating the solution by two freeze–thaw cycles a CO atmosphere of 7 bar was established. The solution was stirred and irradiated with a projector lamp for 20 min in an ice bath whereafter the color had faded. Stirring was continued under CO pressure overnight at rt and the solvent was evaporated. An NMR analysis of the raw product showed the presence of *inter alia* tetrachloro-*o*-isotoluene **20** and tetrachlorotoluene **22** but no signal for the aldehyde proton of the expected tetrachlorophenylacetaldehyde **21**. Digestion of the impure product with *n*-hexane left colourless crystals that were characterized as 1,2-bis(2′,3′,4′,5′-tetrachlorophenyl)ethane **23** (17.6 mg, 22%), mp 213 °C (from hexane); δ_H 2.99 (4 H, s, CH_2), 7.24 (2 H, s, CH); δ_C 34.09 (CH_2), 129.09 (CH), 138.87 (Cq); *m*/*z* 458 (5%, M^+, Cl_8 isotope pattern). The hexane extract was flash chromatographed with cyclohexane yielding tetrachlorotoluene **22**, another portion of **23** and 1-(2′,3′,4′,5′-tetrachlorophenyl)-2-(2″,3″,4″,5″-tetrachlorocyclohexa-2″,4″-dienyl)ethane **24** (14.5 mg, 18%), mp 125 °C; δ_H 1.88 (2 H, m, 2-H), 2.65 (1 H, d, *J* 17, 6″-H), 2.7–2.9 (3 H, m, 1-H, 6″-H), 3.18 (1 H, q, $^{1,3}J$ 8, 1″-H), 7.27 (1 H, s, Ar-H); δ_C 30.31 (CH_2), 31.15 (CH_2), 36.61 (CH_2), 41.87 (CH), 127.80 (Cq), 128.78 (CH); *m*/*z* 460 (12%, M^+, Cl_8 isotope pattern).

2-Hydroxy-2-methyl-3-(2′,3′,4′,5′-tetrachlorophenyl)propionic acid methyl ester 25

The solution of diketone **19** (212 mg, 0.74 mmol) and methyl pyruvate (0.19 g, 1.85 mmol) in diethyl ether (10 ml) was put into a glass ampoule, deaerated and sealed. The reaction mixture was irradiated in an ice bath with a projector lamp for 55 min, when the color had vanished. After 18 h at rt the solution was concentrated in a rotary evaporator at 45 °C and the remaining yellow oil was flash chromatographed with methylene chloride. A first fraction eluted the stabilization products of tetrachloroisotoluene, *i.e*. **22**–**24**, the second fraction contained the product of the oxo-ene reaction. **25** (167 mg, 68%), mp 85 °C (from hexane); δ_H 1.46 (3 H, s, CH_3), 3.19 (2 H, AB, Δ*v* 18.3, *J* 14, CH_2), 3.77 (3 H, s, CH_3 ester), 7.44 (1 H, s, Ar-H); δ_C 25.59 (CH_3), 42.77 (C-3), 53.13 (CH_3 ester), 74.42 (C-2), 130.99 (C-6′), 131.53 (C-4′), 131.62 (C-5′), 133.13 (C-2′), 133.22 (C-3′), 134.86 (C-1′), 176.25 (C-1); *m*/*z* 271 (8%, $M^+ - CO_2CH_3$), 228 (10, $C_7H_4Cl_4^+$), 193 (13, $C_7H_4Cl_3^+$), 157 (12, $C_7H_3Cl_2^+$), 103 (100, $M^+ - C_7H_3Cl_4$).

2,3,4,5-Tetrachlorobenzyl hydroperoxide 26

In a septum capped test tube with a side arm diketone **19** (329 mg, 1.15 mmol) was suspended in diethyl ether (20 ml). A slow stream of argon from a steel capillary was passed through the suspension while it was irradiated in an ice bath with a projector lamp. After 1 h a clear light yellow solution resulted. Changing argon for oxygen, the percolation was continued for 3 h. The reaction mixture was left overnight at room temperature and was brought to dryness in a rotary evaporator. The semi-solid residue was recrystallized from acetone yielding the hydroperoxide **26** (214 mg, 71%), mp 147 °C (decomp.); ν_{max}(KBr)/cm^{-1} 3445 (OH), 3080 (ArH), 2911 (CH_2), 1046 (OO), 826 (ArH); δ_H 4.99 (2 H, s, 7-H), 7.38 (1 H, s, 6-H); δ_C 73.97 (CH_2), 129.43 (CH), 134.6 (Cq), 131.89, 132.16, 132.87, 133.52 (C-Cl); *m*/*z* 243 (100%, $M^+ - OH$) 229 (27, $M^+ - O_2$,+H), 209 (65, $M^+ - OCl$), 193 (15, $M^+ - O_2Cl$). The hydroperoxide **26** was disproportionated into 2,3,4,5-tetrachlorobenzaldehyde (mp 106 °C)[28] and tetrachlorobenzyl alcohol by ferrous sulfate hydrate in ethanol.

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References

1 K. Alder, in *Neuere Methoden der Präparativen Organischen Chemie*, *Teil 1*, ed. W. Foerst, Verlag Chemie, Weinheim, 1949, p. 251; J. Sauer and R. Sustmann, *Angew. Chem.*, *Int. Ed. Engl.*, 1980, **19**, 779.

2 R. Huisgen, R. Grashey and J. Sauer, in *The chemistry of alkenes*, ed. S. Patai, Interscience, London, 1964, p. 739; A. Padwa, *1,3-Dipolar Addition Chemistry*, Wiley, New York, 1984.

3 L. Mock, in *Pericyclic Reactions*, *volume II*, ed. A. P. Marchand and R. E. Lehr, Academic Press, New York, 1977, p. 141.
4 G. V. Boyd, in *The chemistry of double-bonded functional groups*, ed. S. Patai, Wiley, Chichester, UK, 1989, p. 477.
5 W. S. Trahanowsky and S. L. Emeis, *J. Am. Chem. Soc.*, 1975, **97**, 3773.
6 M. E. Jung and C. N. Zimmerman, *J. Am. Chem. Soc.*, 1991, **113**, 7813.
7 R. J. Crawford, S. Lutener and H. Tokunage, *Can. J. Chem.*, 1977, **55**, 3951.
8 W. R. Roth, J. König, *Liebigs Ann. Chem.*, 1966, **699**, 24.
9 A. Bertsch, W. Grimme and G. Reinhardt, *Angew. Chem.*, *Int. Ed. Engl.*, 1986, **25**, 377; W. Grimme, P. Höner, H.-T. Kämmerling, R. Waldraff and J. Wirz, *Angew. Chem.*, *Int. Ed. Engl.*, 1989, **28**, 1353.
10 H. J. Reich and S. Wollowitz, *J. Am. Chem. Soc.*, 1982, **104**, 7051.
11 A. R. Rye and D. Wege, *Aust. J. Chem.*, 1974, **27**, 1943; W. C. Herndon, W. B. Cooper and M. J. Chambers, *J. Phys. Chem.*, 1964, **68**, 2016.
12 W. Grimme, K. Pohl, J. Wortmann and D. Frowein, *Liebigs Ann. Chem.*, 1996, 1905.
13 W. R. Roth, *Tetrahedron Lett.*, 1964, 1009; W. Grimme, J. Lex and T. Schmidt, *Angew. Chem.*, *Int. Ed. Engl.*, 1987, **26**, 1268; T. Grommes, PhD Thesis, University of Cologne, 1991.
14 MM2 + π-VESCF routine MMP1 (both from N. L. Allinger) as contained in PCMODEL, Serena Software, Bloomington, IN.
15 R. Schwesinger, *Chimia*, 1985, **39**, 269.
16 C. Grundmann, in *Methoden der Organischen Chemie*, *volume E5*, ed. J. Falbe, Thieme, Stuttgart, 1985, p. 1611.
17 G. Kohlmaier and B. S. Rabinovitch, *J. Phys. Chem.*, 1959, **63**, 1793.
18 W. J. Bailey and R. A. Baylouny, *J. Org. Chem.*, 1962, **27**, 3476; K. R. Kopecky and M.-P. Lau, *J. Org. Chem.*, 1978, **43**, 525; W. A. Pryor, W. D. Graham and J. G. Green, *J. Org. Chem.*, 1978, **43**, 526; D. Hasselmann and K. Loosen, *Angew. Chem.*, *Int. Ed. Engl.*, 1978, **17**, 1167.
19 W. A. Pryor and W. D. Graham, *J. Org. Chem.*, 1978, **43**, 770.
20 P. Eilbracht, M. Acker and B. Rosenstock, *Chem. Ber.*, 1989, **122**, 151.
21 This measurement was done in the laboratory of the late Professor W. R. Roth, Ruhr-University Bochum; we have enjoyed his expert cooperation for many years and deplore this untimely loss of a leader in the field.
22 R. W. Lang and H.-J. Hansen, *Org. Synth.*, 1982, **62**, 202.
23 A. Ishida and T. Mukaijama, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 1161.
24 R. Schwesinger and H. Schlemper, *Angew. Chem.*, *Int. Ed. Engl.*, 1987, **26**, 1167.
25 1-*tert*-Butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)-phosphoranylideneamino]-2λ^5,4λ^5-catenadi(phosphazene), purchased from Fluka Chemie.
26 T. Tsuchiya, H. Arai and H. Igeta, *Chem. Pharm. Bull.*, 1973, **21**, 1516.
27 M. Raasch, *J. Org. Chem.*, 1980, **45**, 856.
28 E. A. Nodiff, A. J. Saggiomo, K. Tanabe, E. H. Chen, M. Shinbo, M. P. Tyagi, A. Kozuka, H. Otomasu, B. L. Verma and D. Goff, *J. Med. Chem.*, 1975, **18**, 1011.

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