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1-(TRIPHENYLMETHYL)ALLYL POTASSIUM : CONFORMATIONAL PREFERENCE AND [1,2]-REARRANGEMENT

ETIENNE MORET, JÜRG FÜRRER and MANFRED SCHLOSSER *

Institut de Chimie organique de l'Université
Rue de la Barre 2, CH-1005 Lausanne, Switzerland

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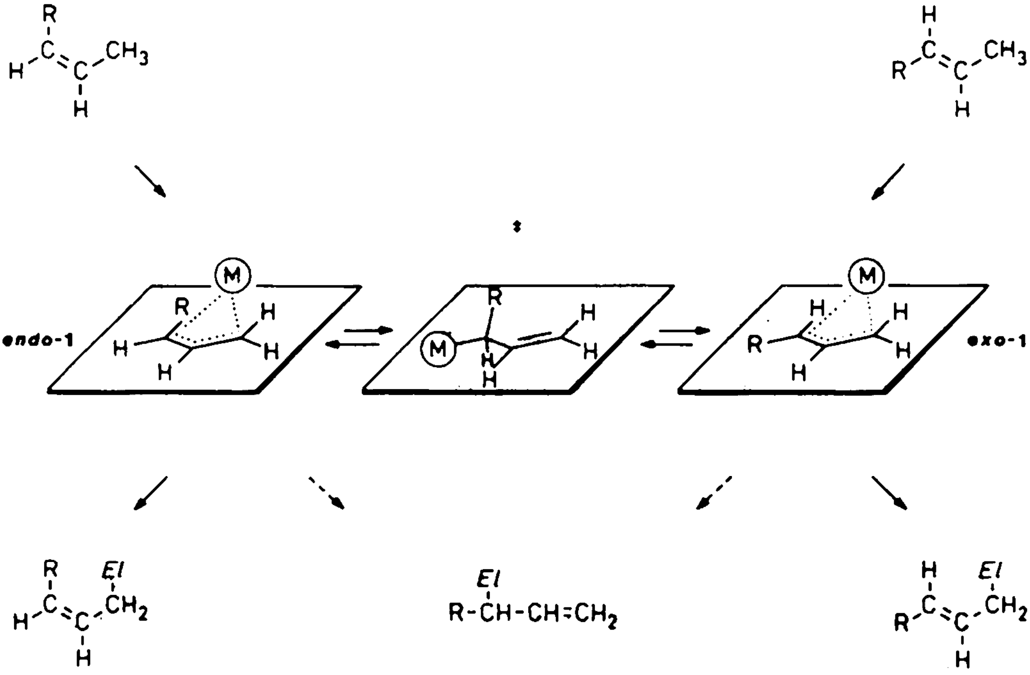
Summary. - Upon treatment with the superbasic 1 : 1 mixture of butyllithium and potassium *tert*-butoxide *cis*- and *trans*-1,1,1-triphenyl-2-butene as well as 4,4,4-triphenyl-1-butene undergo a hydrogen/metal exchange to afford 1-(triphenylmethyl)allyl potassium [4,4,4-triphenyl-2-butenyl potassium] which can exist in two stereoisomeric forms. Torsional equilibration leads to an *endo/exo*-ratio of approximately 50 : 50. Novel *endo*-stabilizing interactions are discussed to rationalize this result. At temperatures around or above 0°C a phenyl 1,2-migration, though no 1,4-migration takes place.

The introduction of our superbasic reagent, the 1 : 1 mixture of butyllithium and potassium *tert*-butoxide, has allowed to carry out the metalation of low acidity hydrocarbons such as benzene [1] or simple alkenes [2] for the first time in a synthetically useful manner. Since, in general, these metalations require only short reaction times even at low temperatures, the selective ("stereodefensive" [3]) conversion of *cis*- and *trans*-2-alkenes to *endo*- and, respectively, *exo*-alkenyl potassium species (*endo*- and *exo*-1, M = K) proved possible [4]. Quite slowly, however, an *endo/exo*-equilibrium is established between these conformers by torsional isomerization [4,5]. Catalysts such as oxygen [6] or magnesium, zink and mercury compounds [7] may be used to accelerate this process.



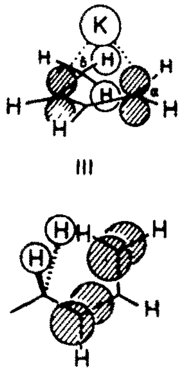
The *endo/exo*-equilibrium positions heavily depend on the nature of the alkyl group and the metal which are attached to the allyl moiety. Solvent effects add to these intrinsic factors. A first, qualitative evaluation of the detailed findings (see table) leads to an astonishing conclusion : straight-chain 2-alkenylsodium, -potassium and -caesium intermediates are thermodynamically more stable in the sterically more congested *endo*-conformation. The *exo*-counterpart becomes preponderant if the alkyl substituent is branched or the heavier alkali metals are replaced by lithium or magnesium. Even in the latter cases, the *endo*-conformer is favored in relative terms, since its proportion is invariably much higher than that of its *cis*-alkene precursor when in equilibrium with the corresponding *trans* olefin. (Estimated *cis/trans* ratio of 15 : 85 for 2-butene, 2-pentene or 4-methyl-2-pentene and of 1 : 10^5 for 4,4-dimethyl-2-pentene).

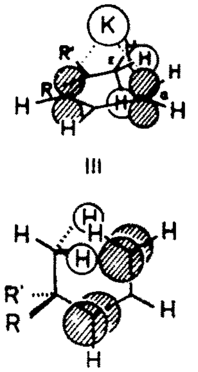
Table. Torsional equilibration of allyl-type magnesium, lithium, sodium, potassium and caesium compounds : ratios of *endo/exo*-conformers 1 in hexane suspension at 25°C or, in parentheses, in tetrahydrofuran solution at -30°C [4-6, 8].

R	M = MgBr	M = Li	M = Na	M = K	M = Cs
CH_3	1 : 1	2 : 1 (6 : 1)	15 : 1	25 : 1 (125 : 1)	1000 : 1
$CH_2CH_2CH_3$	1 : 2	1 : 2 (4 : 1)	2 : 1	15 : 1 (20 : 1)	10 : 1
$CH(CH_3)_2$	1 : 3	1 : 6 (1 : 1)	1 : 2	1 : 1 (4 : 1)	2 : 1
$C(CH_3)_3$	1 : 500	1 : 30 (1 : 25)	1 : 15	1 : 10 (1 : 7)	1 : 10

We have tentatively explained this strange *endo*-preference by intramolcular hydrogen bonding [9] between CH bonds at position 4 as donors and the electron-rich free allyl terminus as the acceptor [5]. This interaction between α- and δ-centers in 2-butenyl potassium (**1a**) may give way to an α,ε-interaction in 2-pentenyl potassium (**1b**, R = R' = H) or in 4-methyl-2-pentenyl potassium (**1c**, R = CH_3, R' = H) and must do so in 4,4-dimethyl-2-pentyl potassium (**1d**, R = R' = CH_3).

1a:



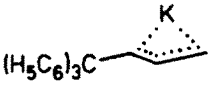


1b: R = R' = H
1c: R = H, R' = CH_3
1d: R = R' = CH_3

What would happen, if the three methyl groups in 4,4-dimethyl-2-butenyl potassium (**1d**) each were replaced by a phenyl group ? Hydrogen bridges between CH bonds and $C^α$-centers could no longer be invoked. Thus, the persisting steric effects should handicap the *endo*-conformer of 4,4,4-triphenyl-2-butenyl potassium (**2**) to the extent of its undetectability under equilibrium conditions unless new stabilizing factors come into play.

In order to answer these questions we have generated the two stereoisomers (*endo*- and *exo*-2) of 4,4,4-triphenyl-2-butenyl potassium ["1-(triphenylmethyl)allyl potassium"] and have equilibrated them. In addition, we have studied the thermal stability of these organometallic intermediates.

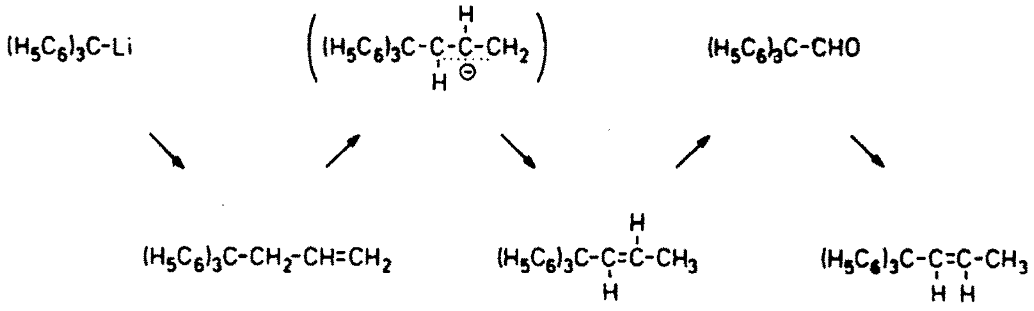
endo-2



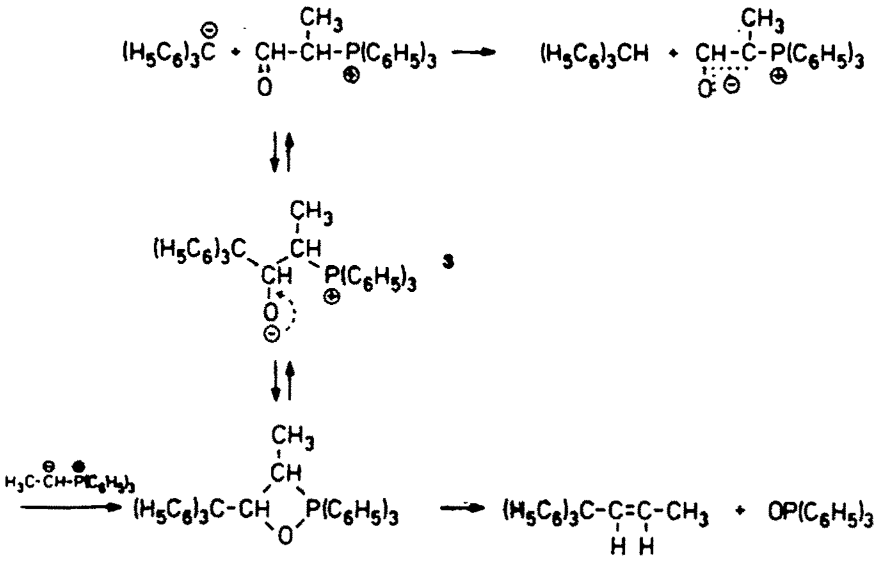
exo-2

Preparation of the starting materials

The terminal olefin, 4,4,4-triphenyl-1-butene, was readily obtained by condensation of triphenylmethyl lithium (from triphenylmethane and butyllithium) with allyl bromide. Base catalyzed isomerization [10] gave *trans*-1,1,1-triphenyl-2-butene in quantitative yield. Ozonolysis of the latter produced triphenylacetaldehyde which was converted to the *cis*-1,1,1-triphenyl-2-butene by Wittig reaction under "salt-free" [11] conditions.

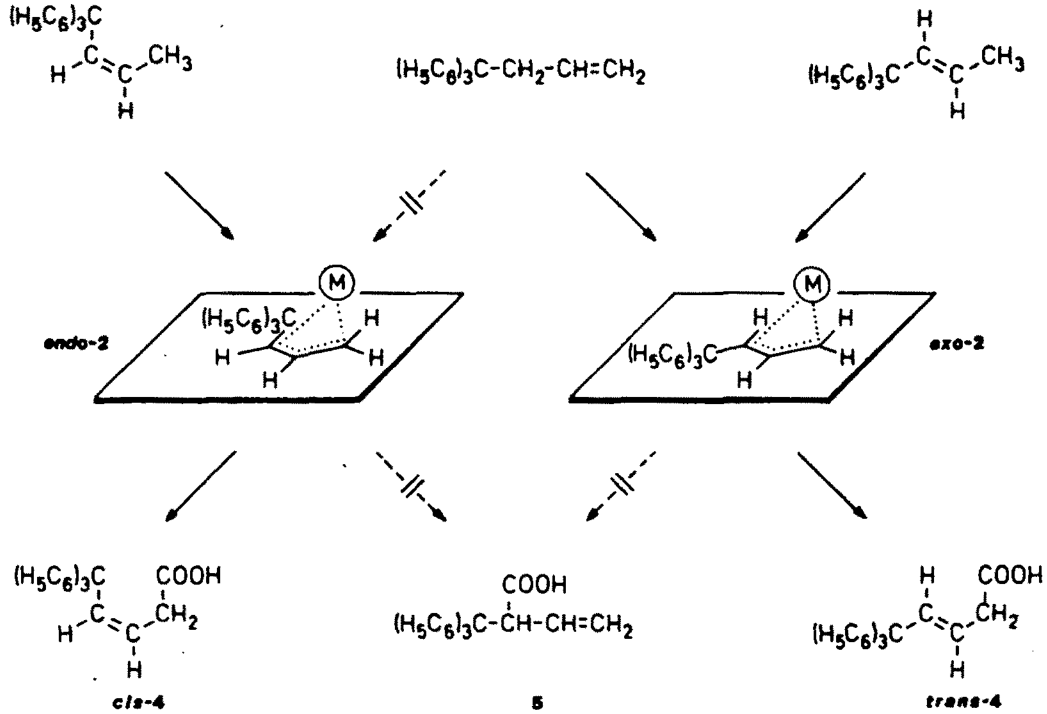


Highest yields of olefin were found, if the ylid was generated with potassium *tert*-butoxide [12] in tetrahydrofuran. With other bases up to 35% of triphenylmethane were isolated as a byproduct. Presumably it arises from a carbon-carbon bond scission at the stage of a betaine (*β*-phosphonioalkoxide) intermediate (3). Such zwitterions exist in equilibrium with the generally more stable oxaphosphetanes [13].

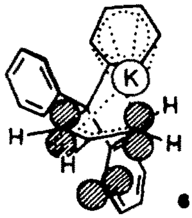


Metalation and trapping of the resulting intermediates

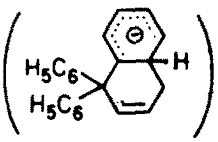
When *cis*-1,1,1-triphenyl-2-butene was treated with butyllithium and potassium *tert*-butoxide in tetrahydrofuran at -75°C the metalation proceeded rapidly as indicated by the immediate appearance of a characteristic deep red color. After 2h at - 50°C, the solution containing the *endo*-4,4,4-triphenyl-2-butenyl potassium (*endo*-2) was poured on dry ice and *cis*-5,5,5-triphenyl-3-pentenoic acid (*cis*-4) was isolated in 80% yield. The *trans*-isomer reacted 5 times more slowly, but the terminal olefin twice as fast as *cis*-4 and much more rapidly than the sterically even less hindered 4,4-dimethyl-1-pentene. Both, the *trans* and the terminal olefin gave the same *exo*-substituted allyl species *exo*-2 as was demonstrated by its conversion to *trans*-5,5,5-triphenyl-3-pentenoic acid (*trans*-4, 55 and 90%). Not even trace amounts of the regioisomeric 2-triphenylmethyl-3-butenoic acid (5) were produced in any of these reactions.



The organometallic intermediates 2 were not particularly prone to torsional isomerization. Despite the presence of a catalyst (dibutylmercury) 100h at -50°C were required to achieve complete equilibration after starting with each of the stereoisomerically pure precursors. More remarkably, however, both conformers, *endo*- and *exo*-2 were found to be represented at equilibrium in roughly equal amounts. This means, the *endo*-isomer must benefit from a special stabilizing interaction to compensate the steric crowding which discriminates against it. Actually we assume two effects to operate side by side. On one face of the allyl moiety a phenyl group might be rotated into the appropriate position to maximize the overlap of a π-orbital at one *ortho*-position with the π-orbital at the free allyl terminus. In that way electron excess can flow into the aromatic moiety (conformation 6 and limiting formula 7). On the opposite face another phenyl ring can orient its center towards the metal and act as a η^6-ligand of the latter.



6

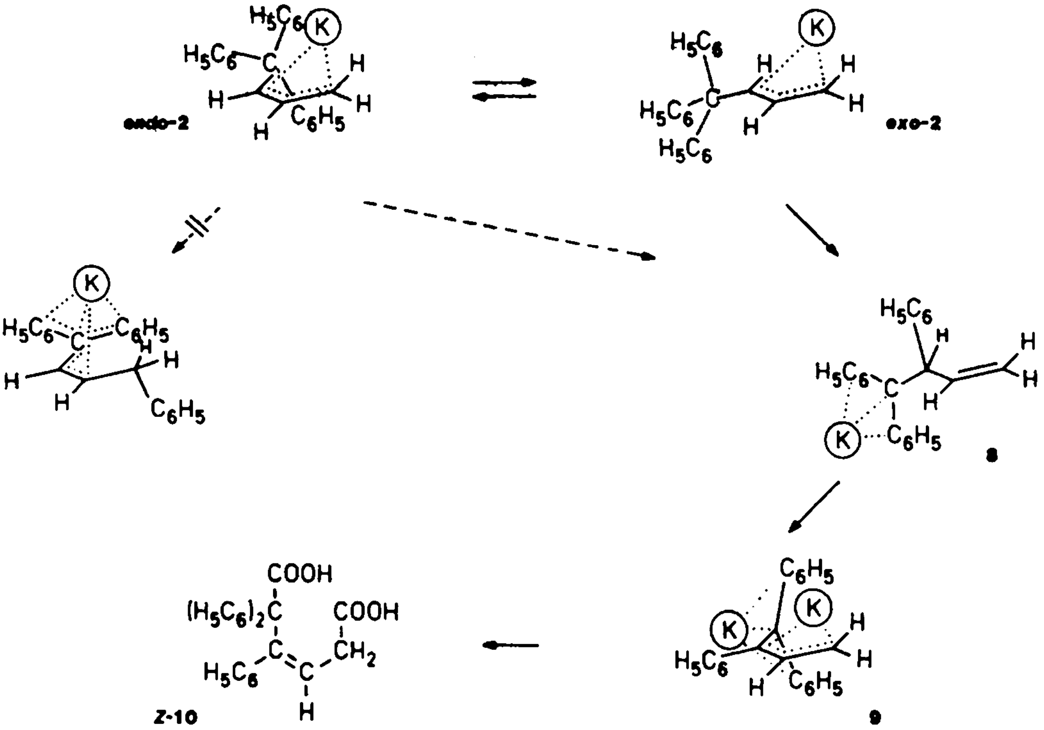


7

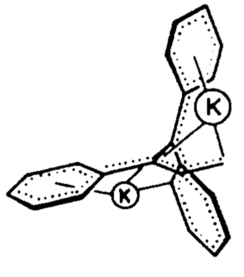
A similar π-complexation of an enolate lithium atom again by a homoallylic aryl group has been postulated previously [14]. The lamellar adducts [15] which spontaneously form by intercalation of potassium into the graphite lattice may also be considered as metal-arene π-complexes.

Phenyl [1,2]-migration

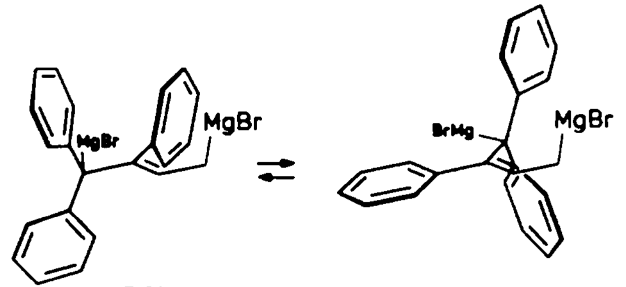
A Grovenstein-Zimmerman-type rearrangement [17] is promoted at temperatures around or above 0°C. The initially formed 1,1,2-triphenyl-3-butenyl potassium (8) transfers immediately a proton to unconsumed *exo*-2, a stronger base. The resulting dimetal species 9 reacts with carbon dioxide to afford (*Z*)-2,2,3-triphenyl-3-hexenedioic acid (*Z*-10).



If, however, a stoichiometric amount of magnesium bromide is added to the dipotassio compound 9 prior to carboxylation, a 1 : 1 mixture of the acid *Z*-10 and its stereoisomer *E*-10 is produced. This difference in conformational preferences may just reflect a change in the nature of metal-allyl interactions. The propensity of the higher alkali metals for symmetrical π-bonding [16] is best satisfied by the conformer carrying the benzhydryl moiety in the *endo*- and the single phenyl ring in the *exo*-position : both potassium atoms can enjoy simultaneous η^3(allyl or benzyl) and η^6(phenyl)-bonding (see *Z*-9a). On the other hand, neither conformer (*Z*- or *E*-9b) offers any special advantage in the case of magnesium derivatives since they form σ-bonds anyway [16].

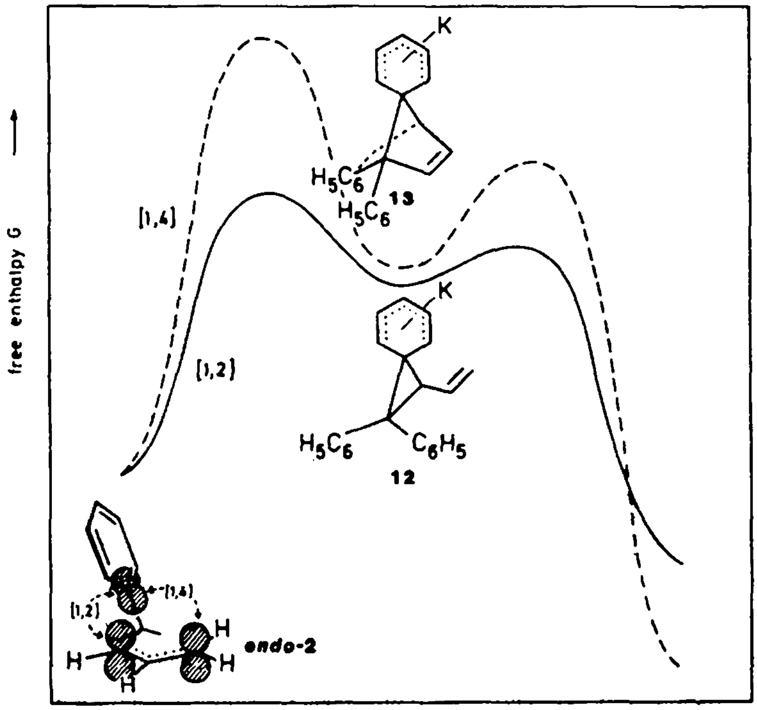


Z-9a



E-9b **Z-9b**

Torsional isomerization being faster than phenyl migration, it is not yet possible to tell whether the latter pathway is accessible to both 1-(triphenylmethyl)allyl species, *endo*- and *exo*-**2**, or to the less hindered *exo*-conformer alone. On the other hand, only *endo*-**2** has a suitable geometry for a phenyl [1,4]-migration. As a matter of fact, *endo*-**2** is the first heteroatom-free model compound which offers a choice between [1,2]- and [1,4]-rearrangements. Then why is the [1,4]-mode so strictly avoided although it would lead to a more efficiently delocalized and hence thermodynamically more stable rearrangement product ? By analogy [17] both, the factual [1,2]- and the hypothetical [1,4]-process, should involve cyclohexadienyl metal intermediates (**12** and **13**, respectively). Norbornene may be considered as a mimic for the geometry of the [1,4]-migration intermediate. Its total ring strain [18] is some 5 kcal/mol lower than that of cyclopropane, the crucial structural feature of the [1,2]-migration intermediate. The fusion of the bridge position with the cyclohexadienyl moiety will considerably attenuate this difference or even slightly inverse it since a spiro-center can much better accomodate one large and one small rather than two large (*e.g.*, 120° wide) CCC-angles. Therefore, the discrimination in favor of the [1,2]- and against the [1,4]-migration mode does not occur at the level of the intermediates but of the preceding transition states : the distance of the phenyl ring to the inner node of the allyl part being much shorter than to its free terminus, orbital overlap and hence bonding is stronger in the former case as soon as the skeleton deformation starts.



EXPERIMENTAL PART

1. General remarks

Starting materials have been purchased from Fluka AG, Buchs, Aldrich-Chemie, Steinheim, or Merck-Schuchardt, Darmstadt, unless literature sources or details for the preparation are given. *Butyllithium* and *potassium tert-butoxide* were supplied by CheMetall, Frankfurt, and Dynamit-Nobel, Troisdorf. All commercial reagents were used without further purification.

Air and moisture sensitive compounds were stored in Schlenk tubes or Schlenk burettes. They were protected by and handled under an atmosphere of 99.995% pure nitrogen.

Diethyl ether was obtained anhydrous by distillation after the characteristic blue color of in situ generated sodium diphenylketyl [19] was found to persist. The same procedure was applied to *tetrahydrofuran*, but in case of poor quality it was, in addition, pretreated with cuprous chloride [20] and potassium hydroxide pellets. *Hexane* and *benzene* were dried by careful azeotropic distillation, *dimethylsulfoxide* by vigorous stirring with finely powdered calcium hydride and distillation from it under reduced pressure.

Ethereal extracts were dried with sodium sulfate. Before distillation of compounds prone to radical polymerization or sensitive to acids a spatula tip of *hydroquinone* or, respectively, *potassium carbonate* was added.

The temperature of dry ice-methanol baths is consistently indicated as -75°C, "room temperature" (22 - 26°C) as 25°C. *Melting ranges* (mp) are reproducible after resolidification, unless otherwise stated ("dec."), and are corrected using a calibration curve which was established with authentic standards. If no melting points are given, it means that all attemps to crystallize the liquid product have failed even at temperatures as low as -75°C.

Infrared spectra were all recorded of potassium bromide pellets. The intensities of absorption bands are abbreviated as s (strong), m (moderate), w (weak) and b (broad).

Nuclear magnetic resonance spectra of hydrogen nuclei were recorded in the 360 MHz field. Unless otherwise stated, deuterochloroform was used as the solvent. Chemical shifts refer to the signal of tetramethylsilane ($\delta = 0$ ppm). Coupling constants (*J*) are measured in Hz. Coupling patterns are described by abbreviations : *s* (singulet), *d* (doublet), *t* (triplet), *q* (quadruplet), *pent* (pentuplet), *td* (triplet of a doublet) and *m* (multiplet).

In general, *mass spectra* were obtained at a 70 eV ionization potential. Whenever no molecular peak was observed under standard conditions, chemical ionization ("c.i.") in an ammonia atmosphere was applied.

2. Starting materials

4,4,4-Triphenyl-1-butene

A solution of triphenyl methane (22 g, 0.10 mol) and butyllithium (0.15 mol) in tetrahydrofuran (100 mL) and hexane (100 mL) is kept 16 h at 0°C. At -30°C allyl bromide (15 mL, 22 g, 0.18 mol) is added dropwise. After 1 h at 25°C, the mixture is washed with water (0.5 L) and brine (0.1 L), the solvents are stripped off and the residue (29 g) is cristallized from hexane (60 mL) to give, upon cooling, 21 g (76%) of colorless needles, mp 68 - 69°C (after recrystallization; lit.: mp 69.5 - 70.5°C [21]).

IR : 3070 + 3040 + 3030 + 3010 (w, $\nu[=\overset{|}{\mathrm{C}}\text{-H}]$), 1590 + 1485 + 1438 (s, $\nu[\mathrm{C=C}]$), 995 + 903 (m, $\delta[\mathrm{CH=CH_2}]$), 755 + 695 (m, $\delta[=\overset{|}{\mathrm{C}}\text{-H}]$).

^{1}H-NMR : 7.2 (15 H, *m*), 5.67 (1 H, *ddt*, *J* 17.0, 10.4, 6.7), 5.03 (1 H, *dq*, *J* 17.0, 1.7), 4.94 (1 H, *ddt*, *J* 10.4, 1.4), 3.44 (2 H, *dt*, *J* 6.7, 1.4).

trans-1,1,1-Triphenyl-2-butene

Immediately after the addition of potassium *tert*-butoxide (3.0 g, 27 mmol) to a solution of 4,4,4-triphenyl-1-butene (28.4 g, 100 mmol) in dimethyl sulfoxide at 50°C a red color appears and a white solid begins to deposit. After 1 h the mixture is allowed to cool before being diluted with water (200 mL). The precipitate is filtered and washed thoroughly. The wet product is dissolved in boiling ethanol (1.5 L). The solution is treated with charcoal and filtered. Upon cristallization 20.2 g (71%) of a colorless product are obtained, mp 126 - 127°C.

IR : 3050 + 3020 (m, $\nu[=\overset{|}{\mathrm{C}}\text{-H}]$), 2948 + 2920 + 2904 + 2868 + 2842 (m, $\nu[-\overset{|}{\underset{|}{\mathrm{C}}}\text{-H}]$), 1590 + 1487 + 1440 (s, $\nu[\mathrm{C=C}]$), 970 (m, $\delta[\mathrm{HC=CH}]$), 752 + 697 (s, $\delta[=\overset{|}{\mathrm{C}}\text{-H}]$).

^{1}H-NMR : 7.2 (9 H, *m*), 7.1 (6 H, *m*), 6.49 (1 H, *dq*, *J* 15.4, 1.6), 5.26 (1 H, *dq*, *J* 15.4, 6.4), 1.80 (3 H, *dd*, *J* 6.4, 1.6).

Analysis : calc. for $C_{22}H_{20}$ (284.4) C 92.91%, H 7.09%; found C 93.08%, H 7.11%.

cis-1,1,1-Triphenyl-2-butene

A stream of ozone is absorbed in a solution of *trans*-1,1,1-triphenyl-2-butene (5.7 g, 20 mmol) in dichloromethane (150 mL) at -75°C. When after approximately 1 h the solution becomes blue, dimethyl sulfide (5.0 mL, 4.3 g, 69 mmol) is added and the mixture is allowed to warm up. Solvent evaporation and crystallisation of the residue from ethanol gives 4.6 g (71%) of **triphenylacetaldehyde**, mp 100.0 - 101.5°C (lit.: mp 104 - 105°C [22]).

Potassium *tert*-butoxide (1.7 g, 15 mmol) is added to a suspension of ethyltriphenylphosphonium bromide (5.6 g, 15 mmol) in tetrahydrofuran (15 mL) and the mixture is stirred 30 min at 25°C. At -75°C, a solution of triphenylacetaldehyde (3.3 g, 12 mmol) in tetrahydrofuran is added dropwise. After 1 h at 25°C, the mixture is diluted with hexane (100 mL) and the precipitated triphenylphosphine oxide is removed by filtration. Evaporation of the solvents leaves a crude product (~ 3.0 g) which according to gas chromatography (10 m, SE-54 quartz capillary, 200 → 260°C [5°C/min]) consists essentially of *cis*- and *trans*-1,1,1-triphenyl-2-butene in the ratio of 97 : 3. After one crystallization from ethanol and another from hexane followed by sublimation a 99.8% isomerically pure sample is obtained, 2.0 g (59%), mp 64 - 65°C.

IR : 3070 + 3050 + 3010 (m, $\nu[=\overset{|}{\mathrm{C}}\text{-H}]$), 2938 + 2905 + 2840 (m, $\nu[-\overset{|}{\underset{|}{\mathrm{C}}}\text{-H}]$), 1645 (m, $\nu[\mathrm{C=C}]$), 1590 + 1487 + 1440 (s, $\nu[\mathrm{C=C}]$), 752 + 697 (s, $\delta[=\overset{|}{\mathrm{C}}\text{-H}]$).

^{1}H-NMR : 7.2 (15 H, *m*), 6.46 (1 H, *dq*, *J* 11.7, 1.7), 5.83 (1 H, *dq*, *J* 11.7, 7.3), 1.07 (3 H, *dd*, *J* 7.3, 1.7).

Analysis : calc. for $C_{22}H_{20}$ (284.4) C 92.91%, H 7.09%; found C 93.08%, H 7.11%.

3. Metalation and carboxylations

trans-5,5,5-Triphenyl-3-pentenoic acid (*trans*-4)

A solution of 4,4,4-triphenyl-1-butene (1.4 g, 5.0 mmol), potassium *tert*-butoxide (0.63 g, 5.6 mmol) and butyllithium (6.0 mmol, 1.5 M in hexane) in tetrahydrofuran (20 mL) is kept 2 h at -50°C before being poured on dry ice. After addition of hexane (60 mL), the organic layer is thoroughly extracted with 0.5 N aqueous sodium hydroxide (2 x 50 mL) and then evaporated whereupon 0.14 g (10%) of starting material (contaminated with some trans-1,1,1-triphenyl-2-butene) is recovered. After acidification (to pH ~ 1), the aqueous layer is extracted with a 3 : 1 (v/v) mixture of diethyl ether and hexane (100 mL). When the dried solvents are stripped off, 1.5 g (90%) of acid *trans*-4 are isolated, mp 187 - 188°C (after recrystallization from toluene and sublimation).

IR : 3000 (s, broad, ν[O-H]), 1700 (s, ν[C=O]), 1590 + 1487 + 1440 (s, ν[C=C]), 970 (m, δ[HC=CH]), 752 + 697 (s, $\delta[=\overset{|}{\mathrm{C}}\text{-H}]$).

^{1}H-NMR : 11.2 (1 H, broad), 7.2 (9 H, *m*), 7.1 (6 H, *m*), 6.66 (1 H. *d*, *J* 15.9), 5.39 (1 H, *dt*, *J* 15.9, 7.0), 4.24 (2 H, *d*, *J* 7.0).

MS (c.i): 346 (100%, $[M + NH_4^+]$).

Analysis : calc. for $C_{23}H_{20}O_2$ (328.4) C 84.12%, H 6.14%; found C 84.15%, H 6.11%.

Metalation and carboxylation of *trans*-1,1,1-triphenyl-2-butene (5.0 mmol) gave only 55% *trans*-4. In addition, 30% of starting material and 15% of a presumably ring substituted by-product were isolated.

Esterification of *trans*-4 with methanol in the presence of boron trifluoride during 2 h at 25°C affords **methyl *trans*-5,5,5-triphenyl-3-pentenoate** (96%), mp 99.5 - 100.0°C (from hexane).

IR : 3060 + 3020 (m, $\nu[=\overset{|}{\mathrm{C}}\text{-H}]$), 2942 + 2896 (m, $\nu[\text{-}\overset{|}{\underset{|}{\mathrm{C}}}\text{-H}]$), 1717 (s, ν[C=O]), 1590 + 1487 + 1440 (s, ν[C=C]), 970 (m, δ[HC=CH]), 752 + 697 (s, $\delta[=\overset{|}{\mathrm{C}}\text{-H}]$).

^{1}H-NMR : 7.3 (15 H, *m*), 6.61 (1 H, *dt*, *J* 16.0, 1.5), 5.41 (1 H, *dt*, *J* 16.0, 6.9), 3.20 (2 H, *dd*, *J* 6.9, 1.5).

Analysis : calc. for $C_{24}H_{22}O_2$ (342.4) C 84.18%, H 6.48%; found C 84.19%, H 6.45%.

cis-5,5,5-Triphenyl-3-pentenoic acid (*cis*-4)

Under the same conditions as described for the *trans*-isomer, *cis*-1,1,1-triphenyl-2-butene (0.58 g, 2.0 mmol) 81% of the acid *cis*-4 were isolated; mp 161 - 162°C (after crystallization from a 1 : 3 mixture of toluene and hexane).

^{1}H-NMR : 10.9 (1 H, broad), 7.3 (15 H, *m*), 6.68 (1 H, *dt*, *J* 11.8, 1.9), 5.95 (1 H, *dt*, *J* 11.8, 7.0), 2.43 (2 H, *dd*, *J* 7.0, 1.9).

Analysis : calc. for $C_{23}H_{20}O_2$ (328.4) C 84.12%, H 6.14%; found C 83.83%, H 6.10%.

Esterification gave the **methyl *cis*-5,5,5-triphenyl-3-pentenoate** (63%), mp 72 - 73°C (from hexane).

^{1}H-NMR : 7.3 (15 H, *m*), 6.64 (1 H, *dt*, *J* 12.0, 7.0), 5.99 (1 H, *dt*, *J* 12.0, 7.0), 3.56 (3 H, *s*), 2.39 (2 H, *dd*, *J* 7.0, 2.0).

Analysis : calc. for $C_{24}H_{22}O_2$ (342.4) C 84.18%, H 6.48%; found C 84.22%, H 6.45%.

Competitive metalations

A 1 : 1 mixture of *cis*- and *trans*-1,1,1-triphenyl-2-butene (2.5 mmol each) is treated 1 h at -50°C with trimethylsilylmethyl potassium [23] (2.2 mmol) in tetrahydrofuran (8 mL). The solution is poured on dry ice and the stereoisomeric acids *cis*- and *trans*-4 (0.44 g, 61%) are extracted. NMR analysis reveals a *cis*/*trans* ratio of roughly 80 : 20 which corresponds to relative reaction rates k_{cis}/k_{trans} ~ 5. A similar competition experiment between *cis*-1,1,1-triphenyl-2-butene and 4,4,4-triphenyl-1-butene leads to a ratio $k_{cis}/k_{terminal}$ ~ 0.5.

4. Torsional equilibration

A number of samples are prepared by adding *cis*- or *trans*-1,1,1-triphenyl-2-butene (2.0 mmol) and dibutylmercury (0.040 mmol) to a solution of trimethylsilylmethyl potassium [23] (2.0 mmol) in pentane (3.0 mL) and tetrahydrofuran (7.0 mL) at -50°C. In intervals the reactions are quenched with dry ice, the neutralized samples treated with diazomethane and the *cis/trans* composition of the resulting methyl esters determined by gas chromatography (10 m, SE-54 quartz capillary, 260°C) and by NMR spectroscopy. After 4 days a 1 : 1 ratio is approached in both stereoisomeric series.

5. Rearrangement

A solution of 4,4,4-triphenyl-1-butene (2.8 g, 10 mmol), potassium *tert*-butoxide (1.1 g, 10 mmol) and butyllithium (11 mmol) in tetrahydrofuran (40 mL) and hexane (10 mL) is kept 2 h at -50°C and 12 h at 0°C before being poured on dry ice. After addition of hexane (200 mL) the insoluble material is extracted with a 0.5 M aqueous solution of sodium hydroxide (2 x 60 mL). The organic layer contains *trans*-1,1,1-triphenyl-2-butene (1.3 g, 4.5 mmol). From the combined alcaline layers **(*Z*)-2,2,3-triphenyl-3-hexenedioic acid (*E*-10)** 1.75 g, 94% can be extracted with a 1 : 1 (v/v) mixture (250 mL) of diethyl ether and hexane after acidification (pH ~ 1), mp 247 - 248°C (dec.; from glycol dimethyl ether and hexane).

IR : 3000 (s, broad, ν[O-H]), 1695 (s, ν[C=O]), 1590 + 1487 + 1440 (s, ν[C=C]).
^{1}H-NMR : (C_3D_6O) 11.0 (2 H, broad), 7.46 (4 H, *d*-like *m*, *J* ~ 7), 7.2 (11 H, *m*), 6.21 (1 H, *t*, *J* 7.0), 2.78 (2 *H*, *d*, *J* 7.0).
MS : 372 (8.3%, M^+), 45 (100%).
Analysis : calc. for $C_{24}H_{20}O_4$ (372.4) C 77.40%, H 5.41%; found C 77.40%, H 5.42%.

Treatment of diacid *E*-10, in methanol, with an ethereal solution of diazomethane gives **methyl (*E*)-2,2,3-triphenyl-3-hexenedioate**; mp 124 - 125°C (from hexane).

^{1}H-NMR : 7.42 (4 H, *d*-like *m*, *J* ~ 7), 7.26 (6 H, *q*-like *m*, *J* ~ 6), 7.13 (5 H, *s*), 6.18 (1 H, *t*, *J* 7.2), 3.57 (3 H, *s*), 3.44 (3 H, *s*), 2.55 (2 H, *d*, *J* 7.2).
Analysis : calc. for $C_{26}H_{24}O_4$ (400.5) C 77.98%, H 6.04%; found C 77.75%, H 6.33%.

With *cis*-1,1,1-triphenyl-2-butene practically the same result is obtained. For control, a small quantity of the reaction mixture is treated with water and then checked on the presence of **1,1,4-triphenyl-1-butene**. No trace of this compound is detected by gas chromatography. Authentic material for comparison (85%, mp 42 - 44°C) had been prepared by olefination of benzophenone with (triphenylphosphonio)-3-phenyl-1-propanide.

^{1}H-NMR : 7.2 (15 H, *m*), 6.09 (1 H, *t*, *J* 7.5), 2.73 (2 H, *t*, *J* 7.7), 2.42 (2 H, *q*, *J* 7.6).
Analysis : calc. for $C_{22}H_{20}$ (284.4) C 92.91%, H 7.09%; found C 92.99%, H 7.13%.

An identical reaction sequence is carried out except that anhydrous magnesium bromide (40 mmol) in diethyl ether (20 mL) is added prior to carboxylation. A solid (90%, mp 215 - 225°C) is obtained the nmr spectrum of which shows with same intensities two signal sets, that of acid *Z*-10 (see above) and a new one corresponding to **(*E*)-2,2,3-triphenyl-3-hexenedioic acid (*E*-10)**.

^{1}H-NMR : (C_6D_6) 7.6 (4 H, *m*), 7.3 (9 H, *m*), 7.0 (2 H, *m*), 5.90 (1 H, *t*, *J* 7.3), 2.93 (2 H, *d*, *J* 7.0).
Analysis : calc. for $C_{24}H_{20}O_4$ (372.4) C 77.40%, H 5.41%; found C 77.33%, H 5.46%.

Treatment with diazomethane converts the acids in the corresponding stereoisomeric esters. The signals which remain after subtraction of the spectrum of the (*Z*)-isomer (see above) are assigned to the methyl (*E*)-2,2,3-triphenyl-3-hexenedioate.

^{1}H-NMR : 7.3 (13 H, *m*), 6.9 (2 H, *m*), 5.69 (1 H, *t*, *J* 7.5), 3.63 (3 H, *s*), 3.33 (3 H, *s*), 2.93 (2 H, *d*, *J* 7.5).

Analysis : calc. for $C_{26}H_{24}O_4$ (400.5) C 77.98%, H 6.04 %; found C 78.17%, H 6.07%.

A mixture of (*Z*)-2,2,3-triphenyl-3-hexenedioic acid (*Z*-**10**; 0.74 g, 0.2 mmol), trifluoroacetic anhydride (0.30 mL, 0.45 g, 2.2 mmol) and pyridine (1.5 mL, 1.5 g, 19 mmol) in tetrahydrofuran (50 mL) is kept 1 h at 25°C. The mixture is diluted with hexane (50 mL), washed with water (50 mL), 2 N sulfuric acid (25 mL), 0.5 N aqueous sodium hydroxide (25 mL) and brine (25 mL). Evaporation of the solvents and crystallization from toluene gives 3,3,4-triphenyl-2,3,6-7-tetrahydro-2,7-oxepinedione, 0.34 g (48%), mp 173 - 174°C (dec.).

IR : 3080 + 3060 + 3020 (w, $\nu[=\overset{|}{\mathrm{C}}\text{-H}]$), 2920 + 2890 (w, $\nu[-\underset{|}{\overset{|}{\mathrm{C}}}\text{-H}]$), 1782 + 1739 (s, $\nu[\mathrm{C=O}]$), 1590 + 1487 + 1440 (s, $\nu[\mathrm{C=C}]$), 760 + 700 (s, $\delta[=\overset{|}{\mathrm{C}}\text{-H}]$).

^{1}H-NMR : 7.2 (10 H, *m*), 7.0 (3 H, *m*), 6.83 (2 H, *d*-like *m*, *J* ~ 7), 6.10 (1 H, *t*, *J* 5.3), 3.47 (2 H, *d*, *J* 5.3).

Analysis : calc. for $C_{24}H_{18}O_3$ (354.4) C 81.34%, H 5.12%; found C 81.22%, H 5.18%.

Hydrolysis (2 N sulfuric acid and ethylene glycol dimethyl ether, 5 mL each, 1 h 25°C) of the anhydride allows to quantitatively recover the acid *Z*-**10**, which subsequently may be converted to its ester (mp 124 - 125°C).

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