

Reactions of the Lithium Salts of the Tribenzylidenemethane Dianion, Diphenylacetone Dianion, and Related Compounds

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Potentially synthetically useful reactions of the dilithium salts of the title dianions have been investigated. Electrophilic quenching with a variety of reagents usually leads to the expected products in good yield. Quenching the diphenylacetone dianion with 1 equiv of trimethylchlorosilane, however, gives a good yield of 1,3-diphenylallene obtained by formal elimination of a trimethylsiloxy anion from an intermediate monoquenched monoanion salt. NMR studies, however, do not reveal the intermediacy of the 1,3-diphenyl-2-(trimethylsiloxy)allyl anion but rather suggest that the initial reaction site is at carbon, rather than oxygen. Oxidation of the dianions leads either to ring closure or dimerization for the tribenzylidenemethane dianion and to dimerization for the diphenylacetone dianion. The dimerization reactions are stereospecific, both with respect to the two new stereocenters produced and for the double bonds of the bis-silyl enol ether products if the dimeric bis-enolate dianion products are quenched with trimethylchlorosilane.

Introduction

The remarkable stability of the guanidinium cation, which is inert to boiling water, was first attributed by Gund¹ to "Y-aromaticity". This suggestion started a controversial discussion about the special thermodynamic stability of cross-conjugated systems. The easy formation of the trimethylenemethane dianion² was attributed to this conjugative stabilization. Optimal Coulomb attraction between the anion and its counterions³ and internal stabilization resulting from charge alternation between the central positive carbon and the negative terminal carbons were proposed to determine the structure.⁴ In contrast, Frenking⁵ explained the preferred geometry by the differences in charge distribution between Y-conjugated dianions and their linear analogues. The negative charge is delocalized over three carbon atoms, whereas in the linear dianion only two atoms are available. Another proposal was that repulsive interactions of π -electrons are minimized in the Y-systems.⁵ However, the calculated pyramidalization of the terminal carbon atoms in the gas phase without counterions found by Frenking has never been observed experimentally. All X-ray structures of Y-conjugated dianions show planar Y-frameworks.^{6,7} However, the ligand TMEDA (*N,N,N,N*-tetramethyl-1,2-ethylenediamine) as well as the lithium cations undoubtedly influence the structures strongly.

Preparation and Structure

Y-Conjugated dianions are prepared easily by metalation of the corresponding olefin, as shown in Scheme

1. Two equivalents of TMEDA and *n*-butyllithium are added to a solution of the olefin in hexane. The color changes to red, and the dilithium salt is isolated as the crystalline adduct with two molecules of TMEDA.⁸ In the case of dianion **9**, the first deprotonation is carried out with 1.3 equiv of lithium hydride and TMEDA.⁹ The second step is as described above for molecules **1–8** and **10**.

Table 1 gives a summary of all dianions prepared this way. Nearly all of them show colors from orange to red. Only **8** was isolated in the form of green needles.

The conformations of the dianions in solution and the solid state have been examined by NMR and X-ray structure determination. Whereas **2** and **8** exist exclusively in the *exo,exo* conformation, **9** is a mixture of two isomers: 65% *exo,endo* and 35% *exo,exo* in solution.⁹ In the solid state, molecule **2** prefers an *exo,exo* conformation.⁷ All X-ray structures show the lithium cations on opposite sides of the dianion plane: one above and one below.

Reactions

Quenching reactions of strong nucleophiles are often carried out to obtain information, such as the nature of reactive centers, or to answer the question of kinetic vs thermodynamic control of reactions. However, in the case of dianion salts, a wide range of synthetically useful molecules can be synthesized. It is possible to introduce two, possibly different (see Scheme 4), functional groups. The reactions are performed at low temperature. The reagents were added by syringe to dissolved (tetrahydrofuran, diethyl ether) or suspended (hexane) dianion. Scheme 2 shows some reactions using tribenzylidenemethane dianion **3** as an example. The percentage yield

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(1) Gund, P. J. *Chem. Educ.* **1972**, *49*, 100.

(2) Klein, J.; Medlik, A. *J. Chem. Soc., Chem. Commun.* **1973**, 275.

(3) Schleyer, P. v. R. *Pure Appl. Chem.* **1983**, *55*, 355.

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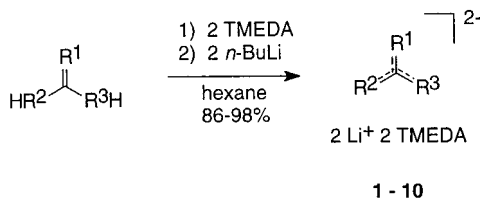
(6) Wilhelm, D.; Dietrich, H.; Clark, T.; Mahdi, W.; Kos, A. J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1984**, *106*, 7279.

(7) Dietrich, H.; Mahdi, W.; Wilhelm, D.; Clark, T.; Schleyer, P. v. R. *Angew. Chem.* **1984**, *96*, 623.

(8) Wilhelm, D.; Clark, T.; Schleyer, P. v. R.; Buckl, K.; Boche, G. *Chem. Ber.* **1983**, *116*, 1669.

(9) Wilhelm, D.; Clark, T.; Schleyer, P. v. R. *J. Chem. Soc., Perkin Trans. II* **1984**, 915.

Scheme 1. Synthesis of Y-Conjugated Dianions 1-10^a



^aFor R¹, R², and R³ see Table 1. For dianion **9**, the first deprotonation step is carried out with 1.3 TMEDA/LiH.

given in Scheme 2 relates to the corresponding olefin (i.e., yields include the double-deprotonation step).

As shown in Scheme 2, all reactions give good yields. In nearly all cases the intermediate monoanion reacts a second time to form disubstituted compounds. Quenching with dimethyldichlorosilane did not lead to a four-membered ring as expected. Ring strain and the very stable oxygen-silicon bond favor **14** after hydrolysis. Methyl iodide does not oxidize the dianion, although Bates¹⁰ has used it to oxidize quinodimethane dianions. The reaction with 1,2-dibromoethane results in a three-membered, **19**, and not a five-membered ring system, in contrast to 1,3-dibromopropane, which gives the six-membered ring **17**. The only reagent that reacts only once is 1,2-dichloroethane. Oxidation with iodine results in a dimerization to **16**.

The other Y-conjugated dianions with carbon frameworks, **1**, **2**, and **4-8**, react in the same general way with quench reagents. The stereochemistry of these reactions must, however, be considered. Monosubstituted trimethylenemethane dianions **1**, **6**, and **7** give two isomers with almost all quench reagents: both substituents at the CH₂ group or one at CH₂ and one at CHAr. Chart 1 shows one example for the quench reaction between dianion **1** and TMSCl (trimethylchlorosilane), the only reagent that reacts exclusively at the CH₂ groups (**20**, yield 94%). With dimethyl disulfide, the expected reaction was found. The product distribution is 60 (**21a**):40 (**21b**), and the yield is 85%.

Dianion **2** poses new problems in addition to constitutional isomerism: *Z,E* isomerism of the double bond and diastereoisomerism. However, once again selectivity problems arise. TMSCl is very selective. Only **22** was found in an excellent yield of 92% (Chart 2). Without exception the product is *E*-configured. Reaction with di-*tert*-butyl peroxide leads to the *E* product **23a** and a mixture of diastereoisomers **23b**. The product distribution is 71 (**23a**):29 (**23b**) in a total yield of 73%.

Dianion **9** shows different reactions because of the oxygen heteroatom. The intermediate monoanion is stabilized by the oxygen and is therefore less reactive than its carbon analogue. Dimethyl disulfide (**25**) and di-*tert*-butyl peroxide (**24**) give only monosubstituted products at CHAr. The peroxide reacts extremely slowly. Decolorization of the red dianion solution occurs in 24 h. Reaction with methyl iodide (**26**) and 1,3-dibromopropane (**27**) lead to the expected compounds. However, neither 1,2-dichloroethane nor 1,2-dibromoethane gives a five-membered ring with dianion **9** under analogous conditions. Double nucleophilic substitution to give an ethylene-bridge (**28**) or dimerization (**29**) was obtained. Scheme

3 shows the products of the quenching reactions of the diphenylacetone dianion, the quench reagents, and the yields.

Attempts to trap the monoanion product formed by the quench-reaction between dianion **9** and dimethyl disulfide with TMSCl lead to a product with two different substituents (**32**, Scheme 4). It is possible to control the product distribution between the kinetically preferred product **32a,b**, which is formed under thermodynamic control. Quenching the intermediate enolate after 5 min with TMSCl leads exclusively to **32a**, whereas addition after 4 h leads to **32b**.

Reactions with TMSCl

The products of the quench reaction between dianion **9** and trimethylchlorosilane are unusual. Excess of TMSCl leads to *Z*-configured disilylated compound **30**. Because of the high affinity between silicon and oxygen, one of the silyl groups is bonded to the heteroatom. The result of the analogous reaction under the same conditions but with an equimolar amount of TMSCl leads to a completely different product: 1,3-diphenylallene (**31**) was formed in a surprisingly good yield of 84%.

To check whether this reaction can be extended to other α,α' -ketone dianions, we used several ketone dianions and treated them with equimolar amounts of TMSCl (Scheme 5). Table 2 shows the reaction conditions and the products.

Dianions **9** and **33**, which could be isolated and purified, lead to good yields of allenes, but with **34** and **35** yields were low. As it was not possible to separate these two dianions from byproducts in THF, the whole reaction was carried out in one flask, without isolation of the intermediate dianion.

NMR experiments show that the elimination reaction of the ⁻OSi(CH₃)₃ fragment begins at -60 °C in the case of **9**. Scheme 6 shows the possible routes to the allene via different intermediates. A possible alternative pathway from **40** via a 1,3-H shift to an α -silylenolate and a subsequent 1,2-elimination would lead to an acetylene.¹¹ The allene could then be formed by rearrangement. However, derivatives of acetylenes have never been observed in this reaction, so this path seems unlikely.

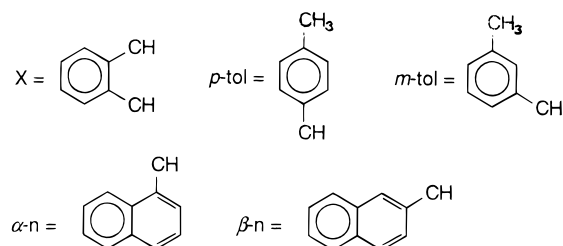
We have tried to differentiate between initial O- and C-silylation. NMR experiments show that the silylation step was complete at -95 °C, and only **40** was observed. We therefore performed several experiments in order to investigate the transfer of the Si(CH₃)₃ fragment from the carbon atom to the oxygen.

First, we mixed dianion **9** with equimolar amounts of disilylated **30**. Neither deprotonation of **30** nor intermolecular transfer of a Si(CH₃)₃ group took place. Second, a desilylation of **30** with methyl lithium leads to the allene and the byproduct α -silyl ketone, the C-silylated compound. Again there is no indication of intermediate **39**. The reaction between the diphenylacetone dianion **9** and trimethylsilyl triflate leads exclusively to the *Z* conformation of **30**. The competition between disilylation and allene formation observed in the reaction with TMSCl is not found with the more reactive trimethylsilyl triflate. This third experiment shows that the formation of **31** is slow.

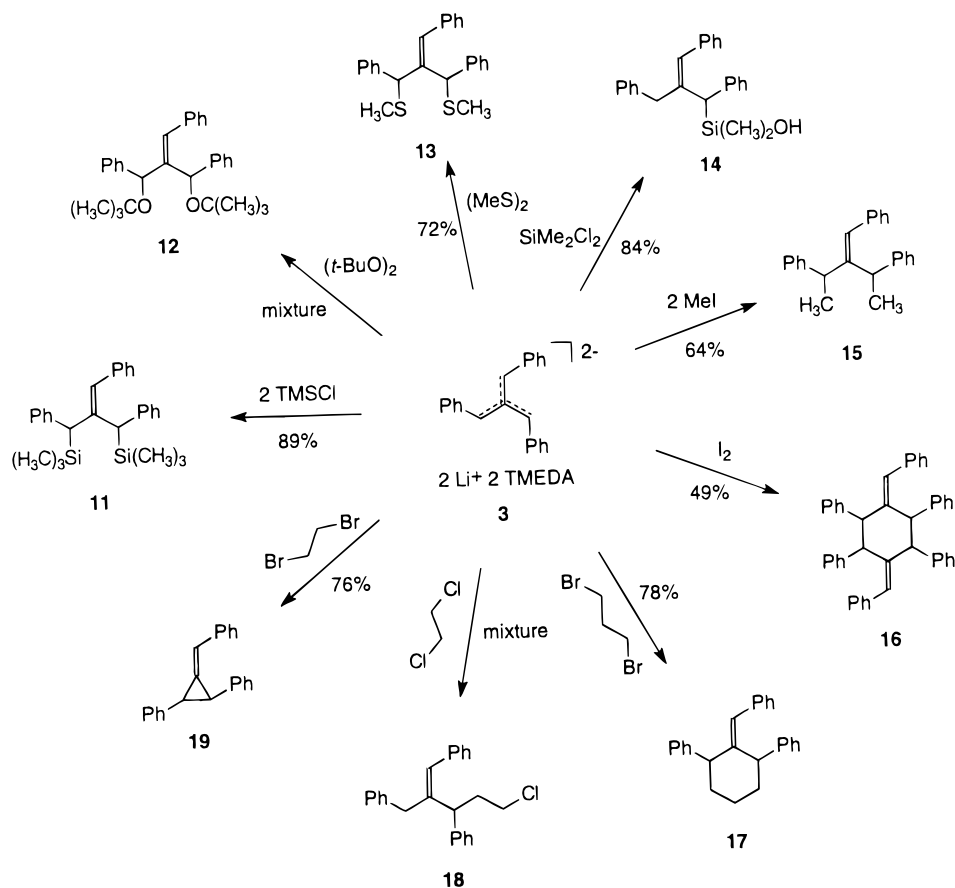
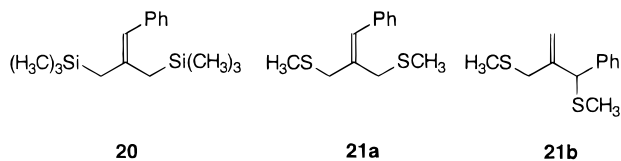
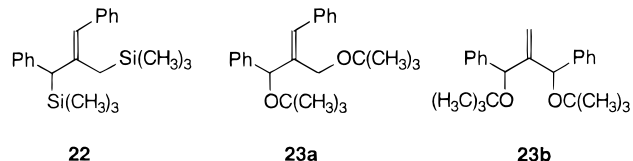
(10) Bates, R. B.; Ogle, C. A. *J. Org. Chem.* **1982**, *47*, 3949.

(11) Bushby, R. J.; Patterson, A. S.; Ferber, G. J.; Duke, A. J.; Whithan, G. H. *J. Chem. Soc., Perkin Trans. II* **1978**, 807.

Table 1. Y-Dianions



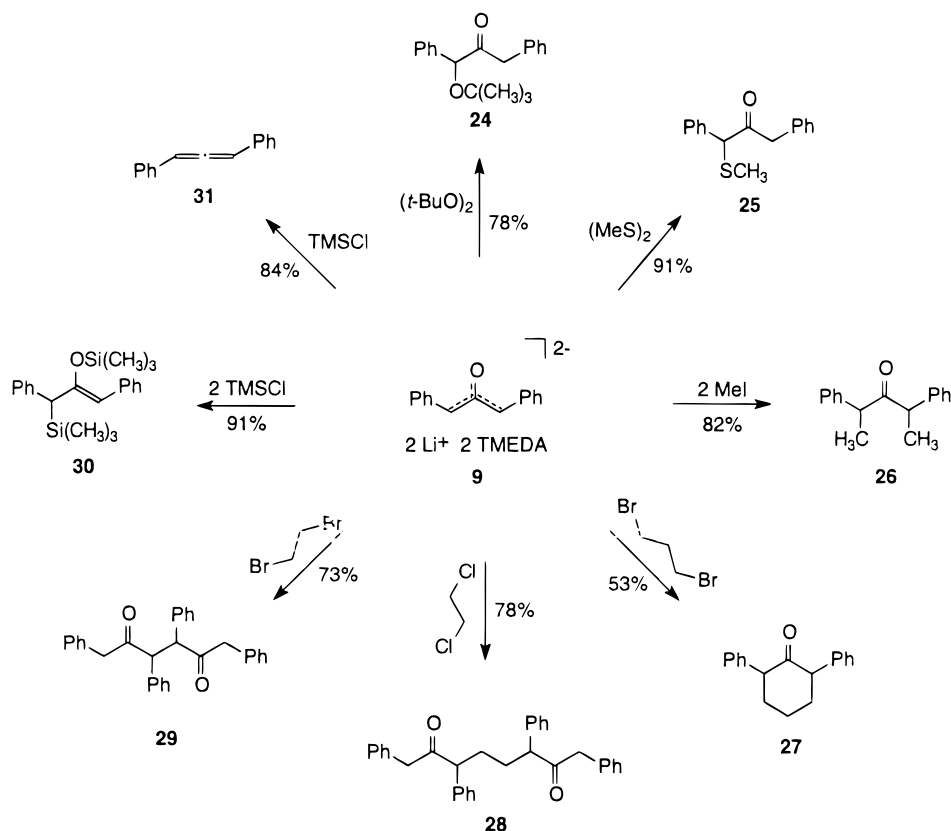
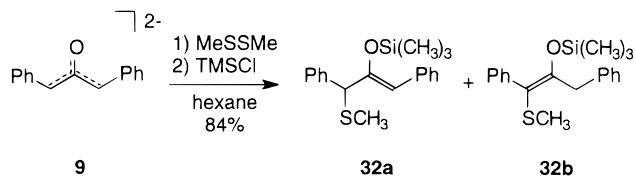
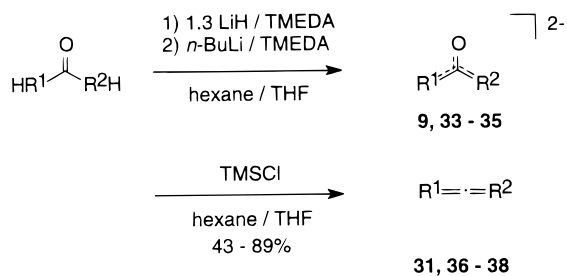
R ¹	CH ₂	CH ₂	CHPh	<i>p</i> -tol	<i>m</i> -tol	CH ₂	CH ₂	CH ₂	O	CHPh
R ²	CHPh	CHPh	CHPh	<i>p</i> -tol	<i>m</i> -tol	α -n	β -n	β -n	CHPh	} X
R ³	CH ₂	CHPh	CHPh	<i>p</i> -tol	<i>m</i> -tol	CH ₂	CH ₂	β -n	CHPh	
dianion	1	2	3	4	5	6	7	8	9	10
yield, %	96	95	97	94	91	98	97	93	96	86

Scheme 2. Quench Reactions of Tribenzylidenemethane Dianion **3**Chart 1. Products of the Quench Reaction of TMSCl or Dimethyl Disulfide with Dimethylenbenzylidenemethane Dianion **1**Chart 2. Products of the Quench Reaction of TMSCl or Di-*tert*-butyl Peroxide with Dibenzylidenemethylenemethane Dianion **2**

Surprisingly, none of these experiments gave any indication of **39**, although the allene must be formed by elimination of $^-\text{OSi}(\text{CH}_3)_3$. The fourth experiment was to deprotonate 1,3-diphenyl-2-(trimethylsilyloxy)-2-propene (**41**) with LDA (lithiumdiisopropylamide) to form the allene **31** (Scheme 7). NMR experiments show that allene formation started at -70°C .

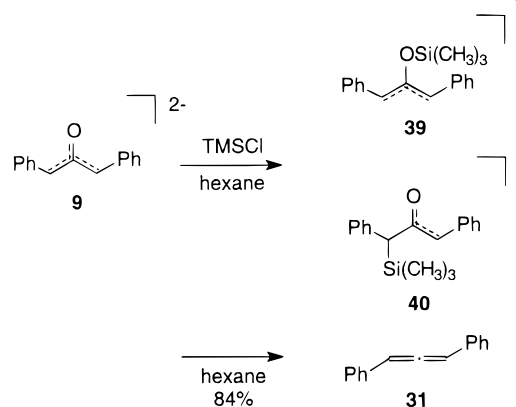
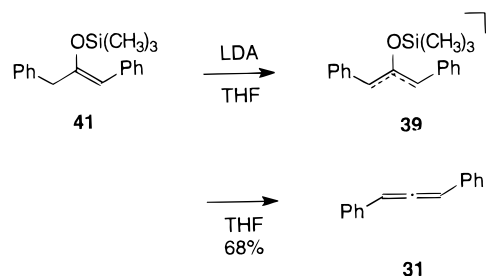
All experiments lead to the following conclusions: The elimination of $^-\text{OSi}(\text{CH}_3)_3$ is fast, the intermediate **39** has never been observed, and the reaction is probably intramolecular. Thus, a cyclic transfer similar to the Peterson olefination¹² is probable, as shown in Scheme 8.

(12) Ager, D. J. *Organic Reactions*; Wiley & Sons: New York, 1990, p 38.

Scheme 3. Reactions of Diphenylacetone Dianion **9****Scheme 4. Mixed Substitution of 1,3-Diphenylacetone Dianion **9******Scheme 5. Reaction of α,α' -Ketones to Allenes^a**^a For R¹ and R² see Table 2.**Table 2. Reactions of Several Ketone Dianions with TMSCl**

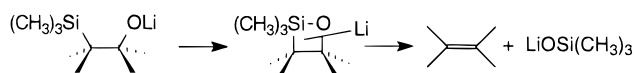
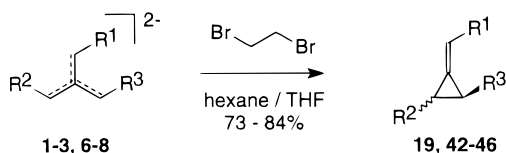
R ¹	R ²	dianion	solvent	product	yield, %
CHPh	CHPh	9	hexane	31	84
CPh ₂	CPh ₂	33	hexane	36	89
CHCOOCH ₃	CHCOOCH ₃	34	THF	37	43
CH(CH ₂) ₇ CH	CH(CH ₂) ₇ CH	35	hexane/THF	38	54

This silicon variation of the Wittig reaction has been known since 1968, but its mechanism is still unclear. A reaction between an α -silyl organic compound and a ketone leads to an intermediate which eliminates to an olefin. In some cases a reaction path via a pentacoordi-

Scheme 6. Possible Routes to the Allene (31**)****Scheme 7. Deprotonation of (*Z*)-1,3-Diphenyl-2-(trimethylsiloxy)propene (**41**)**

nated silicon intermediate has been described.¹³ If the silylating reagent is TMSCl, the Si-O and C-C bonds form synchronously, but all examples lead to a C-C double bond.

(13) Hudrlík, P. F.; Agwaramgbo, E. L. O.; Hudrlík, A. M. *J. Org. Chem.* **1989**, *54*, 5613.

Scheme 8. Key Step in the Peterson Reaction**Scheme 9. Reactions of Dianions with 1,2-Dibromoethane^a**

^a For R¹, R², and R³ see Table 3.

Table 3. Reactions of the Y-Shaped Dilithium Compounds with 1,2-Dibromoethane and Subsequent Hydrolysis

dianion	R ¹	R ²	R ³	product	yield, %
1	H	Ph	H	42	79
2	Ph	Ph	H	43a	63
	Ph	H	Ph	43b	14
	H	Ph	Ph	43c	<2
3	Ph	Ph	Ph	19	76
6	H	α-n	H	44	74
7	H	β-n	H	45	73
8	β-n	β-n	H	46	84

Syntheses of tetraphenylallene with silyl reagents have been described by Gilman¹⁴ and Chan.¹⁵ In another publication Chan describes the route to terminal allenes.¹⁶

However, the facile quench reaction of α,α'-ketone dianions, or even more simply deprotonation of the trimethylsilyloxy enol ether (Scheme 7), provides an attractive alternative synthetic route to allenes.

Oxidations

The reactions of dilithio compounds are not restricted to their nucleophilic or alkaline behavior. They can also be oxidized easily. The resulting CC coupling is an important aspect for synthetic chemistry. In the presence of oxidants, dilithio compounds do not usually react by electrophilic substitution but rather undergo single-electron transfer (SET). We have tested the oxidant/solvent systems I₂/THF, FeCl₃/THF, and 1,2-dibromoethane in hexane or THF. 1,2-Dibromoethane is generally considered to be the best oxidant since the resulting ethylene gas is inert to all reactants. The initial SET from the negatively charged dianion creates a radical anion. The products are either a dimer or, after further oxidation and internal cyclization, a methylenecyclopropane (Schemes 3 and 9). Whereas the oxidation of the dianion of linear 1,5-hexadiene leads to the triene,¹⁷ the Y-shaped homonuclear dianions form methylenecyclopropanes (Scheme 9 and Table 3).

The dibenzylidenethylene dianion **2** gives an isomeric mixture of all possible diphenylmethylenecyclopropanes.

(14) Gilman, H.; Tomasi, R. A. *J. Org. Chem.* **1962**, *27*, 3647.

(15) Chan, T. H.; Chang, E. *J. Org. Chem.* **1974**, *39*, 3264.

(16) Chan, T. H.; Mychajlowski, W. *Tetrahedron Lett.* **1974**, *2*, 171.

(17) Morton, A. A.; Marsh, F. D.; Coombs, R. D. *J. Am. Chem. Soc.* **1950**, *72*, 3785.

**Figure 1.** Twofold degenerate HOMO of the *exo,exo*-(*EE*)-dianion **8** (PM3).

The product range is similar to the hydrolysis of **2**. No radical byproducts were isolated. Therefore, the reaction is assumed to be a fast and selective oxidation of the Y-conjugated carbon core. Semiempirical calculations suggest that these atoms have the highest HOMO coefficients. Figure 1 shows the degenerate HOMO of the most stable conformer of dianion **8** found with PM3. The resulting radical anions and neutral triplet or singlet systems obviously exist only in very low concentrations or are short-lived, so that only internal cyclization is observed. ESR experiments on the tribenzylidenemethane dianion **3**¹⁸ also show no signals due to the radical anion.

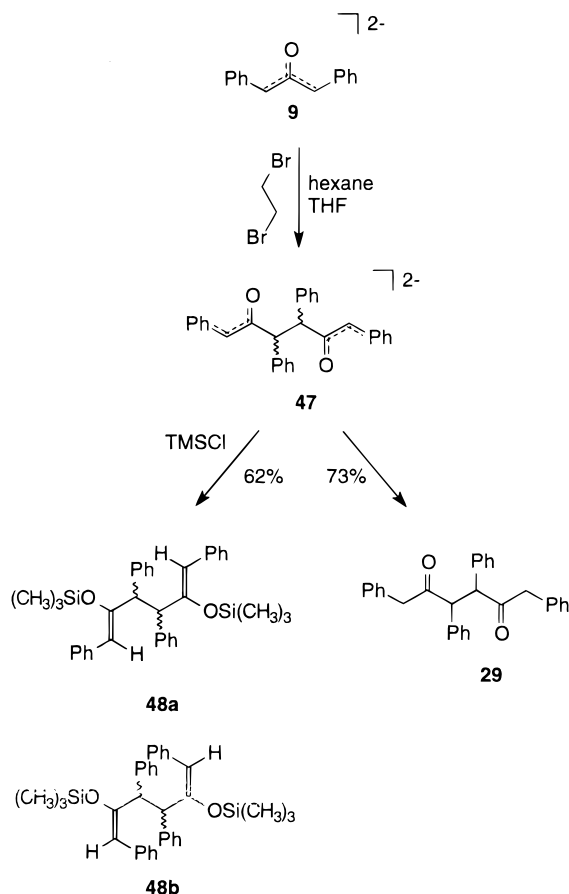
On closer examination of the methylenecyclopropanes, it is evident that the reaction occurs under kinetic control. One aryl group is always bonded to the three-membered ring to give the thermodynamically less-stable product. In general, these oxidative cyclizations of Y-dianions are a useful route to methylenecyclopropanes.

Formal substitution of Y-conjugated core atoms by oxygen leads eventually to the stable carbonate dianion. A theoretical and experimental overview of this relationship has been given by Clark et al.⁹ Oxidation of the 1,3-diphenylacetone dianion **9** gives, in contrast to the homonuclear dianions **2** and **3**, not internal but rather external CC coupling to give the dimer **29**. This difference is probably the result of a strong shift in the oxidation potential of the intermediate radical anion on oxygen substitution. Although we know of no experimental data to support a change in oxidation potential, it is reasonable to assume the replacement of a CHPh group by the very much more electronegative oxygen will have this effect.

After the first electron transfer, the two radical anions form the dienolate **47** (Scheme 10), which is stable in oxygen-free solution. Following hydrolysis, **47** gives the 1,4-diketone **29**. When the dienolate **47** is quenched with TMSCl, only two of three possible regioisomers (*ZZ*)-**48a** and (*EE*)-**48b** are observed; the (*EZ*)-disilyl enol ether is not formed.

As for the other oxidations, the reaction can be carried out in both THF and hexane. In the latter, however, at low temperature and with an excess of 1,2-dibromoethane, the isomers of tetraphenyl dienolate **47** can be

(18) Wilhelm, D.; Clark, T.; Courtneidge, J. L.; Davies, A. G. *J. Chem. Soc., Chem. Commun.* **1983**, 213.

Scheme 10. Oxidation of 1,3-Diphenylacetone Dianion 9


isolated as yellow crystals. Since an X-ray analysis has not yet been possible, the structure of **47** is not fully characterized. The proton NMR, however, shows four signals between 3.35 and 4.76 ppm belonging to eight aliphatic hydrogen atoms. By analogy with the quench reaction with TMSCl, there must be at least two isomers, both symmetrical and therefore chiral.

A comparison of the NOE difference spectra^{19,20} with the calculated PM3 geometries^{21,22} shows good agreement with the internal bridged structures **47a,b** (Figure 2), respectively. Both minimum-energy geometries contain two TMEDA ligands each to saturate the coordinative sphere of the lithium counterions and are very close in energy.

If we assume that structures **47a,b** are correct, the reaction with TMSCl results in a direct electrophilic attack at the oxygens under formation of the enol double bond. The geometry and stereochemistry are fixed. We are now trying to confirm the suggested *RR/SS* stereoselectivity. To verify the results of the dianion reactions with 1,2-dibromoethane, other oxidants were used. We did not observe an oxidative cyclization to 1,2,4,5-tetraphenylhydroquinone on treatment of 1,3-diphenylacetone dianion **9** with iodine in THF and subsequent

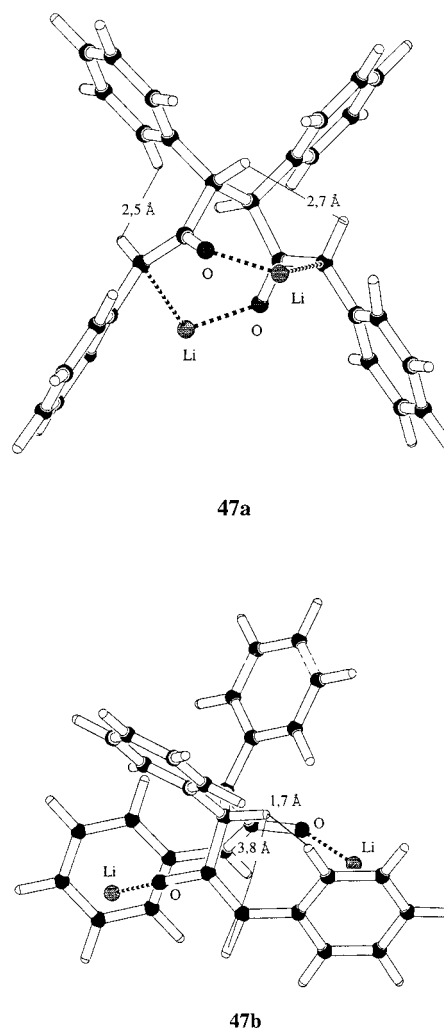


Figure 2. PM3 geometries of the two most probable 1,3,4,6-tetraphenyl dienolate isomers **47a,b**.

quenching in excess of water under absence of oxygen. This oxidative dimerization to 1,2,4,5-tetraphenylhydroquinone was described by Fox et al.,²³ if dianion **9** is oxidized by I_2/THF in the presence of oxygen and worked up with water. Under our conditions, the reaction leads to the products described above, but in lower yields. A significant difference is the formation of a six-membered ring, **16** (Scheme 2), when the tribenzylidenemethane dianion is stirred in a homogeneous reaction with iodine in THF. Treating dianions with other oxidants leads to poorly defined products (Cl_2) or at least worse yields (FeCl_3/THF). When using 1,2-dichloroethane instead of 1,2-dibromoethane, one halogen is substituted by the nucleophilic dianion in an $\text{S}_{\text{N}}2$ reaction. The product range depends on the dilution and ratio of dianion and dihalogen species. In an equimolar ratio we observed linear products **49** (Chart 3).

The same species are also formed by monoanions. Therefore, it is reasonable to propose that the first step is the protonation of the dianion. When working in very high dilution, a second substitution is possible to form a cyclic species. However, in general yields are low. The treatment of tribenzylidenemethane dianion **3** with the

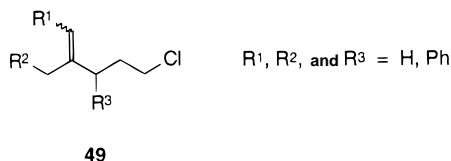
(19) Neuhaus, D.; Williamson, M. *The Nuclear Overhauser Effect in Structural and Conformational Analysis*; VCH: New York, 1989.

(20) Noggle, J. H.; Schirmer, R. E. *The Nuclear Overhauser Effect, Chemical Applications*; Academic Press: New York, 1971.

(21) Stewart, J. J. *J. Comput. Chem.* **1989**, *10*, 209, 221.

(22) Rauhut, G.; Alex, A.; Chandrasekhar, J.; Steinke, T.; Sauer, S.; Beck, B.; Hutter, M.; Clark, T. *VAMP6.5*; Oxford Molecular Ltd., Magdalen Centre, Oxford Science Park, Sandford-on-Thames, Oxford OX4 4GA, England; 1997.

(23) Fox, M. A.; Chen, C.-C. *J. Chem. Soc. Chem. Commun.* **1985**, 23.

Chart 3. Quench Reaction of Dianions with 1,2-Dichlorides

more reactive 1,3-dibromopropane gives a six-membered ring, **17**. Here the dibromoalkane does not react as an oxidant.

Not surprisingly, the 1,3-diphenylacetone dianion **9** shows different behavior than the homonuclear dianions. In contrast to the oxidation with 1,2-dibromoethane, the reaction with 1,2-dichloroethane gives an ethylene-bridged dimer, **28**.

Conclusions

Y-Conjugated derivatives of the trimethylenemethane and α, α' -acetonediyl dianions have proven to be potentially useful reagents for synthetic reactions. They undergo quench reactions with a variety of electrophiles in high yields to yield mono- and disubstituted products. The quench reaction with TMSCl is unusual in that it leads to elimination of the $^-OSi(CH_3)_3$ anion with formation of an allene. These reactions occur in synthetically useful yields as long as the intermediate dianion can be isolated and used pure for the quench reaction. Oxidation of Y-conjugated dianions may either lead to ring closure or to dimerization. The dimerization reaction exhibits an unusual double stereoselectivity that is still under investigation.

Experimental Section

General Preparation of Dianion Compounds 1–10.

We describe the procedure for preparation of dianion **1**. All other dianions are synthesized analogously. To 2-benzyl-1-propene (5 g, 42 mmol) in 100 mL of absolute hexane were added TMEDA (14.4 mL, 95.8 mmol) and *n*-BuLi (1.6 M in hexane, 61.8 mL, 95.8 mmol) under nitrogen atmosphere. Soon deep-red crystals were formed. After 12 h the solvent was separated, and the crude product **1** was washed several times with absolute hexane and dried in vacuum.

In the case of dianion **9**, the first deprotonation step was carried out with LiH (0.43 g, 53 mmol) and TMEDA (8.0 mL, 53 mmol) during 36 h in refluxing solvent. Remaining LiH was separated by filtration. The further reaction was the same as described above with 44 mmol of TMEDA and *n*-BuLi.

Dimethylenebenzylidenemethane Dianion 1. Yield: 96%. 1H NMR (C_6D_6 , 20 °C): δ 1.8 (m, 2H), 2.77 (s, 2H), 3.13 (s, 2H), 4.30 (s, 1H), 6.30 (m, 1H), 7.07 (m, 4H). ^{13}C NMR (C_6D_6 , 20 °C): δ 33.2, 69.9, 110.7, 120.3, 128.3, 147.3, 162.7.

Dibenzylidenemethylenemethane Dianion 2,⁹ Tribenzylidenemethane Dianion 3,⁸ and Tri-*p*-methylbenzylidenemethane Dianion 4. Yield: 94%. 1H NMR (C_6D_6 , 25 °C): δ 2.27 (s, 9H), 5.00 (s, 3H), 7.07 (m, 12H). ^{13}C NMR (C_6D_6 , 25 °C): δ 21.0, 71.6, 120.0, 120.9, 129.5, 142.0, 144.0.

Tri-*m*-methylbenzylidene Dianion 5. Yield: 91%. 1H NMR (C_6D_6 , 20 °C): δ 2.33 (s, 9H), 5.15 (s, 3H), 6.40 (m, 3H), 7.20 (m, 9H). ^{13}C NMR (C_6D_6 , 20 °C): δ 22.5, 73.6, 113.5, 117.9, 121.8, 128.9, 137.0, 142.7, 146.3.

Dimethylene- α -(naphthylmethylene)methane Dianion 6. Yield: 98%. 1H NMR (THF- d_6 , -30 °C): δ 1.60, 1.70, 2.40 (m, 4H), 4.83 (s, 1H), 5.53 (d, 1H, $J = 7.3$ Hz), 6.47 (t', 1H, $J = 8.6, 7.3$ Hz), 6.55 (t', 1H, $J = 8.2, 6.7$ Hz), 6.56 (d, 1H, $J = 8.6$ Hz), 6.76 (t', 1H, $J = 7.6, 6.7$ Hz), 6.90 (d, 1H, $J = 7.6$ Hz), 7.75 (d, 1H, $J = 8.2$ Hz) (t' = pseudotriplet). ^{13}C NMR ($CDCl_3$,

-30 °C): δ 44.7, 77.5, 101.3, 107.2, 118.8, 123.5, 123.8, 127.0, 128.2, 128.7, 138.4, 142.4, 161.4.

Dimethylene- β -(naphthylmethylene)methane Dianion 7. Yield: 97%. 1H NMR (THF- d_6 , -61 °C): δ 1.44 (s, 1H), 1.55 (s, 1H), 2.30 (s, 1H), 2.44 (s, 1H), 3.99 (s, 1H), 6.00 (t', 1H, $J = 7.0, 6.4$ Hz), 6.25 (m, 1H, $J = 8.8$ Hz), 6.39 (s, 1H), 6.44 (m, 1H, $J = 8.8$ Hz), 6.52 (t', 1H, $J = 8.1, 6.4$ Hz), 6.57 (d, 1H, $J = 8.1$ Hz), 6.66 (d, 1H, $J = 7.0$ Hz) (t' = pseudotriplet). ^{13}C NMR ($CDCl_3$, -61 °C): δ 44.0, 45.1, 84.1, 101.4, 113.2, 122.3, 125.1, 125.4, 125.6, 127.0, 130.5, 140.3, 144.8, 162.9.

Bis(β -naphthylmethylene)methylenemethane Dianion 8. Yield: 93%. 1H NMR (THF- d_6 , -85 °C): δ 3.60 (s, 2H), 3.94 (s, 2H), 6.09 (t', 1H, $J = 7.6, 6.7$ Hz), 6.32 (m, 1H, $J = 8.8$ Hz), 6.51 (m, 1H, $J = 8.8$ Hz), 6.57 (s, 1H), 6.60 (t', 1H, $J = 8.2, 6.7$ Hz), 6.67 (d, 1H, $J = 8.2$ Hz), 6.74 (d, 1H, $J = 7.6$ Hz) (t' = pseudotriplet). ^{13}C NMR ($CDCl_3$, -85 °C): δ 59.8, 89.6, 101.1, 113.0, 122.1, 125.1, 125.4, 125.6, 126.8, 131.8, 140.3, 143.7, 152.2.

1,3-Diphenylacetone Dianion 9⁹ and α -Benzylidene Dianion 10. Yield: 86%. 1H NMR (THF- d_6 , -60 °C): δ 4.10 (s, 1H), 5.00 (s, 1H), 5.20 (t, 1H), 5.65 (s, 1H), 5.60–7.20 (m, 8H). ^{13}C NMR ($CDCl_3$, -60 °C): δ 71.5, 81.3, 83.5, 101.7, 110.5, 112.4, 113.8, 118.4, 127.2, 128.9, 130.0, 132.0, 141.1, 146.5.

General Procedure for the Quench Reactions of 11–31, 35–37, 41–47, 49a,b. We describe the procedure for preparation of compound **11**. All other quench reactions are analogous. Dimethylenebenzylidenemethane dianion **1** (5 g, 19 mmol) in 80 mL of hexane was cooled to -40 °C under nitrogen atmosphere. TMSCl (6.4 mL, 50 mmol) was added dropwise under vigorous stirring, and the resulting mixture was stirred for 4 h. The reaction mixture was poured into water. The organic layer was separated, and the aqueous layer was extracted with ether (three times, 50 mL). The combined organic extracts were dried over $MgSO_4$ and concentrated to afford a light-yellow oil, **20**. The crude product was purified by distillation or flash chromatography (silica gel, petroleum ether/dichloromethane 5/1).

1,3-Diphenyl-1,3-bis(trimethylsilyl)-2-benzylidene-1-propane (11)⁸ and 1,3-Diphenyl-1,3-di-*tert*-butoxy-2-benzylidenepropane (12). The product **12** could not be separated completely from the educt 1,3-diphenyl-2-benzylidenepropane. The 1H NMR, ^{13}C NMR, and mass spectrometric data for **12** obtained from the mixture are as follows: mixture of isomers. Bp: 238–240 °C/3.2 Torr. 1H NMR ($CDCl_3$): δ 0.79, 0.80, 1.03, 1.22 (s, 18H), 5.11, 5.32, 5.72 (s, 2H), 6.86–7.60 (m, 16H). ^{13}C NMR ($CDCl_3$): δ 27.81, 28.19, 28.39, 28.46, 28.85, 70.07, 70.25, 72.46, 74.72, 74.78, 74.91, 75.03, 125.84–146.00. IR (liquid): 3080, 3045, 2985, 2950. MS (70 eV): m/e 57, 91, 191 (100), 209 (100), 282, 298, 354, 428.

3,5-Diphenyl-4-benzylidene-2,6-dithiaheptane (13). Yield: 72%. Mp: 86–88 °C. 1H NMR (CCl_4): δ 1.57 (s, 6H), 4.40, 5.20 (2s, 2H), 7.0–7.6 (m, 16H). ^{13}C NMR ($CDCl_3$): δ 15.3, 16.2, 51.5, 51.9, 126.3, 126.9, 127.1, 127.7, 127.9, 128.3, 128.5, 128.7, 131.4, 136.9, 137.4, 140.6, 140.9. IR (KBr): 3060, 3030, 2970, 2960. MS (70 eV): m/e 137, 328, 376 (100). Anal. Calcd for $C_{24}H_{24}S_2$: C, 76.55; H, 6.42. Found: C, 76.21; H, 6.10.

1,3-Diphenyl-2-benzylidene-4-methyl-4-hydroxy-4-silapentane (14). Yield: 84%. Bp: 210–215 °C/0.1 Torr. 1H NMR (CCl_4): δ -0.10, 0.03 (2s, 6H), 3.40, 3.63 (2d, 2H, $J = 15$ Hz), rest of peaks are covered. ^{13}C NMR ($CDCl_3$): δ -0.5, 38.3, 45.7, 125.3, 126.1, 126.4, 128.2, 128.3, 128.5, 128.6, 128.9, 129.7, 129.8, 138.1, 139.5, 140.9, 141.1. IR (liquid): 3590, 3380, 3030, 3000, 2930, 2880, 1640. MS (70 eV): m/e 193 (100), 284, 340, 358. Anal. Calcd for $C_{24}H_{26}SiO$: C, 80.40; H, 7.31. Found: C, 79.76; H, 7.15.

2,4-Diphenyl-3-benzylidenepentane (15). Yield: 64%. Bp: 260–265 °C/0.06 Torr. 1H NMR (CCl_4): δ 1.15, 1.20, 1.50, 1.55 (4d, 12H, $J = 7$ Hz), 3.40 (2q, 2H, $J = 7$ Hz), 4.40 (q, 2H, $J = 7$ Hz), 6.50–7.40 (m, 32H). IR (liquid): 3090, 3060, 3030, 2970, 2940, 2905, 2880, 1640. MS (70 eV): m/e 207 (100), 312. Anal. Calcd for $C_{24}H_{24}$: C, 92.26; H, 7.74. Found: C, 92.20; H, 7.55.

1,4-Dibenzylidene-2,3,5,6-tetraphenylcyclohexane (16). Mixture of isomers, separated with HPLC (silica gel/petroleum ether). Yield: 49%. Mp: 194–198 °C. ¹H NMR (CDCl₃): δ 4.35, 4.50, 4.60, 4.66, 4.80, 4.95 (m, 4H, *J* = 2 Hz), 5.95, 6.15, 6.30 (m, 2H, *J* = 2 Hz), 6.66–7.35 (m, 30H). IR (KBr): 3080, 3050, 3020, 1590, 1460. MS (70 eV): *m/e* 384, 473, 565, 564 (100). Anal. Calcd for C₄₄H₃₆: C, 93.57; H, 6.43. Found: C, 93.35; H, 6.22.

1-Benzylidene-2,6-diphenylcyclohexane (17). Yield: 78%. Bp: 250 °C/0.1 Torr (bath temperature). ¹H NMR (CCl₄): δ 1.6–2.7 (m, 6H), 3.6, 4.45 (2m, 2H), 5.95 (s, 1H), 7.0–7.7 (m, 15H). ¹³C NMR (CDCl₃): δ 22.0, 30.6, 34.6, 40.8, 47.0, 125.7, 126.1, 126.3, 126.5, 127.6, 128.0, 128.2, 128.6, 128.8, 138.0, 142.3, 143.1, 147.7. IR (KBr): 3080, 3060, 3020, 2940, 2860, 1640. MS (70 eV): *m/e* 193, 233, 324 (100). Anal. Calcd for C₂₅H₂₄: C, 92.54; H, 7.46. Found: C, 92.11; H, 7.04.

1,3-Diphenyl-2-benzylidene-5-chloropentane (18). A complex product mixture that was not separated further was obtained. Raw microanalyses and ¹H and ¹³C NMR spectra suggest that the main product is **18** with its hydrolysis products. The ¹H NMR and mass spectrometric data for **18** obtained from the mixture are as follows. Bp: 180–190 °C/0.1 Torr (bath temperature). ¹H NMR (CDCl₃): δ 1.7–2.9 (m, 4H), 3.2–4.5 (m, 3H), 6.2, 6.5, 6.9 (m, 1H), 7.0–7.5 (m, 15H). MS (70 eV): *m/e* 205, 206 (100), 207, 219, 310 (100), 311, 346.

1,2-Diphenyl-3-benzylidenecyclopropane (19). Yield: 76%. Mp: 108–110 °C (ether). ¹H NMR (CCl₄): δ 2.70, 2.90 (2dd, 2H, *J* = 6, 3 Hz), 7.05–7.80 (m, 16H). ¹³C NMR (CDCl₃): δ 32.0, 34.4, 122.1, 126.1, 126.2, 126.4, 127.2, 127.3, 128.6, 130.9, 136.6, 139.8, 141.0. IR (KBr): 3080, 3060, 3030, 2980, 2920. MS (70 eV): *m/e* 191 (100), 282. Anal. Calcd for C₂₂H₁₈: C, 93.57; H, 6.43. Found: C, 93.49; H, 6.74.

1,3-Bis(trimethylsilyl)-2-benzylidenepropane (20). Purification with HPLC (petroleum ether/dichloromethane, 95/5). Yield: 94%. Bp: 140–143 °C/14 Torr. ¹H NMR (CDCl₃): δ 0.0 (s, 9H), 0.1 (s, 9H), 1.6 (s, 2H), 1.8 (s, 2H), 6.1 (s, 1H), 7.2–7.6 (m, 5H). ¹³C NMR (CDCl₃): δ –1.06, –0.58, 24.21, 31.09, 120.07, 124.83, 127.89, 128.41, 139.41, 139.82. IR (liquid): 3090, 3060, 3020, 2960, 2900, 1630, 1600, 1490, 1405, 1245, 1145, 880, 830, 735, 690. MS (70 eV): *m/e* 173, 188, 204, 261, 276 (100). Anal. Calcd for C₁₆H₂₈Si₂: C, 69.48; H, 10.20. Found: C, 69.41; H, 10.16.

4-Benzylidene-2,6-dithiaheptane (21a). Yield: 85% together with **21b**. Bp: 128–130 °C/0.08 Torr. Separated from **21b** with HPLC (petroleum ether/ether, 97/3). ¹H NMR (CDCl₃): δ 2.0, 2.1 (2s, 6H), 3.4 (s, 2H), 3.5 (s, 2H), 6.5 (s, 1H), 7.1–7.5 (m, 5H). ¹³C NMR (CDCl₃): δ 14.50, 15.32, 32.03, 39.68, 126.71, 128.07, 128.53, 130.34, 133.53, 136.39. IR (liquid): 3070, 3030, 2980, 2920, 1645, 1600, 1490, 1440, 1370, 740, 690. MS (70 eV): *m/e* 129 (100), 176, 224. Anal. Calcd for C₁₂H₁₆S₂: C, 64.23; H, 7.19. Found: C, 64.25; H, 7.23.

4-Methylene-3-phenyl-2,6-dithiaheptane (21b). Separated from **21a** with HPLC (petroleum ether/ether, 97/3). Yield: 85% together with **21a**. Bp: 119–122 °C/0.08 Torr. ¹H NMR (CDCl₃): δ 2.0 (s, 6H), 3.1 (dd, 2H, *J* = 14 Hz), 4.7 (s, 1H), 5.2, 5.3 (2s, 2H), 7.2–7.6 (m, 5H). ¹³C NMR (CDCl₃): δ 14.53, 15.44, 38.71, 53.63, 115.30, 127.05, 128.22, 139.57, 142.97. IR (liquid): 3080, 3050, 3020, 2970, 2910, 1630, 1590, 1485, 1445, 1415, 900, 730, 685. MS (70 eV): *m/e* 129 (100), 161, 176, 177, 244. Anal. Calcd for C₁₂H₁₆S₂: C, 64.23; H, 7.19. Found: C, 64.05; H, 7.17.

2-Benzylidene-1-phenyl-1,3-bis(trimethylsilyl)propane (22). Yield: 92%. Bp: 143–148 °C/0.1 Torr. ¹H NMR (CDCl₃): δ –0.1 (s, 9H), 0.0 (s, 9H), 1.8 (dd, 2H, *J* = 13.6 Hz), 6.4 (s, 1H), 7.0–7.4 (m, 10H). IR (liquid): 3060, 3030, 2960, 2900, 1635, 1600, 1495, 1450, 1250, 835, 740, 695. MS (70 eV): *m/e* 135, 174, 249, 264 (100), 352. Anal. Calcd for C₂₂H₃₂Si₂: C, 74.92; H, 9.15. Found: C, 74.99; H, 9.12.

2-Benzylidene-1,3-di-tert-butoxy-1-phenylpropane (23a). Separated from **23b** with HPLC (petroleum ether/ether, 90/10). Yield: 73% together with **23b**. Bp: 142–150 °C/0.08 Torr (bath temperature). ¹H NMR (CDCl₃): δ 1.1, 1.2 (2s, 18H), 3.8 (dd, 2H, *J* = 10 Hz), 5.3 (s, 1H), 6.9 (s, 1H), 7.1–7.6 (m, 10H). ¹³C NMR (CDCl₃): δ 27.56, 28.66, 72.93, 74.91, 126.58, 126.80, 127.64, 127.87, 127.90, 128.76, 128.90, 137.50, 141.94,

143.48. IR (liquid): 3040, 3010, 2950, 2860, 1600, 1490, 1470, 1450, 1390, 1360, 1190, 1055, 1020, 920, 890, 880, 695. MS (70 eV): *m/e* 133, 193, 194, 209, 222 (100), 278, 352. Anal. Calcd for C₂₄H₃₂O₂: C, 81.77; H, 9.15. Found: C, 81.49; H, 9.12.

1,3-Di-tert-butoxy-1,3-diphenyl-2-methylenepropane (23b). Mixture of diastereoisomers, separated from **23a** with HPLC (petroleum ether/ether, 90/10). Yield: 73% together with **23a**. Bp: 138–145 °C/0.08 Torr (bath temperature). ¹H NMR (CDCl₃): δ 0.98, 1.07 (2s, 18H), 4.53, 4.96, 5.17, 5.61 (4s, 4H), 7.17–7.31 (m, 10H). ¹³C NMR (CDCl₃): δ 28.23, 28.52, 74.01, 74.21, 74.68, 74.75, 109.12, 113.95, 126.77, 126.94, 127.61, 127.70, 127.87, 127.96, 143.26, 143.41, 153.15, 153.69. IR (liquid): 3100, 3080, 3040, 2980, 2940, 2905, 2880, 1655, 1605, 1495, 1455, 1390, 1370, 1250, 1230, 1190, 1080, 1050, 1020, 910, 900, 765, 695. MS (70 eV): *m/e* 107, 221, 222 (100), 223, 239, 295, 352. Anal. Calcd for C₂₄H₃₂O₂: C, 81.77; H, 9.15. Found: C, 81.37; H, 9.12.

1-tert-Butoxy-1,3-diphenylacetone (24). Yield: 78%. Mp: 38–40 °C. ¹H NMR (CDCl₃): δ 1.15 (s, 9H), 3.75 (2H, *J* = 16 Hz), 5.00 (s, 1H), 6.90–7.55 (m, 10H). ¹³C NMR (CDCl₃): δ 27.89, 42.94, 75.45, 79.98, 125.90, 126.23, 127.52, 127.92, 128.16, 129.38, 134.12, 138.13, 207.28. IR (liquid): 3090, 3070, 3040, 2980, 2960, 1725, 1390, 1350. MS (70 eV): *m/e* 107 (100), 163 (100), 181, 209, 282. Anal. Calcd for C₁₉H₂₂O: C, 80.79; H, 7.85. Found: C, 80.29; H, 7.76.

3,5-Diphenyl-2-thiapentan-4-one (25). Yield: 91%. Mp: 64–65 °C. ¹H NMR (CDCl₃): δ 1.90 (s, 3H), 3.75 (2H, *J* = 12.5 Hz), 4.62 (s, 1H), 7.00–7.45 (m, 10H). ¹³C NMR (CDCl₃): δ 11.90, 44.54, 57.51, 124.63, 125.90, 126.23, 126.69, 127.57, 132.21, 133.82, 200.25. IR (KBr): 3090, 3060, 3030, 2960, 2915, 1710. MS (70 eV): *m/e* 121, 137 (100), 256. Anal. Calcd for C₁₆H₁₈OS: C, 74.96; H, 6.29. Found: C, 74.67; H, 6.08.

2,4-Diphenylpentan-3-one (26).²⁴ Yield: 82%. Bp: 120–130 °C/0.5 Torr. ¹H NMR (CDCl₃): δ 1.30 (d, 6H, *J* = 7.0 Hz), 3.85 (q, 2H, *J* = 7.0 Hz), 6.80–7.60 (m, 10H). ¹³C NMR (CDCl₃): δ 18.21, 51.39, 126.65, 127.88, 128.24, 140.00, 211.00. IR (liquid): 3080, 3050, 2995, 2950, 2895, 1718. MS (70 eV): *m/e* 105 (100), 133, 238. Anal. Calcd for C₁₇H₁₈O: C, 85.67; H, 7.61. Found: C, 85.57; H, 7.56.

2,6-Diphenylcyclohexanone (27)²⁵ and **1,3,6,8-Tetraphenylcyclohexane-2,7-dione (28).** Yield: 78%. Mp: 164 °C. ¹H NMR (CDCl₃): δ 1.53, 1.76 (2m, 4H), 3.52 (dd, 4H, *J* = 15.3 Hz), 3.56 (m, 2H), 6.98–7.31 (m, 20H). ¹³C NMR (CDCl₃): δ 29.33, 48.66, 57.84, 126.86, 127.36, 128.44, 128.53, 128.97, 129.50, 134.09, 138.43, 207.02. IR (KBr): 3070, 3040, 2960, 2940, 2880, 1710, 1605, 1495, 1450, 1320, 1230, 1075, 1025, 760, 750, 720, 690. MS (70 eV): *m/e* 205, 206, 219, 231, 236, 249, 278, 309, 310 (100), 327, 446. Anal. Calcd for C₃₂H₃₀O₂: C, 86.06; H, 6.77. Found: C, 86.02; H, 6.86.

1,3,4,6-Tetraphenylcyclohexane-2,5-dione (29). Yield: 73%. Mp: 191–192 °C. ¹H NMR (CDCl₃): δ 3.37 (dd, 4H, *J* = 6.46 Hz), 4.67 (s, 2H), 7.25–6.67 (m, 20H). ¹³C NMR (CDCl₃): δ 50.03, 59.14, 126.82, 127.55, 128.53, 128.76, 129.07, 129.49, 133.08, 135.93, 205.27. IR (liquid): 1710, 1600, 1490, 1450, 1410. MS (70 eV): *m/e* 91 (100), 327, 418. Anal. Calcd for C₃₀H₂₆O₂: C, 86.09; H, 6.26. Found: C, 86.04; H, 6.14.

1-(Trimethylsilyl)-2-(trimethylsilyloxy)-1,3-diphenyl-2-propene (30). Yield: 90%. Bp: 140–143 °C/1.8 Torr. ¹H NMR (THF-*d*₆): δ 0.03, 0.11 (2s, 18H), 3.02 (s, 1H), 5.58 (s, 1H), 7.45–7.06 (m, 10H). ¹³C NMR (THF-*d*₆): δ –1.15, 0.96, 47.94, 110.49, 126.17, 126.25, 128.72, 129.06, 129.80, 138.01, 140.85, 154.59. ²⁹Si NMR (THF-*d*₆): δ 0.00, 3.24, 17.25. IR (liquid): 3060, 3025, 2955, 2900, 1635, 1245, 840. MS (70 eV): *m/e* 280 (100), 293, 354. Anal. Calcd for C₂₁H₃₀OSi₂: C, 71.12; H, 8.53. Found: C, 70.94; H, 8.53.

1,3-Diphenylallene (31).²⁶ Yield: 84%. Mp: 48 °C. ¹H NMR (CDCl₃): δ 6.4 (s, 2H), 7.5–7.0 (m, 10H). ¹³C NMR (CDCl₃): δ 98.91, 127.71, 127.98, 129.40, 136.66, 208.37.

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3,5-Diphenyl-2-thia-4-(trimethylsiloxy)-4-pentene (32a). Yield: 84% together with **32b**, separated from **32b** with HPLC (silica gel/petroleum ether). Bp: 128–131 °C/1.5 Torr. ¹H NMR (CDCl₃): δ 0.15 (s, 9H), 2.15 (s, 3H), 4.47 (s, 1H), 6.13 (s, 1H), 7.10–7.73 (m, 10H). ¹³C NMR (CDCl₃): δ 0.79, 15.92, 57.35, 110.73, 126.05, 127.44, 127.96, 128.36, 128.60, 128.63, 136.16, 139.03, 150.09. IR (liquid): 3080, 3040, 2975, 2930, 1640, 1250, 835. MS (70 eV): *m/e* 191 (100), 328. Anal. Calcd for C₁₉H₂₄OSSi: C, 69.57; H, 7.31. Found: C, 69.96; H, 6.96.

3,5-Diphenyl-2-thia-4-(trimethylsiloxy)-3-pentene (32b). Yield: 84% together with **32a**, separated from **32a** with HPLC (silica gel/petroleum ether). Bp: 116–120 °C/1.2 Torr. ¹H NMR (CDCl₃): δ 0.20 (s, 9H), 1.85 (s, 3H), 3.40 (s, 2H), 7.15–7.45 (m, 10H). ¹³C NMR (CDCl₃): δ 0.67, 15.20, 40.04, 117.33, 126.12, 126.97, 128.13, 128.22, 128.75, 130.37, 137.85, 138.23, 148.19. IR (liquid): 3070, 3040, 2960, 2930, 1630, 1250, 840. MS (70 eV): *m/e* 191 (100), 328. Anal. Calcd for C₁₉H₂₄OSSi: C, 69.57; H, 7.31. Found: C, 69.96; H, 6.96.

1,1,3,3-Tetraphenylallene (36),²⁷ Dimethyl 2,3-Pentadienedioate (37),²⁸ and 1,2-Cyclododecadiene (38).²⁹ Bp: 64–65 °C/0.1 Torr.

(Z)-1,3-Diphenyl-2-(trimethylsiloxy)propene (41).³⁰ Yield: 40%. Bp: 138–141 °C/4.9 Torr. ¹³C NMR (CDCl₃): δ 0.87, 44.08, 110.31, 125.60, 126.51, 127.96, 128.17, 128.30, 128.41, 128.58, 128.94, 129.22, 136.63, 137.99, 151.76. IR (liquid): 3080, 3050, 3020, 2950, 2890, 1640, 1250, 1150, 970, 835, 745, 690, mixture of isomers. MS (70 eV): *m/e* 73, 75, 91, 105, 122, 136, 179, 192, 267, 282 (100).

1-Methylene-2-phenylcyclopropane (42).³¹ Purification with HPLC (silica gel/petroleum ether). Yield: 79%. Bp: 66–67 °C/14 Torr. ¹H NMR (CDCl₃): δ 1.18 (m, 1H, *J* = 7.98, 7.26 Hz), 1.70 (m, 1H, *J* = 8.08, 7.98 Hz), 2.56 (m, 1H, *J* = 8.08, 7.76 Hz), 5.55 (m, 2H, *J* = 3.38 Hz), 7.11–7.24 (m, 5H). ¹³C NMR (CDCl₃): δ 14.49, 20.19, 104.40, 125.76, 126.30, 128.24, 135.32, 141.78. IR (liquid): 3030, 3010, 1635, 1590, 1500, 880. MS (70 eV): *m/e* 116, 128, 129 (100), 130. Anal. Calcd for C₁₀H₁₀: C, 92.26; H, 7.74. Found: C, 91.95; H, 7.68.

anti-1-Benzylidene-2-phenylcyclopropane (43a). Yield: 63%. Bp: 72–74 °C/4 Torr. ¹H NMR (CDCl₃): δ 1.46 (m, 1H, *J* = 9.00 Hz), 1.98 (m, 1H, *J* = 9.00, 4.88 Hz), 2.61 (m, 1H, *J* = 9.15, 4.88 Hz), 6.85 (m, 1H), 7.10–7.54 (m, 10H). ¹³C NMR (CDCl₃): δ 15.8, 17.9, 119.4, 125.8, 126.4, 126.8, 127.0, 128.3, 128.5, 137.6, 141.9. IR (liquid): 3090, 3070, 3040, 3020, 2985. MS (70 eV): *m/e* 91 (100), 105, 106, 180, 206. Anal. Calcd for C₁₆H₁₄: C, 93.16; H, 6.84. Found: C, 93.28; H, 6.58.

syn-1-Benzylidene-2-phenylcyclopropane (43b). Yield: 14%. Bp: 72–73 °C/4 Torr. ¹H NMR (CDCl₃): δ 1.19 (m, 1H, *J* = 9.16, 9.01 Hz), 1.74 (m, 1H, *J* = 9.16, 4.88 Hz), 2.80 (m, 1H, *J* = 9.01, 4.88 Hz), 6.88 (m, 1H), 7.11–7.54 (m, 10H). ¹³C NMR (CDCl₃): δ 13.6, 21.5, 120.1, 126.1, 126.3, 127.0, 127.4, 128.4, 128.8, 137.1, 141.0. IR (liquid): 3090, 3070, 3040, 3020, 2985. MS (70 eV): *m/e* 91 (100), 105, 106, 180, 206. Anal. Calcd for C₁₆H₁₄: C, 93.16; H, 6.84. Found: C, 93.28; H, 6.58.

1-Methylene-2-(α-naphthyl)cyclopropane (44). Purification with HPLC (petroleum ether/diethyl ether, 93/7). Yield: 74%. Bp: 78 °C/0.1 Torr. ¹H NMR (CDCl₃): δ 1.22 (m, 1H), 1.77 (m, 1H), 3.00 (m, 1H), 5.61 (m, 1H), 5.72 (m, 1H), 7.39–8.28 (m, 7H). ¹³C NMR (CDCl₃): δ 12.56, 17.38, 104.93, 123.34, 124.04, 125.28, 125.47, 125.74, 126.74, 128.38, 132.34, 133.51, 134.23, 136.51. IR (liquid): 3050, 2990, 1600, 1575, 1510, 1400, 1250, 1120, 1110, 885, 790, 765. MS (70 eV): *m/e* 165, 178, 179 (100), 180. Anal. Calcd for C₁₄H₁₂: C, 93.29; H, 6.71. Found: C, 93.25; H, 6.69.

1-Methylene-2-(β-naphthyl)cyclopropane (45). Purification with HPLC (silica gel, petroleum ether/diethyl ether, 93/7). Yield: 73%. Bp: 73 °C/0.08 Torr. ¹H NMR (CDCl₃): δ

Table 4. PM3 Energies of (EE)-47a, (ZZ)-47b, and (EZ) Isomer 47c

compd	ΔH _f ^o , kcal/mol	
	dianion 2Li ⁺	dianion 2Li ⁺ 2TMEDA
47a	36.76	–20.65
47b	34.59	–25.45
47c	42.44	–16.00

1.29 (m, 1H, *J* = 8.8, 5.2 Hz), 1.79 (m, 1H, *J* = 9.3, 8.8 Hz), 2.74 (m, 1H, *J* = 9.3, 5.2 Hz), 5.63 (m, 2H, *J* = 2.8 Hz), 7.22–7.77 (m, 7H). ¹³C NMR (CDCl₃): δ 14.66, 20.43, 104.75, 124.57, 124.95, 125.09, 125.97, 127.30, 127.59, 127.96, 132.07, 133.50, 135.36, 139.36. IR (liquid): 3040, 2980, 1640, 1590, 1495, 1105, 1005, 895, 880, 810. MS (70 eV): *m/e* 165, 178, 179 (100), 180. Anal. Calcd for C₁₄H₁₂: C, 93.29; H, 6.71. Found: C, 93.17; H, 6.61.

1-(β-Naphthylmethylidene)-2-(β-naphthyl)cyclopropane (46). Yield: 84%. Mp: 94 °C. ¹H NMR (CDCl₃): δ 1.71 (m, 1H, *J* = 9.34, 4.96 Hz), 2.22 (m, 1H, *J* = 9.34, 9.11 Hz), 2.88 (m, 1H, *J* = 9.11, 4.96 Hz), 7.11 (m, 1H), 7.26–7.91 (m, 14H). ¹³C NMR (CDCl₃): δ 16.22, 18.27, 119.87, 124.43, 124.72, 124.97, 125.16, 125.73, 126.04, 126.20, 126.38, 127.32, 127.61, 127.68, 127.94, 128.08, 128.12, 129.17, 132.12, 132.77, 133.50, 133.68, 135.21, 139.51. IR (liquid): 3060, 3020, 2960, 1625, 1600, 1500, 1355, 1260, 880, 850, 805, 735. MS (70 eV): *m/e* 141 (100), 165, 178, 289, 306. Anal. Calcd for C₂₄H₁₈: C, 94.08; H, 5.92. Found: C, 93.97; H, 5.96.

(EE)- and (ZZ)-1,3,4,6-Tetraphenylhexane-2,5-dione Dianions 9 (900 mg, 2.0 mmol) in 40 mL of absolute hexane was added dropwise 1,2-dibromoethane (1.2 mL, 13.0 mmol) under stirring at –50 °C. After 2 h of more stirring the pale-yellow crystals were filtered and washed with hexane (three times, 10 mL). Yield: 62% mixture of **47a,b. The NMR signals of the isomers were separated by a NOE experiment. ¹H NMR (THF-*d*₆): δ 3.35 (s, 2H, *EE*), 3.76 (s, 2H, *EE*), 4.25 (s, 2H, *ZZ*), 4.75 (s, 2H, *ZZ*), 6.64–7.57 (m, 80H). ¹³C NMR (THF-*d*₆): δ 42.3 (*ZZ*), 44.9 (*EE*), 80.7 (*EE*), 97.5 (*ZZ*), 121.0, 125.6, 125.8, 125.9, 126.1, 126.3, 126.7, 127.6, 127.9, 128.0, 128.3, 128.5, 130.0, 131.6, 132.0, 132.3, 140.9, 141.5, 141.7, 143.8.**

Table 4 shows the PM3 energies of (EE)-**47a** and (ZZ)-**47b** in comparison with the third possible isomer (EZ)-**47c**, which is not formed.

(ZZ)-1,3,4,6-Tetraphenyl-2,5-bis(trimethylsiloxy)hexa-1,5-diene (48a). Yield: 33%. Mp: 72–73 °C. ¹H NMR (CDCl₃): δ –0.15 (s, 18H), 4.04 (s, 2H), 5.58 (s, 2H), 6.99–7.55 (m, 20H). ¹³C NMR (CDCl₃): δ 0.0, 54.9, 109.7, 125.0, 126.1, 127.2, 127.4, 128.3, 128.5, 136.2, 142.2, 151.8. IR (KBr): 3070, 3035, 2960, 2905, 1644, 1242, 830. MS (70 eV): *m/e* 77, 281 (100), 327, 369, 562. Anal. Calcd for C₃₆H₄₂O₂Si₂: C, 76.87; H, 7.47. Found: C, 76.94; H, 7.54.

(EE)-1,3,4,6-Tetraphenyl-2,5-bis(trimethylsiloxy)hexa-1,5-diene (48). Yield: 40%. Mp: 68–70 °C. ¹H NMR (CDCl₃): δ –0.06 (s, 18H), 4.11 (s, 2H), 6.13 (s, 2H), 6.99–7.55 (m, 20H). ¹³C NMR (CDCl₃): δ 0.0, 55.4, 108.7, 125.5–128.7, 136.3, 139.4, 152.5. IR (KBr): 3055, 3020, 2950, 2895, 1640, 1242, 835. MS (70 eV): *m/e* 77, 281 (100), 327, 369, 562. Anal. Calcd for C₃₆H₄₂O₂Si₂: C, 76.87; H, 7.47. Found: C, 76.94; H, 7.54.

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