

SILANES IN ORGANIC SYNTHESIS

VI *. CONVERSION OF UNSUBSTITUTED AND 2-ARYL KETONES TO (1-ARYLALLYL)SILANES

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(Received February 5th, 1979)

Summary

Treatment of 2- or 3-phenyl ketone arenesulfonylhydrazones with excess n-butyllithium in TMEDA at 50–60°C for 2–3 h, followed by the addition of chlorotrimethylsilane, gives (1-arylallyl)silanes. Although the method has limitations, its simplicity and the availability of a companion procedure for the direct α -arylation of ketones provide desirable advantages. A number of electrophilic reactions are examined in an effort to assess competitive benzylic resonance stabilization and C–Si bond hyperconjugation in cyclic systems where stereoelectronic considerations also prevail.

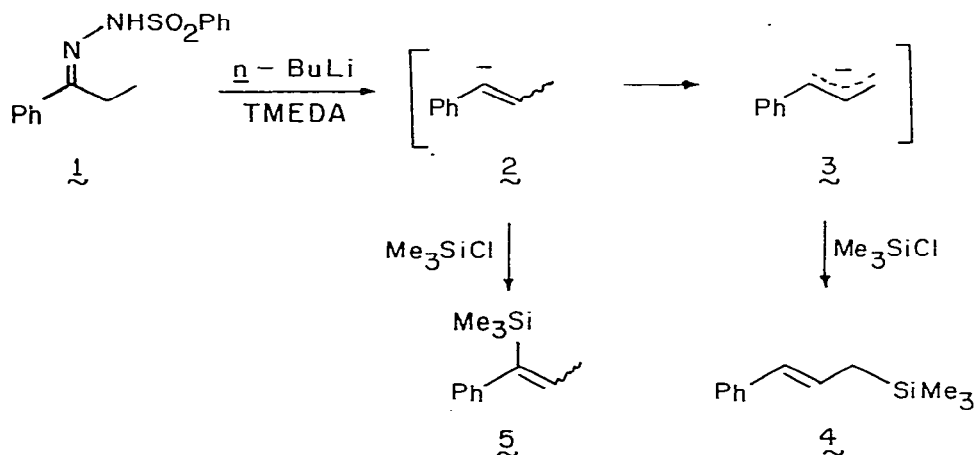
Allylsilanes [2] and their anions [3] have recently emerged as important synthetic reagents [4]. Recent examples include Friedel-Crafts acylation [2a]; allyl transfer to a carbonyl group [2b]; 1,4-addition to α,β -unsaturated enones [2c]; and miscellaneous other reactions [2d]. There exist at the present time several procedures for preparing allylsilanes including the hydrosilylation of dienes [5a], condensation of allylic Grignard reagents [5b] and related organometallics [5c] with chlorotrimethylsilane, Diels-Alder addition of 1-trimethylsilylbutadiene [5d], reaction of β -trimethylsilylethyltriphenylphosphonium ylide with carbonyl compounds [5e] and others [5f]. In this report, we describe a complementary new technique by which unsubstituted and 2-aryl ketones may be transformed expeditiously to 1-aryl substituted allylsilanes, and selected reactions of such compounds.

The methodology is typified by our initial observation that treatment of *N,N,N',N'*-tetramethylethylenediamine (TMEDA) solutions of propiophenone

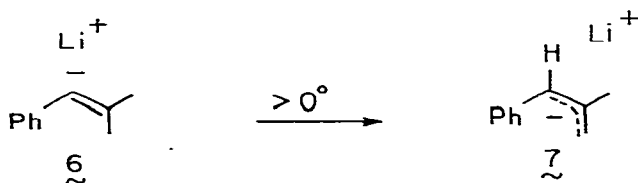
* For part V see ref. 1.

** The Ohio State University Dissertation Fellow, 1978–1979.

benzenesulfonylhydrazone (1) with excess n-butyllithium in hexane at -45°C , followed by heating at 60°C for 3 h and addition of chlorotrimethylsilane, produced the allylsilane 4 (58% isolated yield) instead of the vinylsilane 5 [6]. When conditions were ameliorated somewhat (50°C , 2 h), both 4 (40%) and 5



(49%, *trans/cis* = 2.8) were obtained. At a somewhat later date, Knorr and Lattke reported their independent discovery of a similar vinyl anion (6) to allyl anion (7) rearrangement [7]. Further study on their part revealed the reaction to be governed by a strongly negative entropy of activation, to exhibit 0.5th order in 6, and to likely proceed by an intermolecular transmetalation mechanism involving small amounts of β,β -dimethylstyrene.

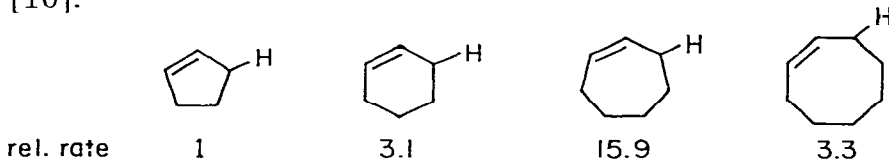


Recent theoretical considerations suggest that allyl anions need not necessarily be thermodynamically favored relative to vinyl anions in every instance [8,9]. The stability of both species appears to be critically dependent upon the geometry of the system, the optimal vinyl anion and allyl anion internal angles being 110° and 132.5° , respectively [9]. Stated differently, an allylic



hydrogen increases in acidity as the $\text{C}-\text{C}-\text{C}$ angle is increased on the vinyl anion, thereby in principle engendering more facile isomerization. Of course, this acidity is also dependent on the $\text{C}-\text{C}-\text{H}$ torsional angle; the closer the $\text{C}-\text{H}$ bond comes to eclipsing the p_{π} orbital, the greater the rate of proton migration. This would represent the least motion pathway in intramolecular processes.

On this basis, the ensuing order of acidity of cyclic olefins has been derived [10]:

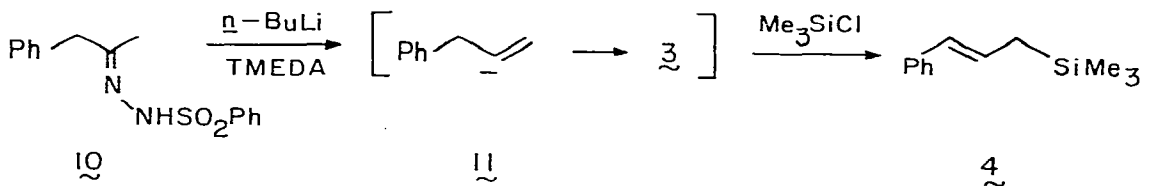


Calculations on the preferred stereochemistry of crotyl anions have also been performed by Schleyer et al., who concluded that the *cis* form **8** is favored over the *trans* form **9** by 1.5 kcal/mol [11]. This analysis warrants comparison with gas-phase ion cyclotron measurements which have shown **9** to be 0.2 kcal/mol lower in free energy than **8** [12] and solution studies which have revealed a 2.2 kcal/mol free energy preference for the *cis* geometry [13].



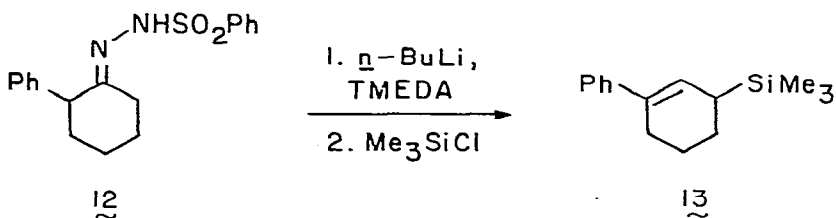
Two important points emerge: (a) all vinyl anions need not be prone to isomerize readily to allylic anions; (b) solvation factors cannot be neglected. As concerns the present work, we have found the vinyl \rightarrow allyl anion rearrangement to proceed at convenient rates only when the allyl anion is additionally conjugated to an aryl substituent. It appears therefore that a rather high energy barrier must be crossed in most, if not all ordinary circumstances. Presumably, the role played by the neighbouring aromatic ring is one of lowering the customarily demanding energetics through inductive and resonance contributions.

These considerations are reflected in the behavior of vinyl anion **11** derived from phenylacetone benzenesulfonylhydrazone (**10**) which rearranged completely within 2 h at 50°C to furnish ultimately **4** in 60% yield. The availability of a

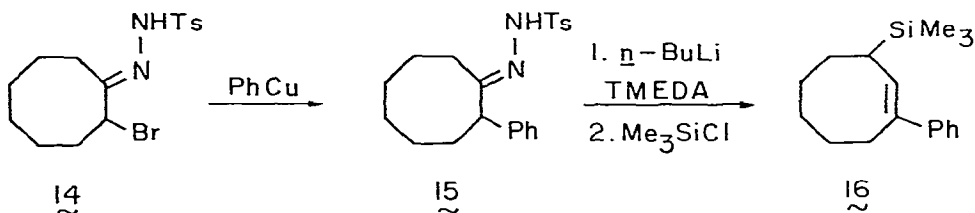


benzylic proton in **11** (as compared to a methyl proton in **2**) is clearly responsible for the heightened rate of isomerization to **3**.

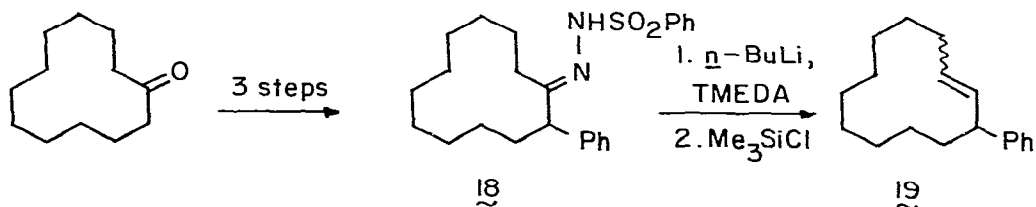
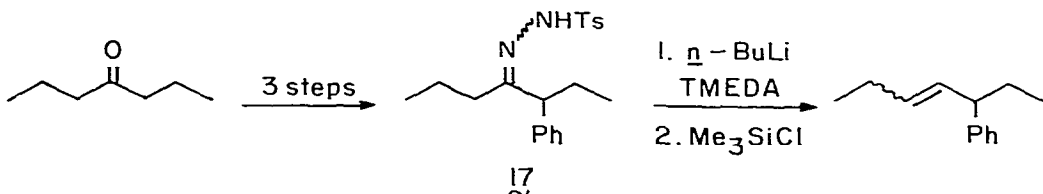
The behaviour of 2-phenylcyclohexanone benzenesulfonylhydrazone (**12**) at these temperatures is essentially comparable, affording **13** in 73% yield despite the smaller internal angle which must prevail in the allylic anion.



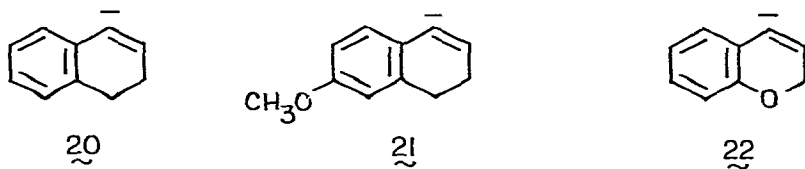
The need for 2-phenyl ketones led us to adapt the methodology developed by Sacks and Fuchs for the α -arylation of carbonyl compounds [14]. As an example, cyclooctanone was brominated [15] and converted to tosylhydrazone 14 in conventional fashion [16]. Treatment with phenylcopper furnished 15 which in turn smoothly gave 16 (70%) accompanied by lesser amounts of 3-phenylcyclooctene.



Despite such successes, the method is not free of complications. For example, comparable handling of 17 and 18 (60°C, 2 h) provided exclusively the related olefins. Therefore, in spite of the incipient stabilization of the derived

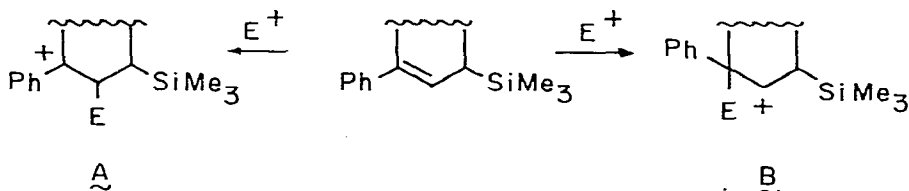


allylic anions, the vinyl anions instead undergo kinetically-controlled protonation by solvent (or other species present). Additionally, we have not found it possible to effect proton migration within the cyclic vinyl anion systems 20–22. Although these limitations do detract from the generality of the synthetic operation, the methodology does have utilitarian value. Further, its scope will undoubtedly expand as our knowledge of the controlling factors underlying vinyl–allyl anionic rearrangements is developed.



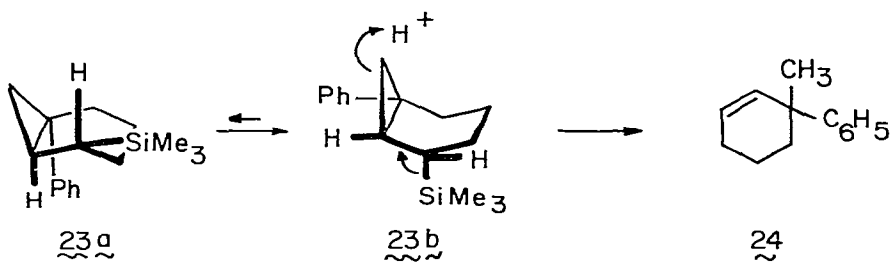
Although carbocations which are benzylic or β to a C–Si bond are recognized to be inherently stabilized, there appear to be only limited instances

where benzylic resonance delocalization has been pitted directly on intramolecular terms against the hyperconjugative ability of silicon [17]. Since phenyl substituted allylsilanes of the present type do allow for examination of this mechanistically informative question (see A and B), several electrophilic reac-



tions were studied in the more conformationally rigid systems where stereo-electronic factors also gain significance.

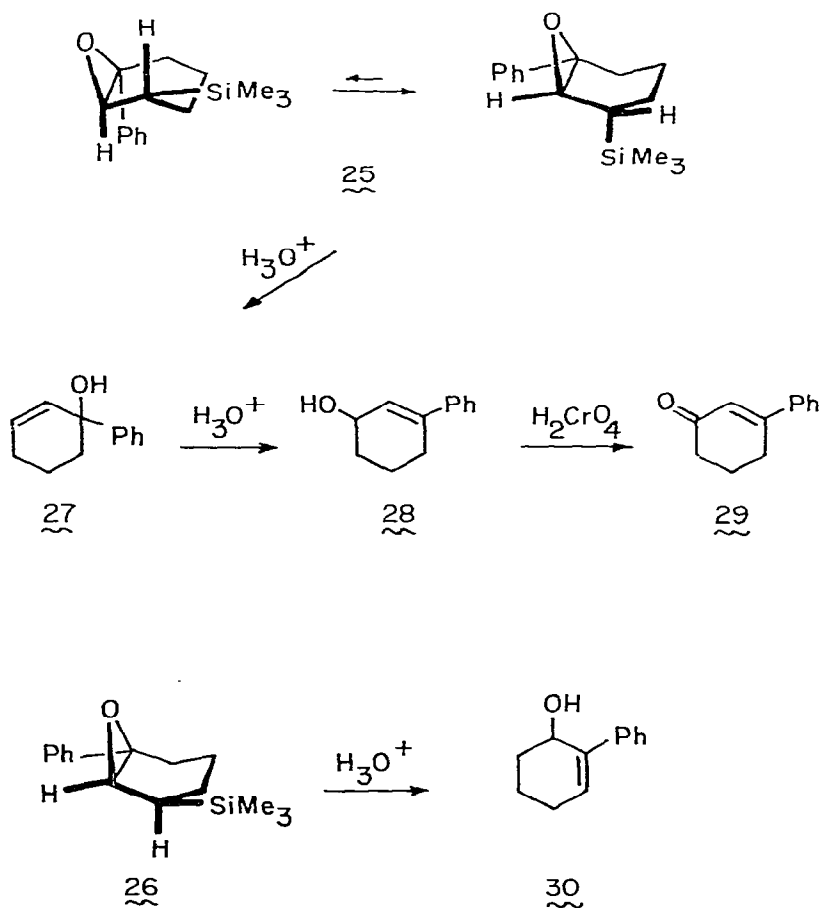
Simmons—Smith cyclopropanation of **13** gave in 86% yield a stereochemically homogeneous bicyclo[4.1.0]heptane assigned structure **23** on the basis of steric considerations and the appearance of the cyclopropylcarbinyl proton adjacent to silicon as a singlet ($W_{1/2}$ 2 Hz) at δ 0.73. Through use of the Karplus equation [18] as modified by Abraham and Gatti for vicinal couplings to cyclopropane rings ($J_{vic} = 10 \cos^2 \Phi$) [19], it can be shown that the experimentally determined signal width agrees with that calculated for H_{2exo} in the *cis*-boat conformation (**23b**) [20,21]. When stirred in acetic acid containing a catalytic quantity of sulfuric acid at 50°C for 2 days, **23** was cleanly converted with loss



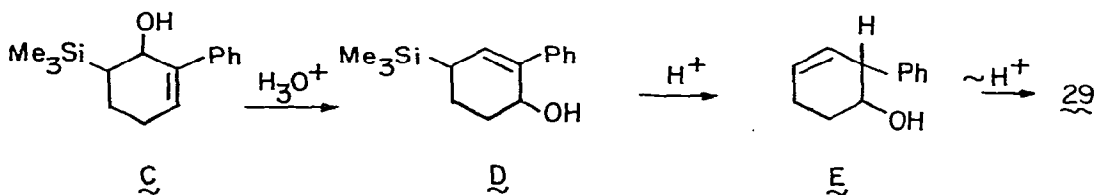
of the trimethylsilyl group to 3-methyl-3-phenylcyclohexene. Thus, the arylcyclopropane, while somewhat unresponsive to ring opening (**23** is unreactive toward mercuric acetate in aqueous tetrahydrofuran [22]), reacts entirely under the control of the silicon substituent. This behaviour, which contrasts with that followed by 1-arylbicyclo[4.1.0]heptanes [22,23] where cleavage operates exclusively in the direction of the benzylic carbon, is attributed to attainment of proper stereoelectronic overlap with the C—Si bond in **23b**.

Although epoxidation reactions of allylsilanes are reported to give poorly characterized mixtures of cleavage products in many instances* [24] **13** reacted with 40% peracetic acid (pretreated with sodium acetate) to provide **25** and **26** in the approximate ratio of 1 : 1 (^1H NMR analysis, see Experimental). Since separation of these isomers could not be achieved chromatographically for lability reasons, the unpurified mixture was treated directly with dilute aqueous sulfuric acid at room temperature. There resulted a mixture of **28** (49%) and **30** (28%). Allylic alcohol **28** results from acid-promoted 1,3-hydroxyl

* A significant exception appears to be the 3-silacyclopentenes [25].

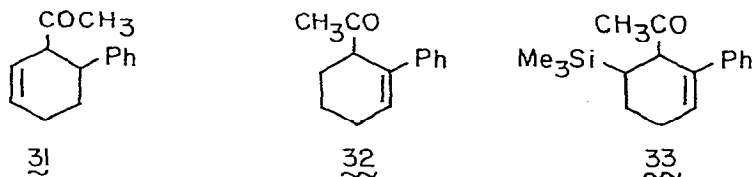


migration within the initially formed 27, an assumption substantiated by independent submission of authentic 27 to the reaction conditions and an earlier literature report [26]. Jones oxidation of 28 furnished the known 3-phenylcyclohexenone (29) [27]. The genesis of 30, a previously described substance [28], is less easily traced. A possible, though unsubstantiated pathway involves regiospecific opening of 26 toward the phenylsubstituent to give C which undergoes 1,3-hydroxyl migration to generate D. Protonolysis of this allylsilane would give E, the less conjugated precursor of 29.

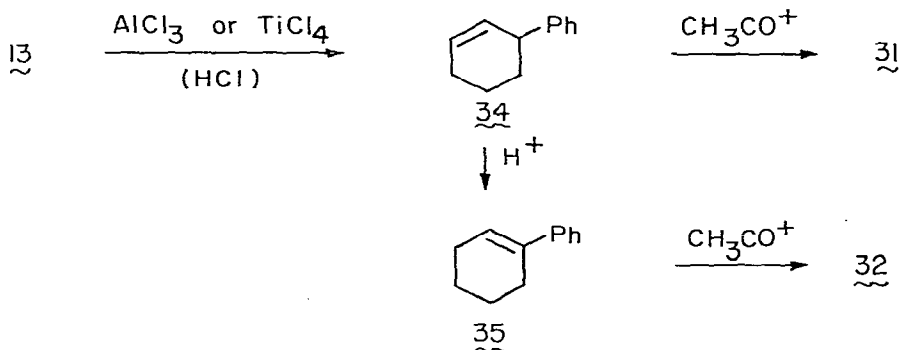


Friedel-Crafts acetylation of 13 afforded a reaction mixture consisting of 31–33 in the relative ratio 39 : 38 : 23. The three components were obtained pure by preparative layer chromatography and isolated in yields of 32, 32, and 19%, respectively. Ketone 33, which was identified by spectral and combustion

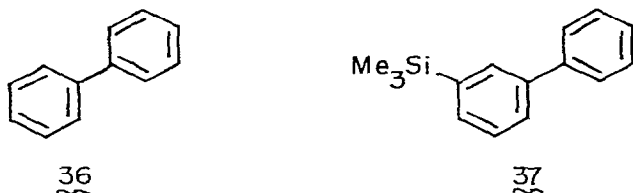
analysis, is clearly the result of phenyl control during acylation. On the other hand, ketones 31 and 32 are believed to arise from acetylation of the phenyl-



cyclohexenes 34 and 35 which were independently shown to be produced upon exposure of 13 to Lewis acids such as AlCl_3 and TiCl_4 .



In a pair of reactions which probably have a sizable free radical component, 13 was treated with *N*-bromosuccinimide in CCl_4 and bromine in cyclohexane. In both instances, a mixture of the biphenyls 36 and 37 resulted, although in differing proportions.



In summary, the variety of reaction mechanisms which can operate with different electrophilic reagents and the wide range of prevailing stereoelectronic factors make sweeping generalizations of the preferred reaction mode of *cyclic* (1-arylallyl)silanes unwarranted.

Experimental

Proton magnetic resonance spectra were obtained with Varian T-60 and EM-360 spectrometers; apparent splittings are given in all cases. Infrared spectra were recorded on a Perkin-Elmer Model 467 instrument. Mass spectra were determined on an AEI-MS9 spectrometer at an ionization potential of 70 eV. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark. Preparative and analytical GLC work was per-

formed on Varian Aerograph A90-P3 instruments equipped with thermal conductivity detectors.

trans-1-Phenyl-3-trimethylsilylprop-1-ene (4)

(A) *from 1.* To a cooled (-45°C) solution of *n*-butyllithium (9.4 ml of 1.6 *M* in hexane, 15 mmol) in dry TMEDA under nitrogen was added portionwise 1.00 g (3.47 mmol) of solid 1 (m.p. $136\text{--}139^{\circ}\text{C}$). During 30 min at this temperature, the solution took on a deep red color. Subsequently, the solution was allowed to warm to room temperature during 2 h and heated at 60°C for 3 h prior to cooling to 0°C and treatment with chlorotrimethylsilane (2.17 g, 20 mmol). After 4 h the dark mixture was diluted with diethyl ether and water. The organic phase was washed with water (2×30 ml), saturated copper sulfate solution (2×30 ml), and brine prior to drying. Solvent evaporation left an oil which was filtered through a short plug of neutral alumina in pentane. Removal of the pentane and molecular distillation at 95°C and 2.2 mm afforded 380 mg (58%) of 4 as a clear colorless liquid [32]. ^1H NMR (δ (ppm), CDCl_3): 7.4–7.1 (m, 5 H), 6.4–6.15 (ABX m, 2 H), 1.68 (dd, $J = 5$ and 2 Hz, 2 H) and 0.17 (s, 9 H).

(B) *From 10.* Reaction of 1.00 g (3.47 mmol) of 10 (m.p. $170\text{--}171^{\circ}\text{C}$, dec.) with *n*-butyllithium in hexane (9.4 ml of 1.6 *M*, 15 mmol) as above, followed by heating at 50°C for 2 h and workup, gave 395 mg (60%) of 4 which was isomerically pure on GLC analysis (6 ft. \times 0.25 in. 5% Carbowax 20M, 120°C).

1-Phenyl-3-trimethylsilylcyclohexene (13)

A mixture of 2-phenylcyclohexanone (8.5 g, 48.8 mmol), benzenesulfonylhydrazine (9.0 g, 52.3 mmol), and a catalytic amount of *p*-toluenesulfonic acid in absolute ethanol (80 ml) was heated at the reflux temperature for 20 min under nitrogen. The white precipitate which formed was filtered after cooling to room temperature (1 h). Recrystallization from dichloromethane/hexane afforded the benzenesulfonylhydrazone (15.11 g, 92%) as white crystals, m.p. $119\text{--}121^{\circ}\text{C}$.

A dry three-necked flask was fitted with a septum, a condenser equipped with a nitrogen inlet tube, and an Erlenmeyer flask containing the benzenesulfonylhydrazone (9.60 g, 29.3 mmol) and connected by means of Gooch tubing. Dry distilled TMEDA (20 ml) was introduced and cooled to -45°C prior to addition of *n*-butyllithium in hexane (90 ml of 1.6 *M*, 0.144 mol). The hydrazone was added slowly in portions and a deep red color was generated immediately. After being stirred at -45°C for an additional hour, the mixture was warmed to room temperature during 60 min. The Gooch tubing was replaced by a glass stopper and the solution was heated in an oil bath at $55\text{--}60^{\circ}\text{C}$ for 2 h. On cooling the dark mixture to 0°C , chlorotrimethylsilane (14 ml) was added and stirring was maintained overnight. Pentane (200 ml) was added before quenching with water. The aqueous phase was separated and extracted with pentane (2×200 ml). The combined organic layers were successively washed with water (2×200 ml), saturated copper sulfate solution (2×200 ml), and saturated brine (200 ml) prior to drying and solvent removal. Distillation in a Kugelrohr apparatus ($80\text{--}90^{\circ}\text{C}/0.03$ mm) gave 4.88 g (72%) of 13 as a colorless oil of 99% purity (2 ft. \times 0.25 in. 5% SE-30, 150°C); $\nu_{\text{max}}^{\text{neat}}$: 3040, 3020, 2930,

1670, 1630, 1600, 1493, 1250, 830, and 743 cm^{-1} ; ^1H NMR (δ (ppm), CDCl_3): 7.43 (m, 5 H), 5.27 (m, 1 H), 3.23–0.97 (series of m, 7 H), and 0.37 (s, 9 H); ^{13}C NMR (ppm, CDCl_3): 143.3, 135.0, 128.2, 126.2, 126.0, 125.0, 27.5, 27.3, 23.4, 23.2, and 2.9; $\lambda_{\text{max}}^{\text{isooctane}}$: 251 nm (13,800); m/e : found 230.1500; calcd. 230.1491. Anal. Found: C, 78.22; H, 9.62. Calcd. for $\text{C}_{15}\text{H}_{22}\text{Si}$: C, 78.19; H, 9.62%.

General procedure for preparation of α -bromo ketone arenesulfonylhydrazones [16]

Equimolar amounts of the α -bromo ketone and tosylhydrazine together with a catalytic amount of *p*-toluenesulfonic acid dissolved in anhydrous ether (approximately 10% solution) was stirred under nitrogen at room temperature for 4 h. The white crystals which formed were filtered and the filtrate concentrated to yield a second crop. The combined lots were recrystallized from dichloromethane/hexane to give the pure product.

2-Bromocyclooctane tosylhydrazone, white crystals, m.p. 118–119°C (66%).

3-Bromo-4-heptanone tosylhydrazone, white crystals, m.p. 105–106°C (70%).

3-Bromo-4-heptanone benzenesulfonylhydrazone, white crystals, m.p. 116–117°C (74%).

2-Bromocyclododecanone benzenesulfonylhydrazone, white crystals, m.p. 105–106°C (57%). In this instance, tetrahydrofuran supplanted ether as solvent.

General procedure for preparation of α -phenyl ketone arenesulfonylhydrazones [14]

A solution of phenylcopper was prepared by adding phenyllithium (3 ml of 1 M, 3.0 mmol) in ether/benzene (3/7) to cuprous iodide (629 mg, 3.3 mmol) in dry ether (5 ml) at 0°C under nitrogen. After 10 min, most of the cuprous iodide dissolved to form a black solution. Anhydrous tetrahydrofuran (5 ml) was added at 0°C and the mixture was cooled to –60°C prior to dropwise addition of 3-bromo-4-heptanone tosylhydrazone (350 mg, 0.97 mmol) dissolved in anhydrous tetrahydrofuran (5 ml). After 15 min, cold acetic acid (5 mmol) was added and the mixture was allowed to warm to room temperature where it was hydrolyzed with saturated ammonium chloride in ammonium hydroxide. The layers were separated and the aqueous layer was extracted twice with ether. The combined organic layers were dried and evaporated to leave a solid which was washed with hexane to remove biphenyl. Recrystallization from dichloromethane/hexane gave 17 (3.23 g, 93%) as colorless crystals, m.p. 119–120°C.

2-Phenylcyclooctanone tosylhydrazone (15), colorless crystals, m.p. 145–146°C (89%).

3-Phenyl-4-heptanone benzenesulfonylhydrazone, white crystals, m.p. 117–118°C (78%).

2-Phenylcyclododecanone benzenesulfonylhydrazone, white crystals, m.p. 163–164°C (99%).

1-Phenyl-3-trimethylsilylcyclooctane (16)

Following the procedure outlined above, 1.11 g (2.9 mmol) of 2-phenylcyclo-

octanone tosylhydrazone in TMEDA (20 ml) was treated with 14.4 mmol of *n*-butyllithium and the resultant vinyl anion was heated at 57°C for 2.5 h. Subsequent to the addition of chlorotrimethylsilane (1.4 ml), the reaction mixture was analyzed by GLC (SE-30 column; 150°C); the presence of 16 (71%) and 3-phenylcyclooctene (29%) was indicated. After the usual workup, distillation in a Kugelrohr apparatus afforded 840 mg of distillate, representing a 70% isolated yield of the allylsilane. Pure samples of the two components were obtained by preparative GLC methods.

For 16: $\nu_{\text{max}}^{\text{neat}}$: 2940, 1600, 1250, 860, 760, and 650 cm^{-1} ; $^1\text{H NMR}$ (δ (ppm), CDCl_3): 7.32 (m, 5 H), 5.78 (d, $J = 10$ Hz, 1 H), 2.63 (m, 2 H), 2.37 (m, 1 H), 2.10–0.80 (series of m, 8 H), and 0.10 (s, 9 H); m/e : found 258.181; calcd. calcd. 258.180. Anal. Found: C, 79.09; H, 10.14. Calcd. for $\text{C}_{17}\text{H}_{26}\text{Si}$: C, 79.00; H, 10.17%.

For 3-phenylcyclooctene [29]: $\nu_{\text{max}}^{\text{neat}}$: 2940, 2865, 1605, 1495, 1455, 745, and 700 cm^{-1} ; $^1\text{H NMR}$ (δ (ppm), CDCl_3): 7.20 (m, 5 H), 5.62 (m, 2 H), 3.73 (m, 1 H), 2.29 (m, 2 H), and 1.70 (br, m, 8 H); m/e found 186.1403; calcd. 186.1408.

5-Phenyl-3-heptene

Submission of 1.07 g (3.0 mmol) of 17 to the previously described reaction conditions afforded 502 mg (94%) of 5-phenyl-3-heptene which was purified by GLC on the SE-30 column. $\nu_{\text{max}}^{\text{neat}}$: 3060, 3025, 3000, 2960, 2925, 2870, 1600, 1490, 1450, 1375, and 690 cm^{-1} ; $^1\text{H NMR}$ (δ (ppm), CDCl_3): 7.17 (s, 5 H), 5.43 (m, 2 H), 3.43 (m, 1 H), 2.10 (m, 2 H), 1.63 (q, $J = 7$ Hz, 2 H), 0.96 (t, $J = 7$ Hz, 3 H), and 0.88 (t, $J = 7$ Hz, 3 H); m/e : found 174.1412; calcd. 174.1408.

3-Phenylcyclododecene (19)

Following the same procedure, 1.23 g (3 mmol) of 18 was converted to 3-phenylcyclododecene (540 mg, 78%). $\nu_{\text{max}}^{\text{neat}}$: 3060, 3020, 2990, 2920, 2850, 1595, 1490, 1460, 720, and 690 cm^{-1} ; $^1\text{H NMR}$ (δ (ppm), CDCl_3): 7.13 (m, 5 H), 5.40 (m, 2 H), 3.80 (m, 1 H), and 3.0–0.7 (series of m, 18 H); m/e : found 242.2040; calcd. 242.2034.

1-Phenyl-4-trimethylsilylbicyclo[4.1.0]heptane (23)

A mixture of zinc powder (1.5 g, 23.7 g-at) and cuprous chloride (0.25 g, 2.5 mmol) in anhydrous ether (8 ml) was heated at reflux with vigorous stirring for 1 h. Upon cooling, 13 (0.85 g, 3.7 mmol) and a small crystal of iodine were added. Subsequently, diiodomethane (3.99 g, 14.9 mmol) was introduced slowly via a syringe and the resulting mixture was refluxed for 6 h, treated with an additional quantity of diiodomethane (2.0 g, 7.5 mmol), and refluxed for an additional 18 h. The ether solution was slowly poured into a saturated solution of ammonium chloride and the aqueous phase was extracted with ether (2 \times 20 ml). The organic phase was dried and evaporated to leave 0.80 g of an oil, GLC analysis (10% SE-30, 135°C) of which showed it to contain 11% of unreacted 13 and 89% of 23 (86% yield based on recovered starting material). Pure 23 was obtained by preparative GLC methods. $\nu_{\text{max}}^{\text{neat}}$: 2940, 2860, 1495, 1450, 1250, 865, 840, 760, and 750 cm^{-1} ; $^1\text{H NMR}$ (δ (ppm), CDCl_3): 7.23 (m, 5 H),

2.47–0.8 (series of m, 9 H), 0.73 (s, 1 H), and 0.17 (s, 9 H); ^{13}C NMR (ppm, CDCl_3): 149.8, 128.2, 128.0, 125.3, 31.8, 25.7, 24.4, 24.1, 22.7, 20.0, 19.5, and 3.4; *m/e*: found 244.1652; calcd. 244.1647. Anal.: Found: C, 78.06; H, 9.93. Calcd. for $\text{C}_{16}\text{H}_{24}\text{Si}$: C, 78.61; H, 9.90%.

3-Methyl-3-phenylcyclohexene (24)

A solution of 23 (123 mg, 0.5 mmol) in acetic acid (0.65 ml) containing a catalytic amount of sulfuric acid (35 mg in 10 ml of acetic acid) was stirred at 50°C for 2 days. The cooled mixture was diluted with pentane and water and the layers were separated. The organic phase was extracted with saturated sodium bicarbonate solution until neutral, dried, and evaporated. The residue was chromatographed on silica gel (elution with 40% ether in hexane) to give 150 mg (86%) of 24 [31]. ^1H NMR (δ (ppm), CDCl_3): 7.28 (m, 5 H), 5.77 (m, 2 H), 1.95 (s, 3 H), and 2.3–1.3 (series of m, 6 H); *m/e*: found 172.1258; calcd. 172.1252.

1-Phenyl-5-trimethylsilyl-7-oxabicyclo[4.1.0]heptane (25 and 26)

Into a flask equipped with an addition funnel and a drying tube was placed 0.43 g (1.9 mmol) of 13 dissolved in ether (5 ml). To this solution was slowly added 0.5 ml of 40% peracetic acid which had previously been treated with sodium acetate to remove traces of sulfuric acid. The progress of the epoxidation was monitored by GLC (10% SE-30, 135°C). After 7 h, when the starting material was consumed, the reaction mixture was diluted with water (10 ml) and extracted with dichloromethane (3 \times 20 ml). The combined organic layers were extracted with 10% sodium carbonate solution and water prior to drying and evaporation. There remained 0.41 g of an oil, GLC analysis of which revealed it to be of 83% purity (79%). Due to the lability of these epoxides, the mixture was utilized without further purification. $\nu_{\text{max}}^{\text{neat}}$: 2950, 1490, 1450, 1250, 840, 760, and 695 cm^{-1} ; ^1H NMR (δ (ppm), CDCl_3): 7.32 (m, 5 H), 3.12 (d, $J = 3.5$ Hz, 0.5 H), 3.02 (s, 0.5 H), 2.60–0.9 (series of m, 7 H), 0.18 and 0.12 (2 s, 4.5 H each); *m/e*: found 246.1444; calcd. 246.1439.

Acid-catalyzed rearrangement of 1-phenyl-5-trimethylsilyl-7-oxabicyclo[4.1.0]-heptane

A suspension of the epoxide mixture (0.19 g, 10.8 mmol) in water (17 ml) and 2 *N* sulfuric acid (2 ml) was stirred at 25°C for 2 days. The products were extracted into ether, washed with water, and dried. The resulting oil was chromatographed on silica gel (elution with 40% ether in hexane) to give 49% of 28 and 28% of 30.

For 28: $\nu_{\text{max}}^{\text{neat}}$: 3340, 1640, 1600, 1495, 750, and 690 cm^{-1} ; ^1H NMR (δ (ppm), CDCl_3): 7.33 (m, 5 H), 6.13 (m, 1 H), 4.37 (br, m, 1 H), 2.43 (m, 2 H), 2.23 (br, s, 1 H), and 1.83 (m, 4 H). Oxidation with Jones reagent gave 3-phenylcyclohex-2-enone (30).

For 30: $\nu_{\text{max}}^{\text{neat}}$: 3340 cm^{-1} ; ^1H NMR (δ (ppm), CDCl_3): 7.30 (m, 5 H), 6.13 (m, 1 H), 4.25 (br, m, 1 H), 2.43 (m, 2 H), and 1.90 (m, 5 H) [28].

Friedel–Crafts acetylation of 13

In a three-necked flask equipped with a septum, magnetic stirring bar, and

nitrogen inlet was placed dry dichloromethane (6 ml), anhydrous aluminum chloride (0.50 g, 3.7 mmol), and acetyl chloride (0.312 g, 4.0 mmol) while cooling the reaction mixture to -25°C . Most of aluminum chloride dissolved within 30 min, whereupon 13 (0.90 g, 3.9 mmol) was added dropwise via syringe. After the reaction mixture had been stirred in the cold for 2 h, it was allowed to warm to 0°C , poured onto ice water, and extracted with ether (2×20 ml). The combined organic phases were washed with water, dried, and evaporated to leave 0.79 g of crude product. GLC analysis (5% SE-30, 150°C) showed the mixture to contain 39% of 31, 38% of 32, and 23% of 33. For characterization purposes, the compounds were separated by preparative layer chromatography on silica gel (elution with 10% ether in hexane). Isolated yields were 32, 32, and 19%, respectively.

For 31: $\nu_{\text{max}}^{\text{neat}}$: 3040, 2940, 1718, 1605, 1585, 1495, 1468, 1365, 1160, and 760 cm^{-1} ; $^1\text{H NMR}$ (δ (ppm), CCl_4): 7.13 (s, 5 H), 5.68 (m, 2 H), 3.68 (m, 1 H), 2.66 (ABq, $J = 10$ and 3 Hz, 1 H), 2.43–1.63 (series of m, 5 H), and 1.83 (s, 3 H); $^{13}\text{C NMR}$ (ppm, CDCl_3): 211.4, 144.4, 130.1, 128.1, 126.6, 55.7, 43.9, 30.0, 25.0, and 24.6; $\lambda_{\text{max}}^{\text{iso-octane}}$: 247.5 (ϵ 225), 253 (260), 259 (175), 264 (200), and 268 nm (150). Anal.: Found: C, 83.94; H, 8.09. Calcd. for $\text{C}_{14}\text{H}_{16}\text{O}$: C, 83.96; H, 8.05%.

For 32: $\nu_{\text{max}}^{\text{neat}}$: 1710 cm^{-1} ; $^1\text{H NMR}$ (δ (ppm), CCl_4): 7.17, (m, 5 H), 6.13 (t, $J = 4$ Hz, 1 H), 3.62 (br, m, 1 H), 2.27 (m, 2 H), 2.03–1.47 (series of m, 4 H), and 1.83 (s, 3 H); m/e : found 200.1206; calcd. 200.1201. This compound proved identical with an authentic sample [32].

For 33: $\nu_{\text{max}}^{\text{neat}}$: 2960, 1710, 1600, 1495, 1355, 1250, 1155, 855, 835, and 755 cm^{-1} ; $^1\text{H NMR}$ (δ (ppm), CCl_4) 7.20 (s, 5 H), 6.13 (t, $J = 5$ Hz, 1 H), 3.60 (m, 1 H), 2.23 (m, 2 H), 2.07–1.50 (m, 2 H), 1.90 (s, 3 H), 1.35 (t, $J = 6$ Hz, 1 H), and 0.15 (s, 9 H); $\lambda_{\text{max}}^{\text{iso-octane}}$: 244 nm (ϵ 1960). Anal.: Found: C, 75.30; H, 8.80. Calcd. for $\text{C}_{17}\text{H}_{24}\text{OSi}$: C, 74.94; H, 8.88%.

Reaction of 13 with *N*-bromosuccinimide

A mixture of 13 (0.41 g, 1.8 mmol) and *N*-bromosuccinimide (0.35 g, 2.0 mmol) in carbon tetrachloride (5 ml) was irradiated with a 150 W sun lamp while heated at the reflux temperature under nitrogen for 1 h. After cooling, the precipitated succinimide was filtered and the concentrated filtrate was analyzed by GLC (5% SE-30, 150°C) showing the presence of biphenyl (36, 72%) and 3-trimethylsilylbiphenyl (37, 28%); $^1\text{H NMR}$ (δ (ppm), CDCl_3) 7.20 (m, 9 H) and 0.43 (s, 9 H); m/e : found 226.1134; calcd. 226.1177 [33].

Bromination of 13

A solution of bromine (3.6 mmol) in cyclohexane (4 ml) was added dropwise to a solution of 13 (0.45 g, 1.95 mmol) in the same solvent (5 ml) at room temperature. The red color disappeared instantaneously. The reaction mixture was concentrated and analyzed by GLC as above, both 36 (58%) and 37 (42%) were again formed.

Acknowledgment

This work was financially assisted by a grant from the National Cancer Institute (CA-12115).

References

- 1 W.E. Fristad, D.S. Dime, T.R. Bailey and L.A. Paquette, *Tetrahedron Lett.*, in press.
- 2 (a) R. Calas, J. Dunogues, J.-P. Pillot, C. Biran, F. Piscioti and B. Arreguy, *J. Organometal. Chem.*, 85 (1975) 149; J.-P. Pillot, J. Dunogues and R. Calas, *Tetrahedron Lett.*, (1976) 1871; (b) W. Abel and R.J. Rwoley, *J. Organometal. Chem.*, 84 (1975) 199; A. Hosomi and H. Sakurai, *Tetrahedron Lett.*, (1976) 1295; A. Hosomi, M. Endo and H. Sakurai, *Chem. Lett.*, (1976) 941; A. Hosomi and H. Sakurai, *J. Amer. Chem. Soc.*, 99 (1977) 1673; I. Ojima, M. Kumagai and Y. Miyazawa, *Tetrahedron Lett.*, (1977) 1385; A. Hosomi, A. Shirahata and H. Sakurai, *ibid.*, (1978) 3043; T.K. Sarkar and N.H. Andersen, *ibid.*, (1978) 3513; A. Hosomi and H. Sakurai, *ibid.*, (1977) 4040; (c) H.O. House, T.S.B. Sayer and C.-C. Yau, *J. Org. Chem.*, (1978) 2153, and certain references cited previously; (d) P.F. Hurdlik and G.P. Withers, *Tetrahedron Lett.*, (1976) 29; M.J. Carter and I. Fleming, *J. Chem. Soc., Chem. Commun.*, (1976) 679; G. Deleris, J. Dunogues and R. Calas, *J. Organometal. Chem.*, 79 (1976) 81; I. Ojima and M. Kumagai, *Chem. Lett.*, (1978) 575; A. Hosomi and H. Sakurai, *Tetrahedron Lett.*, (1978) 2589.
- 3 R.J.P. Corriu and J. Masse, *J. Organometal. Chem.*, 57 (1973) C5; R.J.P. Corriu, J. Masse and D. Samate, *ibid.*, 93 (1975) 71; R.J.P. Corriu, G.F. Lanneau, J.P. Masse and D. Samate, *ibid.*, 123 (1977) 281; D. Ayalon-Chass, E. Ehlinger and P. Magnun, *J. Chem. Soc. Chem. Commun.*, (1977) 772; P.W.K. Lau and T.H. Chan, *Tetrahedron Lett.*, (1978) 2383.
- 4 Reviews: A.W.P. Jarvie, *Organometal. Chem. Rev., A*, 6 (1970) 153; P.F. Hurdlik, in D. Seyferth (Ed.), *New Applications of Organometallic Reagents in Organic Synthesis*, Elsevier, Amsterdam, 1976, p. 127; E.W. Colvin, *Chem. Soc. Rev.*, 7 (1978) 15.
- 5 The following listing provides only leading references and is not meant to be comprehensive: (a) M.S. Wrighton and M.A. Schroeder, *J. Amer. Chem. Soc.*, 97 (1974) 6236; I. Ojima, M. Kumagai and M. Miyazawa, *Tetrahedron Lett.*, (1977) 1385; K. Yamamoto and M. Kumada, *J. Organometal. Chem.*, 13 (1968) 131; (b) J.M. Reuter, A. Sinha and R.G. Salomon, *J. Org. Chem.*, 43 (1978) 2438; (c) D. Seyferth and T.F. Jula, *J. Organometal. Chem.*, 66 (1974) 195; M. Laguerre, J. Dunogues and R. Calas, *Tetrahedron*, 34 (1978) 1823; (d) M.J. Carter and I. Fleming, *J. Chem. Soc. Chem. Commun.*, (1976) 679; I. Fleming and A. Percival, *ibid.*, (1976) 681; D. Seyferth, K.R. Wursthorn and R.E. Mammarella, *J. Org. Chem.*, 42 (1977) 3104; (e) K. Tamao, K. Sumitani and M. Kumada, *J. Amer. Chem. Soc.*, 94 (1972) 3275; K. Itoh, M. Fukui and Y. Kurachi, *J. Chem. Soc. Chem. Commun.*, (1977) 500.
- 6 R.T. Taylor, C.R. Degenhardt, W.P. Melega and L.A. Paquette, *Tetrahedron Lett.*, (1977) 179; T.H. Chan, A. Baldassare and D. Massuda, *Synthesis*, (1976) 801; A.R. Chamberlin, J.E. Stemke and F.T. Bond, *J. Org. Chem.*, 43 (1978) 147.
- 7 R. Knorr and E. Lattke, *Tetrahedron Lett.*, (1977) 4655, 4659.
- 8 W. Gründler, *Tetrahedron*, 26 (1970) 2291.
- 9 D.W. Boerth and A. Streitweiser, *J. Amer. Chem. Soc.*, 100 (1978) 750.
- 10 A. Streitweiser and D.W. Boerth, *J. Amer. Chem. Soc.*, 100 (1978) 755.
- 11 P.v.R. Schleyer, J.D. Dill, J.A. Pople and W.J. Hehre, *Tetrahedron*, 33 (1977) 2497.
- 12 J. Bartness, W.J. Hehre, R.T. McIver Jr. and L.E. Overman, *J. Amer. Chem. Soc.*, 99 (1977) 1976.
- 13 M. Schlosser, J. Hartmann and V. David, *Helv. Chim. Acta*, 57 (1974) 1567.
- 14 C.E. Sacks and P.L. Fuchs, *J. Amer. Chem. Soc.*, 97 (1975) 7372.
- 15 D.P. Bauer and R.S. Macomber, *J. Org. Chem.*, 40 (1975) 1990.
- 16 A. Dondoni, G. Rossini, G. Mossa and L. Caglioti, *J. Chem. Soc. (B)*, (1968) 1404.
- 17 A. Hosomi and H. Sakurai, *Tetrahedron Lett.*, (1976) 1295.
- 18 M. Karplus, *J. Amer. Chem. Soc.*, 85 (1963) 2870.
- 19 R.J. Abraham and G. Gatti, *Org. Magn. Reson.*, 2 (1970) 173.
- 20 A. Aumelas, E. Casadevall and A. Casadevall, *Tetrahedron*, 34 (1978) 2481.
- 21 L.A. Paquette, W.E. Fristad, C.A. Schuman, M.A. Beno and G.G. Christoph, *J. Amer. Chem. Soc.*, 101 (1979) in press.
- 22 A. Balsamo, C. Battistini, P. Crotti, B. Macchia and F. Macchia, *J. Org. Chem.*, 40 (1975) 3233; R.J. Ouellette, R.D. Robin, A. South Jr., *J. Amer. Chem. Soc.*, 90 (1968) 1619.
- 23 C. Battistini, P. Crotti, B. Macchia, F. Macchia and C.H. DePuy, *J. Org. Chem.*, 43 (1978) 1400 and pertinent references contained therein; C.H. DePuy, *Fortschr. Chem. Forsch.*, 40 (1974) 74.
- 24 L.V. Nozdrina, Y.I. Mindlin and K. Andrianov, *Russ. Chem. Rev.*, 42 (1973) 509; E.P. Plueddemann, and G. Fanger, *J. Amer. Chem. Soc.*, 81 (1959) 2632; V. Bažant, V. Matoušek, *Collect. Czech. Chem. Commun.*, 24 (1959) 3758; T. Tsuruta, S. Inone, H. Koenuma, *Makromol. Chem.*, (1968) 112 58; P.F. Hurdlik and G.P. Withers, *Tetrahedron Lett.*, (1976) 29; H.J. Carter and I. Fleming, *J. Chem. Soc. Chem. Commun.*, (1976) 679.
- 25 G. Manuel, P. Mazerolles, J.-C. Florence, *Compt. Rend., Ser. C*, 269 (1969) 1553; *J. Organometal. Chem.*, 30 (1971) 5; G. Manuel, P. Mazerolles and J.-P. Pradel, *ibid.*, 61 (1973) 147; I. Ojima and M. Kumagai, *Chem. Lett.*, (1978) 575.
- 26 A.-M. Mandrou, P. Potin and R. Wylde-Lachazette, *Bull. Soc. Chim. France*, (1962) 1546.

- 27 G. Büchi, J.H. Hansen, D. Knutson and E. Koller, *J. Amer. Chem. Soc.*, 80 (1958) 5517.
- 28 H.J. Reich, I.L. Reich and S.H. Wollowitz, *J. Amer. Chem. Soc.*, 100 (1978) 5981.
- 29 A.C. Cope and R.B. Kinnel, *J. Amer. Chem. Soc.*, 88 (1966) 742.
- 30 S.V. Kessar and K.P. Mahajan, *J. Ind. Chem.*, 39 (1962) 147.
- 31 A.G. Brook, H.W. Kucera and D.M. MacRae, *Can. J. Chem.*, 48 (1970) 818.
- 32 E.W. Garbisch, Jr., *J. Org. Chem.*, 27 (1962) 4243.
- 33 H.A. Clark, A.F. Gordon, C.W. Young and M.T. Hunter, *J. Amer. Chem. Soc.*, 73 (1951) 3798.