Supporting Information for

Carbenoid-mediated nucleophilic “hydrolysis” of 2-(dichloromethylidene)-1,1,3,3-tetramethylindane with DMSO participation, affording access to one-sidedly overcrowded ketone and bromoalkene descendants

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Alternative synthesis of ketone 38b; preparation of [2-D]10, 33, 39a, 39b, 42b, and 43; FBW ring expansion of carbenoid 12; SNV reactions of 12 with PhCH2K and with KN(SiMe3)2

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1. An alternative route to ketone 38b

Epoxidation of the known [S1] olefin S1 with peracetic acid furnished the oxirane S2 (Scheme S1) whose chiral nature became immediately evident through the ¹H NMR nonequivalence of all four methyl groups. We did not succeed in the following two methods of ring-opening nucleophilic bromination of S2 with the intention to arrive at the bromoalkene 42b. Treatment with Li₂NiBr₄ in THF at rt [S2] led to the quantitative recovery of S2, whereas ring-opening by acetyl bromide plus Et₄N⁺Br⁻ in CHCl₃ or by pyridinium bromide in 1,2-dichloroethane at 100 °C furnished 1,1,2,3-tetramethylindene (S3) and benzaldehyde; this provided further examples of the imminent rearrangement [S3] in the 1,1,3,3-tetramethylindane system. Fortunately, deprotonation at C-2’ of S2 by n-BuLi occurred readily in THF as the solvent at rt (but very slowly in hexane with a first half-reaction time of >50 hours). The resultant lithium enolate S4 was trapped with ClSiMe₃ to give the α-Osime₃ derivative S5. Alternatively, the same procedure of generating S4 but trapping by protonation afforded the ketone 38b.

![Scheme S1: An alternative synthesis of ketone 38b.](image-url)
\[\text{1,1,3,3-Tetramethylspiro[2′-phenyloxirane-3′,2-indane} \ (S2): \ [S4] \text{A suspension of the olefin} \ S1 \ (1.80 \text{ g, 6.86 mmol}) \ [S1], \text{suspended in glacial acetic acid} \ (8 \text{ mL}), \text{was stirred at rt during the slow addition of peracetic acid} \ (\text{freshly prepared from} \ H_2O_2 \text{ with acetonhydride}). \text{This batchwise addition was continued until the olefin} \ S1 \text{ had dissolved completely and a peroxide test} \ (\text{KI/starch}) \text{ remained positive, which required several hours. The mixture was diluted with water} \ (40 \text{ mL}) \text{ and stirred for four hours to hydrolyze residual acetonhydride, then rinsed with more water} \ (80 \text{ mL}) \text{ and Et}_2O \ (50 \text{ mL}) \text{ into a separatory funnel. The aqueous layer was extracted with Et}_2O \ (3\times) \text{ and then discarded. The combined four Et}_2O \text{ layers were washed with water} \ (2\times), \text{aqueous NaOH} \ (2 \text{ M, 2}\times) \text{ until the aqueous phase remained alkaline, again with water until neutral, and dried over Na}_2SO_4. \text{The filtered Et}_2O \text{ solution was concentrated and dried in the presence of solid KOH in vacuo to afford the almost pure product} \ S2 \ (1.82 \text{ g, 95%}). \text{After a trap-to-trap distillation at 115–150 °C (bath temp.)/0.02 Torr, analytically pure} \ S2 \text{ was a colorless, viscous material that crystallized very slowly; mp 57–60 °C; }^1\text{H NMR (CDCl}_3, 80 \text{ MHz}) \delta 0.88, 1.13, 1.19, \text{and 1.45 (4 s, 4 × 3H, 2 × 1}-/3\text{-CH}_3), 4.07 (s, 1H, 2′-H), 6.90–7.40 (m, 9H, all aromatic H) ppm; }^1\text{H NMR (CCl}_4, 80 \text{ MHz}) \delta 0.86, 1.10, 1.15, 1.41, 3.95, 6.80–7.35 ppm; \text{IR (film)} \nu: 3090, 3060, 3030, 2960 (s), 2925 (s), 2865, 1607 (w), 1590 (w), 1482, 1450, 1384, 950, 873, 746, 700 cm}^{-1}; \text{UV–vis (cyclohexane)} \lambda_{\text{max}} \text{ (log } \varepsilon) 271 (3.05), 264 (3.03, with vibrational progression by 980 cm}^{-1}), 215 (4.29), 211 (4.22) nm; \text{anal. calcd for} \ C_{20}H_{22}O (278.39): \text{C, 86.29; H, 7.96; found: C, 86.64, H, 8.14.}

\[\text{2-[α-(Trimethylsilyloxy)benzylidene]-1,1,3,3-tetramethylindane} \ (S5): \ [S5] \text{The oxirane} \ S2 \ (460 \text{ mg, 1.65 mmol}), \text{anhydrous THF} \ (10 \text{ mL}), \text{and a magnetic stirring bar were placed in a two-necked, round-bottomed flask} \ (25 \text{ mL}) \text{ fitted with a small pressure-equalizing dropping funnel carrying a gas bubbler. The solution was cooled} \]
under nitrogen gas cover with stirring at −50 °C during the dropwise addition of nBuLi (4 mmol) in hexane (2.00 mL). After 60 min at −50 °C and further stirring at rt for at least 30 min, the yellow solution of the enolate S4 (the in situ 1H NMR showing a multiplet at δ_H = 6.65–7.13 and a quasi-singlet at 7.01 ppm) was cooled in ice and treated with ClSiMe_3 (0.50 mL). After one hour at rt, the mixture was diluted with Et_2O (30 mL) and poured into distilled water. The aqueous layer (pH = 10) was extracted with Et_2O until colorless, then discarded. The combined Et_2O layers were washed with distilled water until neutral, dried over Na_2SO_4, and evaporated to give an orange-colored solid (700 mg) consisting of S5 mainly. Filtration and concentration of the hot solution of this solid in hexane furnished colorless crystals (400 mg, 69%) of pure S5; mp 96–97 °C (2 × from hexane); 1H NMR (CDCl_3, 80 MHz) δ −0.07 (s, 9H, OSiMe_3), 1.11 (s, 6H, 2 × 1-CH_3), 1.60 (s, 6H, 2 × 3-CH_3), 6.95–7.27 (m, ca. 4H, 4-/5-/6-/7-H), 7.27 (quasi-s, 5H, α-phenyl) ppm, assigned as published [S6]; 13C NMR as published [S6]; UV–vis (hexane) λ_max 270.4, 263.3 nm with vibrational progression by ca. 960 cm⁻¹; IR (KBr) ν: 2991, 2956, 2921, 2860, 1662, 1483, 1357, 1291, 1253, 1130, 1091, 1054, 1025, 910, 870, 864, 758, 705 cm⁻¹; anal. calcd for C_{23}H_{30}OSi (350.58): C, 78.80; H, 8.62; found: C, 78.77; H, 8.68. S5 is relatively stable against desilylating reagents.

2-Benzoyl-1,1,3,3-tetramethyldiande (38b): a) From the oxirane S2: [S5] The procedure described above for S5 was repeated but the treatment with ClSiMe_3 was omitted: Colorless crystals; mp 82–84 °C (methanol); 1H NMR (CDCl_3, 80 MHz) δ 1.29 and 1.33 (2 s, 2 × 6H, 2 × 1-/3-CH_3), 4.05 (s, 1H, 2-H), 7.14 (narrow m, 4H, 4-/5-/6-/7-H), 7.42 (m, 3H, p-H and 2 × m-H), 7.90 (m, 2H, 2 × o-H) ppm; IR (KBr) ν: 2960, 2920, 2859, 1673, 1663, 1448, 1370, 1218 (s), 760 cm⁻¹; anal. calcd for C_{20}H_{22}O (278.39): C, 86.29; H, 7.96; found: C, 86.07; H, 7.94.
Without rigorous exclusion of air from the THF solution containing the enolate S4 and n-BuLi, a side-product of uncertain constitution may appear and can be separated from the more soluble ketone 38b through leaching with a hot alkane solvent: Colorless crystals; mp 132–135 °C (cyclohexane); $^1$H NMR (CDCl$_3$, 80 MHz) $\delta$ 1.43 and 1.53 (2 s, 2 $\times$ 6H, 2 $\times$ 1/-3-CH$_3$), 6.90–7.41 (m, ca. 7H), 7.85 (m, 2H) ppm. This CDCl$_3$ solution decayed slowly at rt with formation of a singlet a $\delta$ = 1.31 ppm.

b) From acid 10: n-BuLi (7.33 mmol) in hexanes (3.46 mL) was added dropwise under argon gas cover to a stirred solution of bromobenzene (0.770 mL, 7.33 mmol) in anhydrous Et$_2$O (5.0 mL) cooled to −70 °C. After further stirring at rt for 60 min, this solution of phenyllithium (34b) and n-BuBr was added dropwise at rt to a stirred solution of acid 10 (400 mg, 1.83 mmol) in Et$_2$O (10 mL). Upon further stirring for 24 hours with exclusion of air and moisture, the yellow mixture containing a white precipitate was poured onto solid CO$_2$, warmed up, and dissolved in aqueous NaOH (1 M, 20 mL). The aqueous layer was shaken with Et$_2$O (3 $\times$ 20 mL) and the combined four Et$_2$O layers were washed with distilled water until neutral, dried over Na$_2$SO$_4$, and concentrated. This crude, non-acidic fraction (481 mg) contained the ketone 38b, n-butylbenzene, and the alcohol 39b in a 9:4:1 ratio. (The pure ketone 38b was prepared by the alternative route described above.) The above aqueous NaOH layer was cooled in ice and acidified with conc. hydrochloric acid (white precipitate), then shaken with Et$_2$O (3 $\times$ 20 mL). These latter Et$_2$O extracts were combined and washed with distilled water until neutral, dried over Na$_2$SO$_4$, and evaporated to yield the acidic product fraction (222 mg) containing 10, benzoic acid, and diacid 40 in roughly equal amounts.
2. Products [2-D]10, 33, 39a, 39b, 42b, and 43

[2-D]-1,1,3,3-Tetramethyldiindan-2-carboxylic acid ([2-D]10): This was isolated from a smaller run of the dichloroalkene 6 in [D₆]DMSO after 27 hours at 135 °C and exhibited the following deuterium-induced $^1$H (400 Mz) and $^{13}$C (100.6 MHz) NMR shifts $^0 \Delta = \delta([2-D]10) – \delta(10)$, transmitted over $n$ bonds in CDCl₃ as the solvent: $1-/3$-CH$_3$ syn to CO, $^4 \Delta = 0.002$; $1-/3$-CH$_3$ anti, $^4 \Delta = -0.0043$; $1-/3$-CH$_3$ syn, $^3 \Delta = 0.016$; $1-/3$-CH$_3$ anti, $^3 \Delta = -0.052$; C-1/-3, $^2 \Delta = -0.048$; C-2, $^1 \Delta = -0.448$ ppm; $^1$J$_{C,D} = 19.4$ Hz.

1,1,3,3-Tetramethyl-2-(2-methylsulfinylethen-1-yl)-2-(methylthiomethyl)indane (33): A small amount of this somewhat unstable side-product was isolated through crystallization (pentane) from the nonacidic fraction obtained in a larger (15 mmol) run. The resultant platelets (mp 134–135 °C, fortuitously the same mp as 23) were identified beyond doubt by NMR techniques but could not be recrystallized. $^1$H NMR (CDCl₃, 400 MHz) $\delta$ 1.21 (s, 3H, 1- or 3-CH$_3$ anti$_1$ relative to CH$_2$), 1.28 (s, 3H, 3- or 1-CH$_3$ anti$_2$), 1.39 (s, 3H, 1- or 3-CH$_3$ syn$_1$), 1.41 (s, 3H, 3- or 1-CH$_3$ syn$_2$), 2.19 (s, 3H, CH$_3$S), 2.59 (s, 3H, CH$_3$SO), 2.96 (quasi-s with linewidth 1.6 Hz, 2H, S–CH$_2$), 6.03 (broadened d, $^3 J = 15.8$ Hz, 1H, $\alpha$-H), 6.74 (d, $^3 J = 15.8$ Hz, 1H, $\beta$-H), 7.10 (AB part of an ABMM´ system, 2H, 4-/7-H), 7.22 (MM´ part, 2H, 5-/6-H) ppm, assigned through the NOESY correlations H$_3$C–S ↔ S–CH$_2$ (the only two-proton signal, correlates also with all four 1-/3-CH$_3$) ↔ $\beta$-H ↔ H$_3$C–SO, and $\beta$-H ↔ $\alpha$-H ↔ both anti-1-/3-CH$_3$ ↔ 4-/7-H; $^{13}$C NMR (CDCl₃, 100.6 MHz) $\delta$ 18.0 (qt, $^1 J = 138.0$ Hz, $^3 J = 2.4$ Hz, H$_3$C–S), 26.28 (qq, 3- or 1-CH$_3$ anti$_2$), 26.31 (qq, 1- or 3-CH$_3$ anti$_1$), 29.19 (qq, 3- or 1-CH$_3$ syn$_2$), 29.39 (qq, 1- or 3-CH$_3$ syn$_1$), all of these four 1-/3-CH$_3$ having $^1 J = 126.3$ Hz and $^3 J = 4.2$ Hz, 36.37 (tqi, $^1 J = 138.0$ Hz, $^3 J = 4.9$ Hz, S–CH$_2$), 41.10 (qt, $^1 J = 138.2$ Hz, apparent t $J = 1.5$ Hz, H$_3$C–SO), 49.35 and 49.46 (unresolved, C-
1/-3), 59.06 (m, C-2), 122.74 and 122.81 (2 dm, $^1J = 156$ Hz, C-4/-7), 127.50 and 127.51 (2 ddm, $^1J = 159.5$ Hz, $^3J = 7.4$ Hz, C-5/-6), 132.32 (dq, $^1J = 173.5$ Hz, apparent $J = 4.2$ Hz, C-β), 142.64 (dt, $^1J = 155.5$ Hz, $^3J = 5.5$ Hz, C-α), 148.72 (m, C-3a/-7a) ppm, assigned through HSQC spectra and the $J_{C,H}$ coupling constants.

$p,p'$-Dimethyl-α-(1,1,3,3-tetramethyldiindan-2-yl)benzhydrol (39a): As described for ketone 38a, acid 10 (1.83 mmol) and $p$-methylphenyllithium (34a, from nBuLi, 7.33 mmol) but in refluxing Et₂O (15 mL, 48 hours at 40 °C) provided a 1:1 mixture of 38a and 39a which deposited 39a from pentane as the solvent. The thin needles of pure 39a had a mp of 189.5–191 °C; $^1$H NMR (CDCl₃, 400 MHz, 25 °C) $\delta$ 1.01 and 1.33 (2 s, 2 × 6H, 2 × $p$-CH₃), 2.28 (s, 6H, 2 × $p$-CH₃), 2.84 (s, 1H, variable OH), 3.42 (s, 1H, C-2), 7.05 and 7.17 (AA'BB' system, 2 × 2H, 4/-/6/-7-H), 7.08 (dm, $^3J = 8.3$ Hz, 4H, 2 × 2 m-H), 7.65 (d, $^3J = 8.3$ Hz, 4H, 2 × 2 o-H) ppm; $^1$H NMR (CDCl₃, 400 MHz, −56 °C) $\delta$ 1.01 and 1.37 (broadened), 2.30, 2.97, 3.44, 7.12 and 7.26 (AA'BB' system), ca. 7.14 (d, 2 × 2 m-H), 7.65 and 7.72 (2 d, $^3J = 8$ Hz, 2 × 2 o-H) ppm; $^{13}$C NMR (CDCl₃, 100.6 MHz, 25 °C) $\delta$ 20.84 ($p$-CH₃), 29.46 and 33.54 (2 × 1/-3-CH₃), 47.23 (C-1/-3), 65.30 (C-2), 80.36 (HO-C), 122.00 (C-4/-7), 125.89 (broad, 2 × 2C-o), 126.80 (C-5/-6), 128.34 (2 × 2C-m), 135.77 (2C-p), 145.03 (2C-ipso), 150.52 (C-3a/-7a) ppm, assigned through comparison with benzyl alcohol; $^{13}$C NMR (CDCl₃, 100.6 MHz, −56 °C) $\delta$ 20.96 ($p$-CH₃), 29.48 and 33.14 (broadened, 2 × 1/-3-CH₃), 46.91, 64.46, 79.84, 122.03, 123.30 and 127.78 (2 × 2C-o), 126.77 (C-5/-6), 127.94 and 128.59 (2 × 2C-m), 135.81, 144.32, 150.10 ppm; IR (KBr) ν: 3647 (sharp H–O), 2960, 1506, 1484, 1366, 796, 752 (s), 580 cm⁻¹; anal. calcd for C₂₈H₃₂O (384.56): C, 87.45; H, 8.39; found: C, 87.69; H, 8.26.  

As shown above for 39a at −56 °C in CDCl₃ solution, the diastereotopic o-H, C-o, and C-m nuclei of the α,α-diaryl groups became pairwise chemically nonequivalent, while
the signals of the enantiotopic nuclei (p-CH₃, C-p, C-ipso, and p-CH₃) did not split. This established a restricted mobility at C-α with impeded rotation about the C-α/C-ipso single bonds and implies that the formation of 39a and 39b was retarded by a substantially increasing repulsive resistance.

α-(1,1,3,3-Tetramethylindan-2-yl)benzhydrol (39b): A run with acid 10 (1.83 mmol) and phenyllithium (34b, as in Section 1 for 38b from n-BuLi, 7.33 mmol) in refluxing Et₂O (15 mL, six hours at 40 °C) provided a 2:1 mixture of 38b and 39b. A sample was crystallized from methanol and recrystallized from petroleum ether to give thin needles of pure 39b, mp 205–206 °C; ¹H NMR (CDCl₃, 400 MHz) δ 1.01 and 1.34 (2 s, 2 × 6H, 2 × 1-/3-CH₃), 2.91 (s, 1H, variable OH), 3.48 (s, 1H, 2-H), 7.06 and 7.18 (AA′BB′ system, 2 × 2H, 4-/5-/6-/7-H), 7.17 (tt, ³J = 7.7 Hz, 2H, 2 × p-H), 7.29 (t, ³J = 7.9 Hz, 4H, 2 × 2 m-H), 7.81 (d, ³J = 8.0 Hz, 4H, 2 × 2 o-H) ppm; ¹H NMR (CCl₄, 80 MHz) δ 0.98, 1.31, 2.75, 3.45, 7.12 (broad m, 10 H), 7.77 ppm; ¹³C NMR (CDCl₃, 100.6 MHz) δ 29.46 and 33.52 (2 × 1-/3-CH₃), 47.26 (C-1/-3), 65.34 (C-2), 80.51 (HO–C), 122.01 (C-4/-7), 126.14 (very broad, 2 × 2C-o), 126.40 (2 × C-p), 126.88 (C-5/-6), 127.67 (broadened, 2 × 2C-m), 147.65 (2 × C-ipso), 150.38 (C-3a/-7a) ppm, assigned through comparison with benzyl alcohol; IR (KBr) ν: 3643 (sharp H–O), 3591 (w, H–O), 2982, 2958, 2867, 1486, 1447, 1366, 1065, 1029, 766, 711, 585 cm⁻¹; anal. calcd for C₂₆H₂₈O (356.51): C, 87.60; H, 8.27; found: C, 87.92; H, 8.27.

2-(α-Bromobenzylidene)-1,1,3,3-tetramethylindane (42b): The brominative deoxygenation of ketone 38b by reagent 41 (1.25 equiv) was conducted as described for 42a but in EtOH-free CH₂Cl₂ in place of 1,2-dichloroethane as the solvent. The half-reaction time was ca. 48 hours at 47 °C with 42b as the only product, while complete conversion had previously [S7] been attained within 75 hours at 60 °C in chloroform as the solvent. ¹H NMR (CDCl₃, 80 MHz) δ 1.17 (s, 6H, 2 × 1-CH₃), 1.77 (s, 6H, 2 ×
3-CH₃), 6.88 (m, 1H, 7-H), 7.09 (m, 3H, 4-/5-/6-H), 7.25 (quasi-s, 5H, α-phenyl) ppm, assigned through comparison with 42a; for ¹³C NMR, see ref [S8].

2-{Bis[p-(bromomethyl)phenyl]methylidene}-1,1,3,3-tetramethylindane (43): This unwanted side-product was isolated from the brominative deoxygenation of a sample of ketone 38a that was contaminated by the tertiary alcohol 39a. After separation from the desired bromoalkene 42a through chromatography on silicagel (60 Å, 63–200 μm) with low-boiling petroleum ether/Et₂O (60:1), the almost pure fraction of 43 had a mp of 161–163 °C; ¹H NMR (CDCl₃, 400 MHz) δ 1.28 (s, 12H, 2 × 1-/3-CH₃), 4.46 (s, 4H, 2 × CH₂Br), 7.08 (m, AA’-part of an AA’BB’ system, ca. 2H, 4-/7-H), 7.20 (m, BB’-part, ca. 2H, 5-/6-H), 7.29 (quasi-s, 8H, 4 × m-H and 4 × o-H) ppm; ¹³C NMR (CDCl₃, 100.6 MHz) δ 31.8 (2 × 1-/3-CH₃), 33.4 (2 × CH₂Br), 48.5 (C-1-/3), 122.1 (C-4-/7), 127.0 (C-5-/6), 128.6 (4 × C-m), 129.8 (4 × C-o), 135.7 (2 × C-p), 137.7 (C-α), 143.8 (2 × C-ipsos), 149.8 (C-3a-/7a), 156.9 (C-2) ppm, assigned through comparison with benzyl bromide and tetraphenylethene.
3. Alternative generations and the behavior of the Cl,K-carbenoid 12

3.1. FBW ring expansion of 12

Potassium tert-butoxide (KOt-Bu), but not LiOt-Bu, is a sufficiently active base to deprotonate the monochloride 14 (Scheme S2) slowly at 70 °C. The resultant Cl,K-carbenoid 12 did not add to cyclohexene in THF as the solvent and was not trapped (at least not irreversibly) by di-tert-butyl ketone (t-Bu₂C=O) in cyclohexane. In both of these solvents, 12 expanded its five-membered ring to generate the hitherto unknown cycloalkyne S6 in analogy with the earlier [S9] examples involving unsaturated Br,K- and Cl,Li-carbenoids. A run in heptane as the solvent (50 hours at 90 °C) provided evidence for the unknown enolate S7 through quenching with solid CO₂, which furnished the β-ketoacid S9 along with the known [S10] ketone S8. The chiral constitution of S9 followed from its ¹H NMR spectrum in CDCl₃ which exhibited four nonequivalent methyl groups (δ_H = 1.29, 1.49, 1.55, and 1.61 ppm) and for the center of chirality a one-proton signal (δ_H = 3.98 ppm). The thermal lability of S9 prevented its isolation and further characterization: The complete decarboxylation in CDCl₃ solution within four days at rt afforded the ketone S8, whose constitution [S10] established the ring expansion of carbenoid 12. Because tert-butyl ethers deriving from 12 or S6 were never detected, it remains unknown whether the enolate S7 arose through hydration of S6 by adventitious moisture or through a base-induced decay of a tert-butyl ether derived from S6.
**Scheme S2:** FBW ring expansion of the Cl,K-carbenoid 12.

**1,1,4,4-Tetramethyl-2-tetralone (S8):** A dry NMR tube (5 mm) was charged with the monochloride 14 (110 mg, 0.50 mmol), KOt-Bu (166 mg, 1.47 mmol), anhydrous THF (0.8 mL), and cyclohexene (0.2 mL). The tightly stoppered tube was heated at 70 °C for ca. 40 hours, emptied into aqueous hydrochloric acid (2 M, 10 mL), and shaken with Et₂O (3 × 10 mL). The combined Et₂O layers were washed with distilled water until neutral, dried over MgSO₄, and concentrated. After distillation at 75–90 °C (bath temp.)/0.001 mbar, some contaminations were removed through column chromatography on silica gel with low-boiling petroleum ether, whereupon the ketone S8 was eluted from the column with Et₂O (yield 27%) and washed with cold pentane: mp 68–71 °C (ref [S10]: 75 °C); ¹H NMR (CDCl₃, 200 MHz) δ 1.31 and 1.46 (2 s, 2 × 6H, 2 × 1-3-H), 2.65 (s, 2H, CH₂), 7.20–7.40 (m, 4H, aromatic protons) ppm.

**3.2. The S₅V reaction of benzyl potassium (S11) with carbenoid 12**

The easily prepared (Scheme S3) and purified [S11] benzyl potassium (S11) guides the dichloroalkene 6 into and through an efficient carbenoid chain reaction: S11 acts not only as a chlorine acceptor in step 1 and as a nucleophile in step 2; it is also consumed by the coproduct PhCH₂Cl of step 1 (giving dibenzyl), by the primary chain...
product S13 to produce the allene S14, and by deprotonating S14 to afford S15 which was recognized through carboxylation that generated the acid S16.

$$\text{H}_3\text{C-Ph} + n\text{BuLi} + \text{KO}t\text{Bu} \rightarrow \text{KCH}_2\text{-Ph} + n\text{BuH} + \text{LiO}t\text{Bu}$$

Scheme S3: Carbenoid chain $S_{NV}$ of the Cl,K-carbenoid 12.

2-Phenyl-3-(1,1,3,3-tetramethyl-2-ylidene)propenoic acid (S16): The solid dichloroalkene 6 (153 mg, 0.60 mmol) was added to an ice-cooled, red solution of PhCH$_2$K (S11, max. 3.0 mmol) [S11] in anhydrous THF (2.0 mL) under argon gas cover. The instantaneously blackened mixture was stirred at rt for 30 min, then poured onto solid CO$_2$, warmed up, and dissolved in aqueous NaOH and Et$_2$O. The aqueous layer was washed with Et$_2$O, acidified with conc. hydrochloric acid, and extracted with Et$_2$O which afforded the crude acid S16 together with phenylacetic acid. Crystallization from CCl$_4$ yielded colorless S16 (11%), mp 230–231 °C after recrystallization (CCl$_4$); $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 1.52 and 1.56 (2 s, 2 $\times$ 6H, 2 $\times$ 1-/3-CH$_3$), 7.18 (m, 2H, 4-/7-H), 7.27 (m, 3H, $p$-H and 5-/6-H), 7.33 (tm, $^3$J = 7.7 Hz, 2H, 2 $\times$ m-H), 7.64 (dm,
\(3J = 7.7 \text{ Hz}, 2\text{H}, 2 \times \alpha-\text{H})\), 10.46 (broad s, \text{CO}_2\text{H}) \text{ ppm}, assigned through comparison with compound \text{S9} in ref [S12]: \(^{13}\text{C}\) NMR (CDCl\textsubscript{3},100.6 MHz) \(\delta\) 30.89 and 31.43 (2 \times 1-/3-\text{CH}_3), 49.03 (C-1-/3), 107.35 (C-\(\beta\)), 122.44 (C-4-/7), 127.62 (C-5-/6 and C-p), 127.99 (2 \times C-\(\alpha\)), 128.30 (2 \times C-\(m\)), 129.30 (C-2), 132.80 (C-ipso), 148.15 (C-3a-/7a), 170.53 (\text{CO}_2\text{H}), 207.08 (C-\(\alpha\)) ppm, assigned through comparisons with compound \text{S9} in ref [S12], with phenylallene, and with phenylacetic acid.

The product of workup through protolysis instead of \text{CO}_2 quenching contained \text{S13}, \text{S14}, and dibenzyl. After distillation at 90–190 °C (bath temp.)/0.1 mbar, fractional crystallizations from low-boiling petroleum ether and from methanol furnished enriched samples of \text{S13} and \text{S14}, respectively.

\textbf{S13}: Identified through the \(^{37}\text{Cl}/^{35}\text{Cl}\) mass spectral intensity ratio of 1:3 and \(^1\text{H}\) NMR comparison with compound \text{4f} in ref [S12]. \(^1\text{H}\) NMR (CCl\textsubscript{4}, 80 MHz) \(\delta\) 1.55 (s, 6H, 2 \times 1-\text{CH}_3), 1.68 (s, 6H, 2 \times 3-\text{CH}_3), 4.00 (s, 2H, \text{CH}_2\text{Cl}), 7.21 (quasi-s, 9H, all aromatic protons) ppm; EI\text{MS} \textit{m/z} (%): 312.2 and 310.2 (ca. 1:3, 8\%, [M\textsuperscript{+}]), 297.2 and 295.2 (31\% + 94\%).

\textbf{S14}: Identified through a weak allene vibration in the IR (KBr) at \(\nu: 1949 \text{ cm}^{-1}\); \(^1\text{H}\) NMR (CCl\textsubscript{4}, 80 MHz) \(\delta\) 1.44 and 1.49 \(2\ s\), \(2 \times 6\text{H}, \ 2 \times 1-/3-\text{CH}_3\), 6.39 \(s\), 1H, \(\beta\)-H), 7.14 (quasi-s, 9H, all aromatic protons) ppm.

\textbf{3.3. No ring expansion during deprotonation and S\textsubscript{N}V of monochloride 14 by the potassium amide KHMDS}

It remained to demonstrate that a less reactive potassium nucleophile than \text{S11}, provided that it is more soluble than KO\textsubscript{t}-\text{Bu}, is also able to perform the S\textsubscript{N}V reaction before the ring expansion becomes perceptible. We observed by in situ \(^1\text{H}\) NMR spectroscopy how mixtures of KN(SiMe\textsubscript{3})\textsubscript{2} (KHMDS, potassium 1,1,1,3,3,3-hexamethyldisilazide) and \text{HN(SiMe}_3)_2 \text{ (HMDS, 1,1,1,3,3,3-hexamethyldisilazane)} [S13]
deprotonated the monochloride 14 (Scheme S4). The consumption of 14 required six days at rt in toluene with t-BuOMe (6:5 vol/vol) but only three hours in THF (where LiHMDS did not react over days at rt). In t-BuOMe as the solvent, 14 (0.07 M) was consumed by KHMDS (0.13 M) and HMDS (0.14 M) at rt with a first half-reaction time of ca. seven hours. In all cases, the enamine S18 was the main (and the only identified) product; ring expansion generating the cycloalkyne S6 did not take place. Final evidence for the S_N_V reaction was obtained through hydrolysis of the crude material containing the enamine S18 which furnished the known [S14] aldehyde S19 as the only descendant.

**Scheme S4:** No FBW ring expansion of 12 with KN(SiMe_3)_2.

**KN(SiMe_3)_2 as a base and nucleophile:** A weighed, dry NMR tube (5 mm) was charged with potassium hydride in mineral oil (49 mg) and pentane (0.3 mL). The suspension was whirled up through gentle shaking, and the turbid supernatant was withdrawn by syringe from the heavy precipitate of KH. After twofold repetition of such leaching, the residual pentane was removed in a soft stream of dry argon gas emanating from a long pipette for at least 5–15 seconds, leaving dry KH powder (29
mg, \( \leq 0.72 \) mmol) which was suspended in anhydrous -tBuOMe (0.65 mL) and treated with HMDS (0.040 mL, 0.20 mmol) and \([D_{12}]\)cyclohexane (0.040 mL). As expected [S15,S16] for such an unactivated specimen of KH, the proton transfer from HMDS (evolution of \( H_2 \)) took five days at rt for a partial (ca. 50%) formation of KHMDS (0.11 mmol). The monochloride 14 (11 mg, 0.05 mmol) was added and observed to be consumed over two days at rt. The final mixture was dissolved in Et\(_2\)O/water (vivid but short evolution of \( H_2 \)), and the Et\(_2\)O layer was washed with distilled water until neutral, dried over \( Na_2SO_4 \), and gently evaporated to afford the slightly contaminated enamine S18 (15 mg, 94%): \(^1\)H NMR of S18 (CDCl\(_3\), 200 MHz) \( \delta \) 0.17 (s, 18 H, 2 \( \times \) SiMe\(_3\)), 1.39 (s, 6H, 2 \( \times \) 3-CH\(_3\)), 1.53 (s, 6H, 2 \( \times \) 1-CH\(_3\)), 5.99 (s, 1H, \( \alpha \)-H), 7.12–7.24 (m, 4H, 4-/5-/6-/7-\( \alpha \)) ppm, assigned through comparison with the analogous \( \alpha \)-OSiMe\(_3\) derivative [S17].

Upon treatment of this CDCl\(_3\) solution with aqueous hydrochloric acid (2 M, three drops), the enamine S18 vanished within 150 min, and the known [S14] aldehyde S19 emerged: \(^1\)H NMR (CDCl\(_3\), 200 MHz) \( \delta \) 1.43 and 1.44 (2 s, 2 \( \times \) 6H, 2 \( \times \) 1-/3-CH\(_3\)), 2.54 (d, \( ^3J = 4.0 \) Hz, 1H, 2-H), 7.17 (AA´ part of an AA´BB´ system, 2H, 4-/7-H), 7.25 (BB´ part, 2H, 5-/6-H), 10.03 (d, \( ^3J = 4.0 \) Hz, 1H, CHO) ppm.

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