Unusual traits of cis and trans-2,3-dibromo-1,1-dimethylindane on the way from 1,1-dimethylindene to 2-bromo-, 3-bromo-, and 2,3-dibromo-1,1-dimethylindene

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Abstract
Do not rely on the widely accepted rule that vicinal, sp³-positioned protons in cyclopentene moieties should always have more positive ³J NMR coupling constants for the cis than for the trans arrangement: Unrecognized exceptions might misguide one to wrong stereochemical assignments and thence to erroneous mechanistic conclusions. We show here that two structurally innocent-looking 2,3-dibromo-1,1-dimethylindanes violate the rule by means of their values of ³J(cis) = 6.1 Hz and ³J(trans) = 8.4 Hz. The stereoselective formation of the trans diastereomer from 1,1-dimethylindene was improved with the tribromide anion (Br³⁻) as the brominating agent in place of elemental bromine; the ensuing, regiospecific HBr elimination afforded 3-bromo-1,1-dimethylindene. The addition of elemental bromine to the latter compound, followed by thermal HBr elimination, furnished 2,3-dibromo-1,1-dimethylindene, whose Br/Li interchange reaction, precipitation, and subsequent protolysis yielded only 2-bromo-1,1-dimethylindene.

Introduction
The basic mechanistic features of competing suprafacial and antarafacial additions of elemental bromine to an olefin are reasonably well established [1-3]. With indene as a cyclic olefin, the major product trans-1,2-dibromoindane was formed through antarafacial addition; the accompanying cis diastereomer resulted through the suprafacial bromine addition and rarely [4] exceeded 30% of the diastereomeric trans/cis product mixture. For the cis/trans assignments, common wisdom [5] commends the simple criterion that three-bond NMR coupling constants (³JH,H) should be more positive for a cis than for a trans relationship of the vicinal, sp³-positioned protons in five-membered rings. Indeed, cis-1,2-dibromoindane displayed ³J(1-H,2-H) = 5.0 Hz, whereas the trans diastereomer exhibited ³J(1-H,2-H) = 1.3 Hz [6]. However, we report here on the
closely related trans diastereomer of 2,3-dibromo-1,1-dimethylindane (trans-1) whose grossly deviating value of $^{3}J(2-H,3-H)$ = 8.4 Hz violates the above $^{3}J_{H,H}$ rule.

**Results and Discussion**

The addition of elemental bromine to 1,1-dimethylindene (2, see Supporting Information File 1) in $\text{CCl}_{4}$ as the solvent afforded a 7:3 mixture of trans-1 and cis-1 (Scheme 1). A more useful 9:1 mixture was obtained through the slow titration of a well-stirred chloroform solution of equimolar amounts of 2 and tetraethylammonium bromide with elemental bromine in chloroform. Such a higher trans selectivity is typical of the very rapidly [1] formed tribromide anion (Br$_3^-$) as the reactive species.

What kind of evidence supports our stereochemical assignments of trans-1 and cis-1? Although the three-bond NMR coupling constant $^{3}J(2-H,3-H)$ = 6.1 Hz of cis-1 is close to normal, trans-1 exhibits the abnormally high value of 8.4 Hz (compare with 1.3 Hz for trans-1,2-dibromoindane [6]), violating the commonly accepted $^{3}J_{H,H}$ rule that was mentioned in the Introduction. A more reliable criterion may be visualized from the envelope shape (expected puckering ca. 22–33°) of the cyclopentene parts of 1 (lines 2 and 3 of Scheme 1): the distance between two vicinal, sp$^3$-positioned protons in indanes clearly must be substantially longer for the pseudodiaxial (2ax-H,3ax-H) trans than for the pseudoaxial/pseudoequatorial (2ax-H,3eq-H) cis interproton relationships. Such distances may be estimated through nuclear magnetic Overhauser enhancements (NOE). As expected if trans-1 populates predominantly the 2ax-H,3ax-H conformation shown in Scheme 1, our one-dimensional NOE difference experiments revealed an approximately eight-fold stronger enhancement of the 3-H doublet signal of cis-1 than of trans-1 on irradiation of the almost coincident two 2-H NMR doublets of the two diastereomers; this established our assignments. In addition, a two-dimensional NOESY experiment displayed a cross-peak between 3-H and one of the two 1-CH$_3$ signals of trans-1. The necessary short distance of the involved protons can be traced to a 1,3-pseudodiaxial arrangement of 3-H and one of the methyl groups in the 2ax-H,3ax-H conformation. Thus, a close to 160° torsional relationship between the C(2)–H and C(3)–H bonds gives rise to the surprisingly high value of $^{3}J(2-H,3-H)$ = 8.4 Hz [7,8]. The hyperconjugative interaction of this pseudoequatorial C(3)–H bond with the aromatic π system causes a long-range (hence weak) magnetic coupling ($J = 0.7$ Hz) between 3-H and (presumably) 4-H in trans-1 (but not found in cis-1). The different conformational preference of trans-1 as compared with the methyl-free trans-1,2-dibromoindene ($^{3}J = 1.3$ Hz [6]) may obviously be ascribed to the two 1-Me groups [9]. In accord with the pseudoequatorial C(3)–H bond, HMBC (hetero multiple bond correlation) cross peaks of 3-H in trans-1 were absent with both C-1 and C-7a. On the other hand, the corresponding cross peaks were strong in cis-1 between 3eq-H and both C-1 and C-7a.
which indicated a significant $J_{C,H}$ NMR coupling via the intervening single bonds in their roughly coplanar arrangement shown in Scheme 1. It may also be noticed that the small C(2)–H/C(3)–H torsional angles in either one of the two cis-1 conformations are of similar sizes and do not permit a conformational differentiation. On the other hand, the close to 90° torsional angle between 3-H and 2-H in the 2eq-H,3eq-H conformation of trans-1 would imply an almost vanishing $J_{C,H}$ value, in contrast with the observed value of 8.4 Hz that is explained by the predominant 2ax-H,3ax-H conformation.

Distillation of the trans/cis product mixture led to some enrichment of the thermally more stable diastereomer trans-1 due to the “base-free” HBr elimination from cis-1 with formation of 2-bromo-1,1-dimethylinedene (4 in Scheme 2) [10]. We observed a less distinct kinetic preference in the corresponding base-induced processes: In di(2-methoxyethyl) ether (diglyme) as the solvent, a substoichiometric amount of KOt-Bu (potassium tert-butoxide) reacted faster with cis-1 than with trans-1 by a factor of roughly 9 at room temperature (rt). With an excess (>2 equiv) of KOt-Bu, both of these weakly exothermic HBr elimination reactions were completed within less than 30 min. With KOt-Bu (at rt) or KOEt (at 50 °C) but not with NEt$_3$ (no reaction at rt), the exclusive formation of 3-bromo-1,1-dimethylinedene (3) from trans-1 and of 4 from cis-1 became evident through the similarity of the emerging 3/4 ratios as compared with the trans-1/cis-1 ratios in the employed mixtures [11]. This regiospecificity is readily understandable since trans-1 has no anti relationship of vicinal Br and H available (Scheme 1), whereas each cis-1 conformer holds a pseudoaxial, vicinal Br/H anti relationship and hence is (presumably) able to react somewhat faster.

We abstained from separating trans-1 and cis-1 since the availability of two different mixtures facilitated the NMR assignments and because any cis-1 → trans-1 mixture or the ensuing 3/4 mixtures may be used for preparing 2,3-dibromo-1,1-dimethylinedene (7). Both 3 and 4 can add elemental bromine and the adducts (5 or 6, respectively) eliminated HBr either spontaneously (5) or in the presence of KOt-Bu or NEt$_3$ (6) at rt to furnish the same product 7. We found through NOESY and HMBC analyses that the thermally more stable tribromide 6 populates the conformation which has a pseudoaxial 3-H (and hence a pseudoequatorial 3-Br) orientation (like trans-1). Therefore, the unusually high thermolability of 5 seemed to be due to the unavoidable presence of one pseudoaxial C(3)–Br bond [12]. If so, the hitherto unknown 3,3-dibromo-1,1-dimethylinedene (8) might also be prone to such thermal HBr elimination. For comparison, treatment of 1,1-dimethylinedene (9) with one equivalent of N-bromosuccinimide (NBS) furnished the expected 3-bromo-1,1-dimethylinedene (see Supporting Information File 1), which decomposed already on distillation to yield 1,1-dimethylinedene (2). With two equivalents of NBS, however, 9 afforded a mixture of 3 and 7 through the following sequence in the bottom part of Scheme 2: $9 \rightarrow 8 \rightarrow 3 \rightarrow 5 \rightarrow 7$. Under these conditions, the spontaneous HBr elimination from 8 had produced 3, which added Br$_2$ to generate the thermolabile tribromide 5, whose HBr elimination gave 7; the required Br$_2$ was visible in the weakly brownish gas phase and had been provided through the well-known reaction of HBr with the accompanying NBS. Consequently, three equivalents of NBS would be necessary for obtaining 7 in a maximum yield. This encouraged us to reflux 9 in CCl$_4$ with NBS (4 equiv), which furnished mainly 7 along with succinimide (3.6 equiv) and remnant NBS (0.4 equiv). As a side-reaction, the slower thermal HBr elimination from the intermediate 3-bromo-1,1-dimethylinedene (see Supporting Information File 1) generated
1,1-dimethylindene (2), whose in situ bromination furnished 1 (ca. 1%) in a trans/cis ratio of ca. 3:2. Since both dibromides trans-1 and cis-1 were stable under the reaction conditions and would distill together with 7, they were destroyed through HBr elimination by KOH or Bu (or KOH in EtOH) to produce the bromomides 3 and 4. It may be noticed that 4 (from cis-1) cannot have been an intermediate in the initial step of the above "base-free" conversion of 9 to 7, since 4 would generate the thermally stable tribromide 6 that was not detected in the initial product mixture of 1 and 7.

For practical purposes, 7 may be useful as an alternative starting material in place of 2,3-diiodo-1,1-dimethylindene that had been employed [13,14] in cross-coupling studies. We actually used crude 7 as follows for a first specific route to 2-bromo-1,1-dimethylindene (4). The rapid Br/Li interchange reaction of 7 in hexane as the solvent with n-butyllithium (n-BuLi) occurred predominantly at the 3-position of 7 with formation of 2-bromo-3-lithio-1,1-dimethylindene (10, Scheme 3). In the absence of cycloalkanes or benzene from the hydrocarbon solvent, rather concentrated mixtures of 7 and n-BuLi slowly deposited unsolvated 10, which opened the possibility of purifying 10 through simple washings with dry pentane under inert gas cover. Like the related 3-chloro-2-lithio-1,1-dimethylindene [15], 10 did not eliminate LiHal at rt, so that its final hydrolytic work-up provided clean 4 even from moderately contaminated 7. As a well-known mixing problem [16,17], this final protolysis will be successful only in the absence (or at least after an adequate washing-out) of residual n-BuLi. Since protonation of n-BuLi and 10 is comparably rapid, a local depletion of the added proton source will leave the generated portion of 4 together with remnant n-BuLi, so that a very rapid Br/Li interchange reaction of 4 with n-BuLi will produce 1,1-dimethyl-2-lithioindene, whose protolysis forms 1,1-dimethylindene (2).

Conclusion

cis/trans differentiation in the saturated part of cyclopentene moieties should be based on 1H nuclear magnetic Overhauser enhancements rather than on the magnitudes of vicinal cis and trans 1H,1H NMR coupling constants which are not always reliable. The deceptively high value of 8.4 Hz in trans-2,3-dibromo-1,1-dimethylindene (trans-1) is explained in this work by a preferentially populated envelope conformation with pseudoequatorial 2-Br and hence pseudodiadixial 2-H and 3-H. The alternative (incorrect) stereoadsignment ("cis-19") in reference [8] and "cis-33" in reference [7] for the presently analyzed trans-1 would have misguided us to claim erroneously that we discovered a most unusual, highly cis selective olefin bromination.

What else may appear unusual with 1 and its congeners? Trans-1 and cis-1 undergo regiospecific HBr eliminations even in the absence of bases, cis-1 does so more rapidly than trans-1. The products 3 and 4, respectively, can serve as precursors for the same product 2,3-dibromo-1,1-dimethylindene (7). Exploiting the unusually high inclination of 3,3-di- (8) and 2,3,3-tribromo-1,1-dimethylindane (5) toward "base-free" HBr elimination at close to rt [12], we were able to convert 1,1-dimethylindane (9) with NBS directly to 7. The preparation of clean 2-bromo-1,1-dimethylindene (4) became possible through purification and hydrolysis of crystalline 2-bromo-3-lithio-1,1-dimethylindane (10).

Experimental

General remark. 1H and 13C NMR chemical shifts δ (ppm) were referenced to internal tetramethylsilane.

2,3-Dibromo-1,1-dimethylindene (1). a) Trans-1: Tetraethylammonium bromide (18.32 g, 87.2 mmol) was dissolved with magnetic stirring in a minimum volume of chloroform (120 mL), treated with 1,1-dimethylindene (2, 12.55 g, 87.1 mmol, see Supporting Information File 1), and then cooled in an ice-bath. Elemental bromine (4.44 mL, 13.9 g, 87.1 mmol) in chloroform (40 mL) was added dropwise at such a rate that each drop was quickly decolorized (65 min). After warm-up to rt within the next hour, the mixture was immediately shaken with aqueous Na2CO3 (2 M) until alkaline, washed with distilled water until neutral, dried over Na2SO4, and concentrated. The crude material (23.1 g, 87%) was a colorless, liquid mixture of trans-1 and cis-1 (9:1) with bp 145–149 °C/11 Torr (no data given in reference [7]).

1H NMR (CDCl3, 400 MHz) δ 1.22 (s, 3H, pseudoaxial 1-CH3), 1.42 (s, 3H, pseudoequatorial 1-CH3), 4.35 (d, J = 8.4 Hz, 1H, 2-H), 5.40 (dd, J = 8.4 Hz, J = 0.7 Hz, 1H, 3-H), 7.17 (m, 1H, 7-H), 7.28 (m, 1H, 5-H), 7.31 (m, 1H, 6-H), 7.41 (m, 1H, 4-H)
residue was poured into distilled water (ca. 400 mL) and the following NOEY correlations: J = 7 Hz, 1H, C-6; 7.28 (m, 1H, 7-H), 7.30 (m, 1H, 5-H), 7.33 (dm, J = 7.5 Hz, 1H, 4-H ppm, assigned through HSQC and 1H/13C HMBC (see below); 13C NMR (CDCl3, 100.6 MHz) δ 24.17 (2 × 1-CH3), 49.97 (C-1), 118.19 (C-3), 120.48 (C-4), 120.81 (C-7), 126.41 (C-6), 126.87 (C-5), 140.84 (C-3a), 145.13 (C-2), 151.74 (C-7a) ppm, assigned through HSQC and the following 1H/13C HMBC interactions. 1-CH3 → C-2 and C-7a, 2-H → C-3a and C-7a, both 1-CH3 → C-1. Anal. calcd for C11H12Br2 (304.02): C, 43.46; H, 3.98; found: C, 44.06; H, 3.92.

b) Cis-1: This was analyzed in the 3:7 mixture with trans-1 as obtained from 1,1-dimethylindene (2) through titration with elemental bromine (not Br2). 1H NMR (CDCl3, 400 MHz) δ 1.33 and 1.42 (2 s, 2 × 3H, 2 × 1-CH3), 4.34 (d, J = 6.1 Hz, 1H, 2-H), 5.55 (d, J = 6.1 Hz, 1H, 3-H), 7.20 (m, 1H, 7-H), 7.27 (m, 5-H), 7.34 (m, 6-H), 7.42 (m, 4-H) ppm, assigned through HSQC, HMBC (see below), and the following NOESY correlations: 2-H ↔ both 1-CH3 ↔ 7-H, but pseudoequatorial 3-H ↔ 4-H only (not 1-CH3); 1H NMR (D2O, C=O, 200 MHz) δ 4.54 and 5.76 (AB system, J = 6.0 Hz, 2 × 1H, 2-H and 3-H) ppm; 13C NMR (CDCl3, 100.6 MHz) δ 26.07 and 26.58 (2 × 1-CH3), 47.23 (C-1), 55.70 (C-3), 62.07 (C-2), 123.00 (C-7), 125.56 (C-4), 127.83 (C-5), 130.00 (C-6), 139.30 (C-3a), 148.67 (C-7a) ppm, assigned through HSQC and the following 1H/13C HMBC interactions. 3J: 2-H ↔ both 1-CH3, pseudoequatorial 3-H ↔ C-1 (strong) and C-7a (strong), both 1-CH3 → C-2 and C-7a, C-3a → 5-H and 7-H, C-4 → 6-H, C-7 → 5-H, C-7a → 4-H and 6-H, pseudoequatorial 1-CH3 → pseudoequatorial 1-CH3; 2J: 2-H → C-3, 3-H → C-2 and C-3a, both 1-CH3 → C-1. Anal. calcd for C11H12Br2 (304.02): C, 43.46; H, 3.98; found: C, 44.06; H, 3.92.

3-Bromo-1,1-dimethylindene (3). A crude sample of the 9:1 mixture of trans-1 and cis-1 (23.0 g, max. 75 mmol) was added to a saturated solution of solid KOH (30.0 g, 833 mmol) in ethanol (190 mL) and heated to 50 °C for 4 hours. After cautious removal of some ethanol (ca. 130 mL) in vacuo, the residue was poured into distilled water (ca. 400 mL) and extracted with Et2O (4 × 100 mL). The combined Et2O extracts were washed with distilled water until neutral, dried over CaCl2, concentrated, and distilled to yield a pure 92:8 mixture (11.19 g, ≥96%) of 3- and 2-bromo-1,1-dimethylindene (3 and 4) with bp 115–117 °C/12 Torr.

1H NMR of 3 (CDCl3, 400 MHz) δ 1.32 (s, 6H, 2 × 1-CH3), 6.46 (s, 1H, 2-H), 7.25 (tm, J = 7 Hz, 1H, 6-H), 7.28 (m, 1H, 7-H), 7.30 (m, 1H, 5-H), 7.33 (dm, J = 7.5 Hz, 1H, 4-H ppm, assigned through HSQC and 1H/13C HMBC (see below); 13C NMR (CDCl3, 100.6 MHz) δ 24.17 (2 × 1-CH3), 49.97 (C-1), 118.19 (C-3), 120.48 (C-4), 120.81 (C-7), 126.41 (C-6), 126.87 (C-5), 140.84 (C-3a), 145.13 (C-2), 151.74 (C-7a) ppm, assigned through HSQC and the following 1H/13C HMBC interactions. 1-CH3 → C-2 and C-7a, 2-H → C-3a and C-7a, C-3 → 4-H → C-6, C-3a → 7-H → C-5, C-4 → 6-H, C-7 → 5-H, C-7a → 2-/-6-H; Anal. calcd for C11H11Br (223.13): C, 59.22; H, 4.97; found [18]: C, 58.79; H, 4.91. The alternative HBr elimination with KOt-Bu was rapid and exothermic in diglyme as the solvent.

2-Bromo-1,1-dimethylindene (4). A sample of contaminated 2,3-dibromo-1,1-dimethylindene (7, 8.43 g, 27.7 mmol) in pentane (5.0 mL) was treated with n-BuLi (ca. 40 mmol) in hexane (35 mL) at −70 °C under argon gas cover. Since this reaction was run in an acyclic, saturated hydrocarbon as the solvent (no cyclopentane, no benzene), a voluminous precipitate began to emerge slowly at rt within ca. one hour. When this colorless powder of 2-bromo-3-lithio-1,1-dimethylindene (10) had settled after 20 hours at rt, the supernatant was withdrawn by syringe, and the residue was washed with dry pentane (3 × 15 mL). This purified, solid material was suspended in pentane at −70 °C under argon gas and quenched with methanol (2.0 mL). After dilution with water and Et2O, the aqueous layer was extracted with Et2O (2×). The combined Et2O phases were washed with water until neutral and dried over Na2SO4. The crude material contained 4 and 1,1-dimethylindene (2, 77:23) without any other indene derivative. Pure 4 (2.10 g, 34%) distilled at 101–103 °C/12 Torr. 1H NMR (CDCl3, 400 MHz) δ 1.25 (s, 6H, 2 × 1-CH3), 6.75 (s, 1H, 3-H), 7.15 (tm, J = 7.5 Hz, 1H, 6-H), 7.18 (tm, J = 7.5 Hz, 1H, 5-H), 7.23 (dm, J = 7.5 Hz, 1H, 4-H), 7.27 (dm, J = ca. 7 Hz, 1H, 7-H) ppm, assigned through comparisons with 3 and 7, HSQC and 1H/13C HMBC (see below), and the NOESY correlation 1-CH3 ↔ 7-H; 1H NMR (D2O, C=O, 200 MHz) δ 1.25 (s, 6H, 2 × 1-CH3), 6.89 (s, 1H, 3-H) ppm; 13C NMR (CDCl3, 100.6 MHz) δ 23.94 (2 × 1-CH3), 52.05 (C-1), 120.48 (C-4), 121.51 (C-7), 125.11 (C-6), 126.70 (C-5), 128.99 (C-3), 139.86 (C-2), 141.07 (C-3a), 151.66 (C-7a) ppm, assigned through HSQC, comparison with 7, and the following 1H/13C HMBC interactions. 3J: 1-CH3 → 1-CH3, 1-CH3 → C-2 and
C-7a, 3-H → C-1 and C-7a, 7-H → C-3a and C-5, 6 → 4-H; \( \stackrel{2}{\text{J}} \): 1-CH\(_3\) → C-1, 3-H → C-3a; MS (EL, 70 eV, 80 °C) m/z (%): 224 and 222 (2 × 11, M\(^+\)), 143 (100, M – Br\(^-\)), 128 (56, M\(^+\) – CH\(_2\)Br); HRMS (EI) m/z 224.0026 (C\(_{11}\)H\(_{11}\)Br\(_2^+\), M\(^+\)), 222.0045 (C\(_{11}\)H\(_{11}\)Br\(_2^+\), M\(^+\)); Anal. calcd for C\(_{11}\)H\(_{11}\)Br (223.13): C, 59.22; H, 4.97; found: C, 60.55 H, 4.97.

2,3,3-Tribromo-1,1-dimethylindene (5): This thermolabile adduct of 3-bromo-1,1-dimethylindene (3) and elemental bromine (see 7) was not purified but recognized through its \(^1\)H NMR chemical shifts and its thermolysis product 7. \(^1\)H NMR (CDCl\(_3\), 200 MHz) \( \delta \) 1.36 (s, 3H, 1-CH\(_3\)), 1.39 (s, 3H, 1-CH\(_3\)), 4.78 (s, 1H, 2-H) ppm; \(^13\)C NMR (CDCl\(_3\), 100 MHz) \( \delta \) 125.64 (C-4), 128.03 (C-5), 129.77 (C-6), 137.56 (C-7), 143 (100, M – Br\(^-\)), 150.0 (C-7a) ppm, assigned through HSQC and the NOESY correlation 1-CH\(_3\) ↔ 7-H; \(^13\)C NMR (CDCl\(_3\), 100.6 MHz) \( \delta \) 24.2 (2 × 1-CH\(_3\)), 55.18 (C-1), 63.97 (C-3), 84.42 (C-2), 120.0 (C-3), 120.3 (C-4), 121.3 (C-7), 126.4 (C-6), 127.2 (C-5), 138.9 (C-2), 139.9 (C-3a), 150.0 (C-7a) ppm, assigned through HSQC, comparison with 3, and the following \( \stackrel{2}{\text{J}} \) and \( \stackrel{3}{\text{J}} \) HMBC cross peaks. \( \stackrel{2}{\text{J}} \): 1-CH\(_3\) → C-2 and 3-Ch; 4-H → C-3 and C-6 and C-7; 7-H → C-3a and C-5; C-4 → 6-H, C-7 → C-3a and C-5; C-4 → 6-H, C-3a → 5-H; \( \stackrel{3}{\text{J}} \): both 1-CH\(_3\) → C-2 and C-7a, 3-H → C-4 and C-7a (but not C-1 since 3-H is pseudosaxial), 4-H → C-6 and C-7a, 7-H → C-3a and C-5, C-4 → 6-H, C-3a → 5-H; \( \stackrel{2}{\text{J}} \) both 1-CH\(_3\) → C-1, 3-H → C-3a; HRMS and MS (EI) m/z (%) 303.9135 (14, C\(_{11}\)H\(_{10}\)Br\(_2^+\), calcd 303.9103, M\(^+\)), 301.9119 (25, C\(_{11}\)H\(_{9}\)Br\(_3^+\), calcd 301.9123, M\(^+\)), 299.9146 (14, C\(_{11}\)H\(_{10}\)Br\(_2^+\), calcd 299.9144, M\(^+\)), 222.9936 (83, C\(_{11}\)H\(_{10}\)Br\(_2\), M – Br\(^-\)), 220.9974 (77, C\(_{11}\)H\(_{10}\)Br\(_2\), M – Br\(^-\)); Anal. calcd for C\(_{11}\)H\(_{10}\)Br\(_2\) (302.0): C, 43.75; H, 3.34; Br, 52.92; found: C, 44.06; H, 3.42; Br, 52.00.

b) From 2-bromo-1,1-dimethylindene (4) via 2,2,3-tribromo-1,1-dimethylindene (6): A small sample (44 mg, 0.11 mmol) of distilled tribromide 6 (obtained as above from 4 and containing no trace of 7) in CCl\(_4\) was placed in an NMR tube (5 mm) and treated with an excess of solid KO\(_2\)-Bu, which consumed 6 within less than 2 hours at rt. Aqueous work-up with Et\(_2\)O afforded the dibromide 7 (29 mg, 87%) as the only product (hence, no S\(_2\) reaction by KO\(_2\)-Bu). N\(_2\)Et\(_3\) as the base in place of KO\(_2\)-Bu required 12 days at rt.

c) From 1,1-dimethylindene (9): A mixture of 1-\(\text{N}\)-bromosuccinimide (NBS, 7.13 g, 40 mmol), 1,1-dimethylindane (9, 1.46 g, 10 mmol, see Supporting Information File 1), and CCl\(_4\) (50 mL) was treated with azobis(isobutyronitrile) (40 mg) and warmed slowly up to 85 °C. After 30 min of viced refluxing, the dark red suspension showed traces of elemental bromine in the gas phase and was cooled in an ice bath (15 min). A \(^1\)H NMR spectrum of the solution revealed that the starting material 9 was completely consumed and that a mixture containing three gem-dimethyl compounds had been generated: 2,3-dibromo-1,1-dimethylindene (7, 76%), 1 (1%, \(\text{trans} \), ca. 3:2), and an unknown side-product (20%). The suspension was filtered, and the undissolved portion was washed with CCl\(_4\) (2 × 5 mL), affording a colorless, powdery mixture of NBS and succinimide (4.36 by \(^1\)H NMR). The dark red CCl\(_4\) filtrate became colorless on shaking with an aqueous solution of sodium sulfite (at least 0.6 g) and was washed with distilled water (10 mL),
then dried through stirring with granulated CaCl₂ (30 min). After removal of CaCl₂, the colorless solution became violet on stirring with a sufficient amount of solid KOt-Bu (2.6 g) for 30 min, which destroyed the two dibromides 1 and other small contaminations. The CCl₄ solution was shaken with H₂O (10 mL), aqueous HCl (2 M, 10 mL), and H₂O until neutral, then dried as above with CaCl₂ (30 min). Evaporation of CCl₄ and subsequent distillation in vacuo furnished the colorless liquid 7 (1.35 g, 45%).

Supporting Information

Supporting Information File 1

Alternative synthetic routes to 1,1-dimethylindene (2) and congeners; experimental procedures for 1,1-dimethylindane (9), 3-methyl-1-phenylbutan-2-ol, congeners; experimental procedures for N,N’-bis(1,1-dimethylindan-3-ylidene)hydrazine, and N, N’-bis(1,1-dimethylindan-3-ylidene)hydrazine. [http://www.beilstein-journals.org/bjoc/content/supplementary/1860-5397-12-113-S1.pdf]

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