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# Syntheses of dispiro[2.1.4.1]decane and dispiro[2.0.3.3]decane

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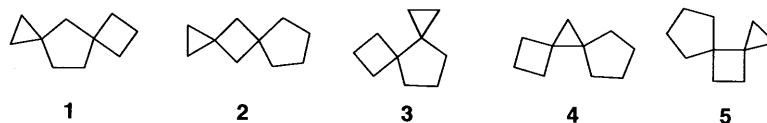
## Abstract

Efficient syntheses of the hitherto unknown hydrocarbons dispiro[2.1.4.1]decane and dispiro[2.0.3.3]decane have been realized through reaction sequences involving spiro[3.4]octan-2-one and spiro[3.4]octan-5-one as key intermediates. © 2000 Elsevier Science Ltd. All rights reserved.

*Keywords:* cyclopropanes; hydrocarbons; polycyclic aliphatic compounds; spiro compounds.

Five of the eleven possible dispirodecanes incorporate one three-membered, one four-membered, and one five-membered ring (**1–5**). These five hydrocarbons combine the comparatively large strain energies and thermal reactivities associated with cyclopropane and cyclobutane sub-structures with the geometrical limitations imposed by the cyclopentane element and the spirocyclic linkages. These features in various geometrical dispositions offer novel opportunities for exploring just how subtle mutual accommodations of structural constituents may influence ground-state heats of formation and favored conformations, and the rates of alternative thermal isomerization and fragmentation reactions. The influences of conformational restrictions on access to and reactivity of thermally generated diradicals<sup>1</sup> derived from **1** to **5** as cyclopropane or cyclobutane rings cleave homolytically may be particularly revealing.

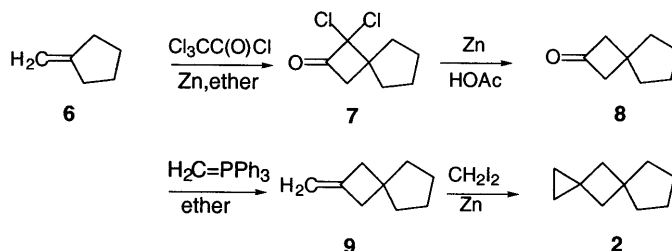
The first of these five isomers, dispiro[2.1.3.2]decane (**1**), was synthesized for the first time only last year;<sup>2</sup> efficient preparations of the second and third hydrocarbons in this set, dispiro[2.1.4.1]decane (**2**) and dispiro[2.0.3.3]decane (**3**), are now reported.



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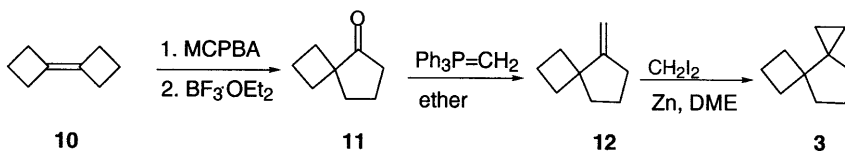
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From the many possible synthetic approaches to these polycyclic hydrocarbons a common strategy was selected, based on the generally reliable two-step transformation of a cycloalkanone to a methylenecycloalkane to a cycloalkanespirocyclopropane, a sequence used in one of our two syntheses of dispiro[2.1.3.2]decane (**1**).<sup>2</sup> Thus the four-step sequence from methylenecyclopentane to dispirodecane **2** outlined in Scheme 1 was selected and realized. It takes advantage of a readily accessible starting material and a brief sequence of suitable well-established reactions.



Scheme 1.

Spiro[3.4]octan-2-one (**8**), the key intermediate, has apparently been made only once before, inefficiently, through the photodecarboxylation of 3,3-tetramethyleneglutaric anhydride.<sup>3</sup> The alternative preparation of Scheme 2 provided ketone **8** much more conveniently. Methylenecyclopentane was combined with dichloroketene generated in situ<sup>4</sup> to give the (2+2) cycloaddition product 1,1-dichlorospiro[3.4]octan-2-one (**7**) with very high regioselectivity and fair yield, 78%. The dichloroketone was reduced with zinc in acetic acid<sup>5</sup> to provide the known spiro[3.4]octan-2-one (**8**)<sup>3,6</sup> in 63% yield. A Wittig reaction converted this ketone in 80% yield to 2-methylenespiro[3.4]octane (**9**).<sup>7</sup> Finally, a Simmons–Smith reaction employing activated zinc<sup>8</sup> rather than the more traditional zinc–copper couple afforded dispiro[2.1.4.1]decane (**2**). It showed the expected six resonances in the <sup>13</sup>C NMR spectrum,<sup>9</sup> the fewest to be anticipated from the dispirodecane isomers **1** to **5**.



Scheme 2.

The tactically identical preparation of dispiro[2.0.3.3]decane (**3**) outlined in Scheme 2 depended on access to spiro[3.4]octan-5-one (**11**), a long known and readily accessible compound.<sup>10</sup> It was made through an epoxidation of bicyclobutyliene (**10**)<sup>11</sup> followed by a  $\text{BF}_3$  etherate catalyzed isomerization to afford ketone **11**.<sup>12</sup> A Wittig condensation converted **11** into 5-methylenespiro[3.4]octane, a known olefin.<sup>12</sup> A cyclopropanation then provided the target hydrocarbon **3**.<sup>13,14</sup>

These preparations of dispirodecanes **2** and **3** are quite direct, reasonably efficient, and amenable to scale-up. They demonstrate the attractive features of the routes outlined in Schemes 1 and 2 and provide clean, isomer-free samples of these polycyclic hydrocarbons. With these syntheses and characterizations, three of the five dispirodecanes **1** to **5** are now in hand and available for comparative studies of thermal reactions and reactivities. Efficient preparations of

the remaining two isomers in this set, dispiro[3.0.4.1]decane (**4**) and dispiro[2.0.4.2]decane (**5**), are currently being developed.

## Acknowledgements

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6. Spiro[3.4]octan-2-one (**8**):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.7–1.9 (m, 8H), 2.9 (m, 4H);  $^{13}\text{C}$  NMR  $\delta$  24.2, 36.6, 39.0, 57.3, 208.5; MS  $m/z$  124 ( $\text{M}^+$ ), 67.
7. 2-Methylenespiro[3.4]octane (**9**):  $^1\text{H}$  NMR  $\delta$  1.50–1.80 (m, 8H), 2.40–2.70 (m, 4H), 4.8 (s, 2H);  $^{13}\text{C}$  NMR  $\delta$  24.0, 39.1, 42.0, 43.2, 105.8, 146.3; MS  $m/z$  122 ( $\text{M}^+$ ).
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13. Dispiro[2.0.3.3]decane (**3**):  $^1\text{H}$  NMR  $\delta$  0.2–0.3 (m, 2H), 0.4–0.5 (m, 2H), 1.50–1.90 (m, 12H);  $^{13}\text{C}$  NMR  $\delta$  8.3, 15.7, 21.1, 28.4, 29.4, 33.7, 39.2, 48.3; MS  $m/z$  136 ( $\text{M}^+$ ), 121.
14. Compare ‘Three, Five, Four’, 1973, 38”x50”, charcoal on paper, a graphic by Mel Bochner, reproduced in *Mel Bochner: 1973–1985* (a catalog to accompany an exhibit organized by Elaine A. King); Carnegie-Mellon University Press: Pittsburgh, 1985. See also Richardson, B. *Mel Bochner: Number and Shape*; The Baltimore Museum of Art: Baltimore, 1976, and Field, R. S. *Mel Bochner: Thought Made Visible 1966–1973*; Yale University Art Gallery: New Haven, 1995.