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Two Syntheses of Dispiro[2.1.3.2]decane

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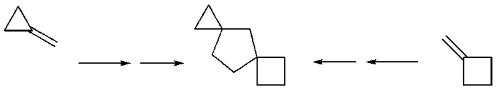
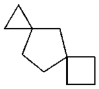
ABSTRACT



Dispiro[2.1.3.2]decane, the first of the five possible dispirodecanes constituted from one three-membered, one four-membered, and one five-membered ring to be synthesized, has been prepared efficiently in four steps from methylenecyclopropane and again in five steps from methylenecyclobutane.

Dispiro[2.1.3.2]decane (**1**), one of the five possible dispirodecanes constituted from one three-membered, one four-membered, and one five-membered ring, contains structural features which are rarely encountered and potentially well worth close investigation. All five have remained unknown.



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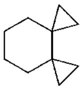

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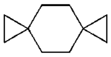

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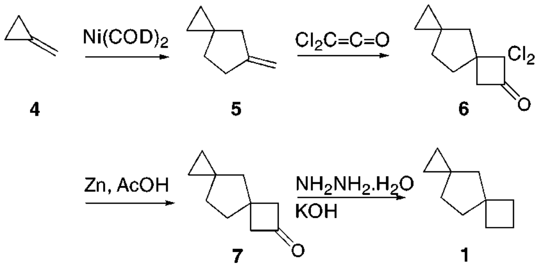
Only 2 of the full set of 11 possible dispirodecanes have been recorded in the literature, dispiro[2.0.2.4]decane (**2**)[1] and dispiro[2.2.2.2]decane (**3**).[2] Both hydrocarbons have been the subject of worthy experimental and theoretical investigations.[1,2] The other nine isomers in this set, including the five based on cyclopropyl, cyclobutyl, and cyclopentyl substructures, have not been prepared and studied.

Two of the many imaginable synthetic approaches to structure **1** which proceed rather directly from readily accessible starting materials were selected and implemented. In the first preparation of this novel $C_{10}H_{16}$ hydrocarbon, outlined in Scheme 1, methylenecyclopropane (**4**)[3] was dimerized under the catalytic influence of bis(1,5-cyclooctadiene)nickel(0) and maleic anhydride by the method of Binger to afford 5-methylenespiro[2.4]heptane (**5**).[4] The (2 + 2) cycloaddition of this olefin with dichloroketene[5] gave adduct **6**, which was reduced with zinc and acetic acid to provide dispiro[2.1.3.2]decan-7-one (**7**).[6] Finally, a Wolff−Kishner reduction in di(ethylene glycol) at temperatures up

Scheme 1



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[1] (a) Magrill, D. S.; Altman, J.; Ginsburg, D. *Isr. J. Chem.* **1969**, *7*, 479−482. (b) De Meijere, A. *Chem. Ber.* **1974**, *107*, 1684−1701. (c) Kaufmann, D.; De Meijere, A. *Chem. Ber.* **1983**, *116*, 833−837. (d) Spanget-Larsen, J.; Gleiter, R.; Gubernator, K. *J. Org. Chem.* **1982**, *47*, 3082−3089.

[2] (a) Buchta, E.; Kröniger, A. *Chimia* **1969**, *23*, 225−229. (b) Lambert, J. B.; Gosnell, J. L.; Bailey, D. S.; Greiferstein, L. G. *J. Chem. Soc. D* **1970**, 1004. (c) Lambert, J. B.; Gosnell, J. L.; Bailey, D. S. *J. Org. Chem.* **1972**, *37*, 2814−2817. (d) Bailey, D. S.; Lambert, J. B. *J. Org. Chem.* **1973**, *38*, 134−147. (e) Asmus, P.; Klessinger, M.; Meyer, L. U.; De Meijere, A. *Tetrahedron Lett*. **1975**, 381−384. (f) Proksch, E.; De Meijere, A. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 761−762. (g) Kiwus, R.; Schwarz, W.; Rossnagel, I.; Musso, H. *Chem. Ber.* **1987**, *120*, 435−438. (h) Bowry, V. W.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1991**, *113*, 5687−5698. (i) Bowry, V. W.; Ingold, K. U. *J. Am. Chem. Soc.* **1991**, *113*, 5699−5707.

[3] Köster, R.; Arora, S.; Binger, P. *Liebigs Ann. Chem.* **1973**, 1219−1235.

[4] (a) Binger, P. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 309−310. (b) Binger, P.; Brinkmann, A.; Wedemann, P. *Chem. Ber.* **1983**, *116*, 2920−2930.

[5] Brady, W. T.; Liddell, H. G.; Vaughn, W. L. *J. Org. Chem.* **1966**, *31*, 626−628.

[6] Dispiro[2.1.3.2]decan-7-one (**7**): ^{1}H NMR ($CDCl_3$) δ 0.30−0.60 (m, 4H), 0.90−1.10 (m, 4H), 1.30 (s, 2H), 2.30 (s, 4H); ^{13}C NMR δ 13.5, 17.0, 36.8, 37.2, 45.0, 49.8, 50.1, 216.0; MS m/z 150 (M^+).

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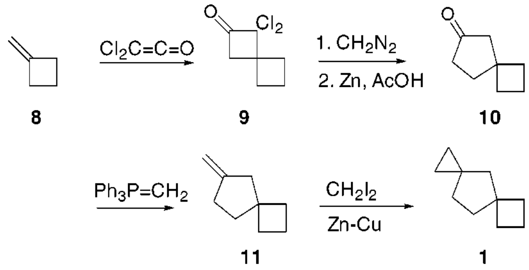
to 175 °C generated the synthetic target, **1**, as a colorless oil, one easy to obtain in high purity through preparative GC on an SE−30 column.[7]

The reduction of **7** gave only a 26% yield of **1**—a disappointing outcome that may well be improved upon through further synthetic trials. Meanwhile, an alternative route was developed (Scheme 2): it confirmed the outcome of the first preparation and provided **1** in a substantially higher overall yield.

Scheme 2



This second synthetic sequence started from methylenecyclobutane (**8**), obtained through the chemistry developed by Fitjer and Quabeck.[8] It was converted to the known spiro-[3.4]octan-6-one (**10**) using the three-step sequence reported by Erden and Sorenson:[9] a (2 + 2) cycloaddition with dichloroketene to give the intermediate 1,1-dichlorospiro-[3.3]heptane-2-one (**9**), followed by ring expansion with diazomethane[10] and a reductive dechlorination with zinc and acetic acid.[11] Ketone **10** was combined with methylenetriphenylphosphorane to generate 6-methylenespiro[3.4]octane (**11**),[12] and finally a Simmons−Smith reaction provided the dispirodecane **1,** identical by analytical GC and NMR spectroscopic criteria with the sample prepared through the route of Scheme 1.

With these synthetic routes to dispiro[2.1.3.2]decane now realized (though not optimized) and hydrocarbon **1** in hand, work on the conformational forms and dynamics of this molecule and on the thermal chemistry of this system has now been initiated.

One stimulus to review the literature for information on dispirodecane structures and then to synthesize **1** was provided by a work of art, a pastel by the artist Mel Bochner.[13,14]

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(7) Dispiro[2.1.3.2]decane (**1**): ^{1}H NMR δ 0.2−0.5 (m, 4H), 1.40−2.10 (m, 12H); ^{13}C NMR δ 13.3, 16.6, 21.1, 34.2, 34.7, 40.4, 48.1, 49.2; MS m/z 136 (M$^+$).

(8) Fitjer, L.; Quabeck, U. *Synthesis* **1987**, 299−300.

(9) Erden, I.; Sorenson, E. M. *Tetrahedron Lett.* **1983**, *24*, 2731−2732.

(10) Greene, A. E.; Deprés, J. P. *J. Am. Chem. Soc.* **1979**, *101*, 1, 4003−4005.

(11) Spiro[3.4]octan-6-one (**10**): ^{1}H NMR δ 1.80−2.10 (m, 8H), 2.2 (m, 2H), 2.30 (s, 2H); ^{13}C NMR δ 15.7, 32.4, 34.3, 35.7, 37.5, 43.3, 51.6, 219.3; MS m/z 124 (M$^+$).

(12) 6-Methylenespiro[3.4]octane (**11**): ^{1}H NMR δ 1.60 (t, 2H, J = 14.7 Hz), 1.90 (m, 6H), 2.3 (m, 4H), 4.50 (m, 2H); ^{13}C NMR δ 16.3, 35.3, 36.1, 36.3, 39.6, 47.5, 51.6, 105.6, 139.4; MS, m/z 122 (M$^+$).

(13) For an introduction to the work of this remarkable artist, see (a) *Mel Bochner: 1973−1985* (a catalog to accompany an exhibit organized by Elaine A. King); Carnegie-Mellon University Press: Pittsburgh, PA, 1985. (b) Richardson, B. *Mel Bochner: Number and Shape*; The Baltimore Museum of Art: Baltimore, MD, 1976. (c) Field, R. S. *Mel Bochner: Thought Made Visible 1966−1973*; Yale University Art Gallery: New Haven, CT, 1995, and its extensive bibliography.

(14) Mr. Bochner's immediate preoccupations in this work titled TRIPLEX were not derived in any way from the realm of organic chemistry, yet, to an organic chemist, this pastel had to be taken as both a creative expression and as a one-to-one correspondence with a structural representation of dispiro[2.1.3.2]decane (**1**). Only later did it become evident that this structure and other closely related isomers had never been prepared and studied. The more common pattern of interchange between science and art runs the other way: wonder and intuition inspired by nature and science may lead to original artistic expressions.[15] Here Mr. Bochner's pure imagination, powered by a thoughtful concern with geometrical shapes and spatial relationships, and some exposure to mathematical and tiling issues, led to TRIPLEX. The exact correspondence of his image with the then unknown but surely accessible and very real dispirodecane **1** led to the syntheses of Schemes 1 and 2.

(15) Compare: Hoffmann, R.; Torrence, V. *Chemistry Imagined: Reflections on Science*; Smithsonian Institution Press: Washington, DC, and London, 1993.