Notes

The Synthesis of *cis*- and *trans*-Tricyclo[6.4.0.$0^{2,7}$]dodeca-2,12-diene by the Intramolecular Coupling of Disilver Reagents[1a]

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Several simple alkenylsilver(I) compounds have been prepared and shown to undergo thermally induced decomposition to give conjugated dienes derived from coupling of the alkenyl groups. Thus vinylsilver affords 1,3-butadiene,[2a] 1-propenylsilver affords 2,4-hexadiene,[2b] and 2-butenylsilver affords 3,4-dimethyl-2,4-hexadiene.[2b] In the last two cases, the coupling was found to occur with retention of configuration indicating that free radicals were not involved. These reactions represent intermolecular coupling. It appeared to us that, if *intramolecular* coupling could be achieved, one would have a potentially useful way to effect unique ring closures. We have examined this possibility in a case of particular interest to us and have found that derivatives of 1,2-dimethylenecyclobutane can be prepared in good yield by intramolecular coupling of the appropriate disilver reagents.

Coupling of dibromide **1**[3] with magnesium affords a 1:1 mixture of *meso*- and *dl*-2,2′-dibromo-3,3′-bicyclohexenyl (**2**) from which the pure crystalline isomers can be obtained by fractional crystallization. The configurational assignments are based on the results reported below.

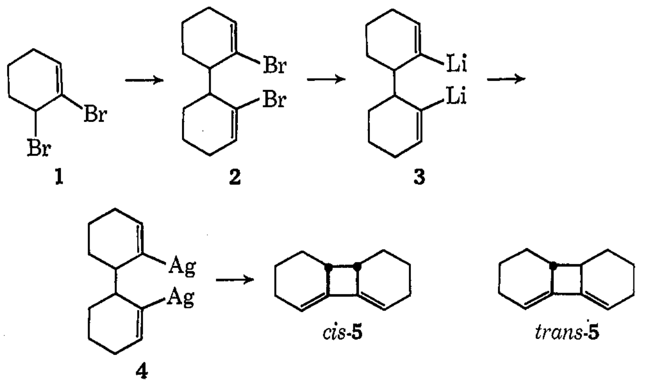
Treatment of either stereoisomer with excess *n*-butyllithium in ether at 25° gave the corresponding dilithium reagent **3**.[4] Reaction of the latter with anhydrous silver iodide at $-78°$ gave the disilver reagent **4**, which upon warming to room temperature decomposed to give tricyclo[6.4.0.$0^{2,7}$]dodeca-2,12-diene (**5**) in *ca.* 70% yield (based on **3**). As was anticipated, stereochemistry was retained; *meso*-**2** gave only *cis*-**5** and *dl*-**2** gave only *trans*-**5**.

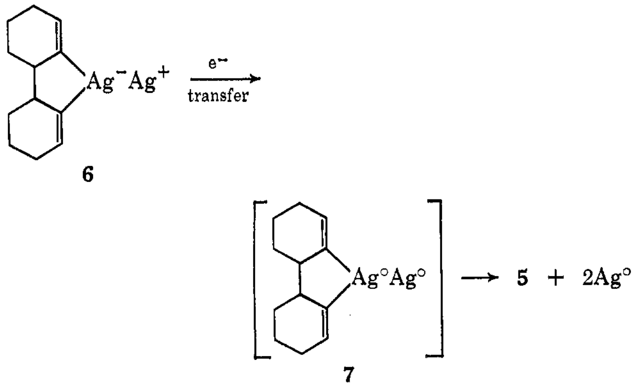
The structure of *trans*-**5** was established unequivocally by spectral and glc comparison with an authentic sample.[5] This structural assignment also establishes the configurational identity of the stereoisomers of **2** inasmuch as the coupling reaction, irrespective of mechanism, cannot affect the stereochemistry at the two centers in question (the 3,3′ positions of **2**).

The structure of *cis*-**5** is clearly confirmed by the mass, infrared, nmr, and ultraviolet spectra. The cis fusion can be deduced from the nmr spectrum since each of the tertiary allylic protons is deshielded by an adjacent trans C–C bond, causing a shift to δ 2.72, *ca.* 0.4 ppm downfield from the signal arising from the corresponding protons in *trans*-**5**.[6]

cis-Diene **5** is extremely reactive toward oxygen and it polymerizes readily when it is neat or in concentrated solutions. Examination of molecular models will show that *cis*-**5** must suffer substantial torsional strain which must be the cause of its high reactivity. Such strain is greatly diminished in *trans*-**5** by puckering of the four-membered ring.

The fact that dienes **5**, and the cis isomer in particular, can be obtained in good yield by this method[7] supports an absence[2b] of free radicals during the thermal decomposition of the disilver reagent since the high reactivity of *cis*-**5** clearly will make it serve as an efficient radical trap. The transition state for carbon–carbon bond formation thus must include at least one silver atom. Since coupling led to cyclization rather than polymerization, it appears likely that the carbon–carbon bond is formed between two ligands attached to a common silver atom. The disilver reagent formulated as **4** may in fact either be, or lead to, an "ate





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[1] (a) Supported in part by the National Science Foundation (GP8181); (b) National Institutes of Health Predoctoral Fellow, 1967–1970.

[2] (a) A. K. Holliday and R. E. Pendlebury, *J. Organometal. Chem.*, **7**, 281 (1967); (b) G. M. Whitesides and C. P. Casey, *J. Amer. Chem. Soc.*, **88**, 4541 (1966).

[3] J. Sonnenberg and S. Winstein, *J. Org. Chem.*, **27**, 748 (1962).

[4] Dienes **5** were formed in very low yields in the preparation of **3**.

[5] W. R. Moore and W. R. Moser, *J. Amer. Chem. Soc.*, **92**, 5469 (1970).

[6] The signal for the tertiary allylic protons of *trans*-**5** is not resolved from the signals arising from other protons, but it cannot fall below *ca.* δ 2.3, where a shoulder appears on a broad band centered at *ca.* δ 2.2.

[7] The excess butyllithium employed to facilitate formation of **3** apparently does not interfere in subsequent steps probably because the butylsilver, which is formed, is decomposed before the decomposition of **4** starts.

complex"[8] such as **6**. While **6** probably oversimplifies the total structure,[9] it represents the essential structural features. Based on the proposed intermediacy of **6**, a rational reaction pathway can be envisioned. With both alkenyl moieties attached to the same silver atom, electron transfer from the anion to the cation, possibly producing an intermediate **7**, should lead to a concerted breaking of the C–Ag bonds and forming of the C–C bond. Stretching of the C–Ag bonds in the sense of a homolytic cleavage must cause an overlap of the carbon orbitals resulting in bond formation.

Experimental Section[10]

2,3-Dibromocyclohexene (1).—6,6-Dibromobicyclo[3.1.0.]-hexane[3,5] (105 g, 0.44 mol) was added dropwise over 0.5 hr to a flask maintained at 155° to effect rearrangement to **1**. Distillation afforded 95 g (90%) of **1**, bp 70° (1.7 mm), $n^{25}\text{D}$ 1.5761 (lit.[3] $n^{25}\text{D}$ 1.5764).

2,2′-Dibromo-3,3′-bicyclohexenyl (2).—2,3-Dibromocyclohexene (95 g, 0.41 mol) was added rapidly to a suspension of 5.9 g (0.24 g-atom) of magnesium in 120 ml of refluxing ether. Refluxing was continued for 1 hr, water was added, and the ether layer was separated and dried (Na_2SO_4). Distillation afforded 35 g (57%) of **2**, bp 135° (0.4 mm), $n^{25}\text{D}$ 1.5780. Glc analysis (silicone nitrile XF-1150, 180°) indicated that the product was a 1:1 mixture of the *meso* and *dl* isomers. The ir and nmr spectra were superpositions of the spectra of the individual isomers reported below. The mass spectrum showed peaks at *m/e* 322, 320, and 318 in a 1:2:1 ratio (molecular ions of a dibromide).

Anal. Calcd for $C_{12}H_{16}Br_2$: C, 45.03; H, 5.04; Br, 49.92. Found: C, 44.87; H, 4.89; Br, 50.08.

The 1:1 mixture of *meso*- and *dl*-**2** was found to crystallize from methanol to give lead fractions enriched in the less soluble *dl* isomer. Repeated fractional crystallization eventually produced pure samples of each isomer as shown by glc analysis. From *ca.* 30 g of the 1:1 mixture, 3–4 g of each pure isomer was obtained (prior to recycling).

meso-**2**: mp 54–55°; ir (CCl_4) 3035, 1635, and fingerprint bands (not in *dl*) at 1240, 1200, 1040, 1020, 965 (broad), 950, 915, 860 cm^{-1}; nmr (CCl_4) δ 1.75 (~8 H, m), 2.0 (~4 H, m), 2.84 (2 H, m), 6.13 (2 H, m).

dl-**2**: mp 67.5–69.5°; ir (CCl_4) 3035, 1640, and fingerprint bands (not in meso) at 1250, 1210, 1108, 1030, 980, 940, 922, 870 cm^{-1}; nmr (CCl_4) δ 1.72 (~8 H, m), 2.0 (~4 H, m), 3.02 (2 H, m), 6.15 (2 H, m).

***cis*-Tricyclo[6.4.0.0^{2,7}]dodeca-2,12-diene (*cis*-5).**—A solution of 12 ml of 1.6 *M* *n*-butyllithium in hexane and 1.51 g (4.7 mmol) of *meso*-**2** in 45 ml of ether was stirred for 4 hr at room temperature. Analysis of an aliquot (the method is presented below) indicated a 65% yield of 2,2′-dilithio-3,3′-bicyclohexenyl (**3**). The dilithium reagent **3** was added to a suspension of 4.76 g (20 mmol) of anhydrous silver iodide in 40 ml of ether (to which 0.8 ml of 1.6 *M* *n*-butyllithium had been added to remove any traces of water) cooled to −78°. After being stirred for 25 min at −78°, the mixture was allowed to warm to room temperature. After 16 hr, the reaction mixture was filtered under nitrogen through Celite and the filtrate, diluted to 100 ml, was stored under nitrogen at −10°. In some instances, the reaction mixture was hydrolyzed and the ether layer was washed with water and dried (K_2CO_3) before storing. The yield of **5** was not changed.

Glc analysis (Carbowax 20M, 120–170°, using *n*-tridecane as in internal standard) established that *cis*-**5** was formed in 70% yield based on the dilithium reagent (46% from **3**). A small amount of 3,3′-bicyclohexenyl (2%) was found along with small amounts of several higher molecular weight materials which were not identified. Several repetitions of the reaction gave essentially the same overall yield of *cis*-**5**.

Pure *cis*-**5** was obtained by preparative glc (Carbowax 20M, 150° and silicone SE 30, 90°) with the collected material being stored at liquid nitrogen temperatures prior to spectral and analytical measurements: ir (CCl_4) 3020, 2930, 2880, 2860, 2830, 1670, 1645 (w), 1450, 1435, 1335, 1250, 1205, 1135, 1065, 935, 875 cm^{-1}; nmr (CCl_4) δ 0.8–1.9 (complex m, 8 H), 2.1 (broad m, ~4 H, $CH_2CH{=}C$), 2.72 (broad m, 2 H, $CH{=}CCH$), 5.40 (m, 2 H, $CH{=}C$); mass spectrum *m/e* (relative intensity) 39 (28), 65 (21), 67 (21), 77 (32), 79 (44), 81 (22), 91 (91), 104 (37), 105 (30), 115 (25), 117 (90), 118 (27), 119 (31), 131 (59), 132 (37), 145 (65), 160 (100, M$^+$); uv (hexane) λ_{max} 256 [log ϵ 4.15 (5)], sh 246 and 265 nm.

Anal. Calcd for $C_{12}H_{16}$: C, 89.94; H, 10.07. Found: C, 89.60; H, 10.20.

Attempts to obtain pure samples of *cis*-**5** by distillation led to extensive polymerization with formation of a nonvolatile white solid. The pure liquid diene (from glc) was found to polymerize readily under helium at room temperature. It is extremely reactive toward oxygen; initial attempts to obtain a mass spectrum led to a peak at *m/e* 192 (*cis*-**5** + O_2) and only a weak molecular ion peak at *m/e* 160.

Analysis of the dilithium reagent can be accomplished by quenching an aliquot with water and determining the yield of 3,3′-bicyclohexenyl by glc (Carbowax 20M, 120–170°) using *n*-tridecane as an internal standard. The amount of 3,3′-bicyclohexenyl formed in preparing the dilithium reagent, typically 2–3%, can be determined by quenching an aliquot with 1,2-dibromoethane followed by glc analysis. A small amount of methyllithium should be added to the dibromoethane immediately before use to ensure complete removal of traces of water or HBr. Very small amounts of **5** were formed during the preparation of **3**; the maximum yields were in the range of 2–3%. This material presumably is derived from coupling of the 2-lithio-2′-bromo intermediate which is a precursor to **3**.

***trans*-Tricyclo[6.4.0.0^{2,7}]dodeca-2,12-diene (*trans*-5).**—Using the same molar ratios of reactants employed in the preparation of *cis*-**5**, *dl*-**2** was converted into *trans*-**5** in overall yields of 41–45%. The product was identified by glc and infrared comparison with an authentic sample.[5]

The 1:1 mixture of *meso*- and *dl*-**2** similarly gave a 1:1 mixture of *cis*- and *trans*-**5** in essentially the same yields. On several glc columns employing different liquid phases (both polar and nonpolar), *cis*-**5** was found to have a retention time *ca.* 10–20% longer than that of *trans*-**5**.

Registry No.—*meso*-**2**, 28229-12-1; *dl*-**2**, 28229-13-2; *cis*-**5**, 28229-14-3; *trans*-**5**, 28229-15-4.

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[8] G. Wittig, *Quart. Rev., Chem. Soc.*, **20**, 191 (1966).

[9] The Ag$^+$ would probably be coordinated to the solvent and possibly halide ions and/or the ate complex **6** may be a part of a larger aggregate.

[10] Spectral measurements were determined with the following instruments: ir, Perkin-Elmer Model 237; nmr, Varian T-60; uv, Cary Model 14; mass spectra, Hitachi Perkin-Elmer RMU-6. Melting points are corrected and boiling points are not. All reactions were conducted under a nitrogen atmosphere.

A Convenient Synthesis of Alkyl-1,3,5-hexatrienes by Reaction of Dienyl Halides with 1,5-Diazabicyclo[4.3.0]non-5-ene[1]

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Most reported preparations of substituted 1,3,5-hexatrienes either yield mixtures or require several steps. The most common impurities from either acid-catalyzed or high temperature preparations are substituted 1,3-cyclohexadienes resulting from electrocyclic ring closure[2] and aromatics from dehydrogenation of the cyclic dienes.[3] Trienes free of these impurities may be obtained *via* a modified Hofmann elimination

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[2] C. W. Spangler and N. Johnson, *J. Org. Chem.*, **34**, 1444 (1969).

[3] C. W. Spangler, *ibid.*, **31**, 346 (1966).