## References and Notes

(1) This work was reported in part at 2nd IUPAC Symposium on Organic Synthesis, Jerusalem–Haifa, Sept 11–15, 1978. Synthesis and Reactivity of Compounds with Cyclobutane Ring(s). 11. For part 10 see D. Belluš, *J. Org. Chem.*, submitted for publication.
(2) R. W. Hoffmann, U. Bressel, J. Gehlhaus, and H. Häuser, *Chem. Ber.*, **104**, 873 (1971).
(3) (a) R. J. Cole, J. W. Kirksey, H. G. Cutler, B. L. Doupnik, and J. C. Peckhan, *Science*, **179**, 1324 (1973); (b) J. P. Springer, J. Clardy, R. J. Cole, J. W. Kirksey, R. K. Hill, R. M. Carlson, and J. L. Isidor, *J. Am. Chem. Soc.*, **96**, 2267 (1974).
(4) D. Belluš, H.-P. Fischer, H. Greuter, and P. Martin, *Helv. Chim. Acta*, **61**, 1784 (1978).
(5) J. W. Scheeren, R. J. F. M. Staps, and R. J. F. Nivard, *Recl. Trav. Chim. Pays-Bas*, **92**, 11 (1973).
(6) The cycloadditions of in situ formed ketenes HXC=C=O with **2** could not be a priori expected, since Hoffmann et al.[2] failed to obtain cyclobutanones on reacting **2** with dimethyl- and diphenylketene, respectively.
(7) **9** (X = Me) was prepared via addition of MeMgBr to diethyl squarate: (a) J. S. Chickos, *J. Am. Chem. Soc.*, **92**, 5749 (1970). For an approach to some 2-aryl-substituted compounds **9** via bromine oxidation of arylcyclobutenediones, which were, in turn, prepared by [2 + 2] cycloadditions of fluoroethylenes with arylacetylenes, see (b) E. J. Smutny, M. C. Caserio, and J. D. Roberts, *ibid.*, **82**, 1793 (1960); (c) A. H. Schmidt and W. Ried, *Synthesis*, 1 (1978).
(8) This requires 1.3–2.6 equiv of **1** if X = alkyl or dichlorovinyl group (reflux, 2–4 h) or 2.1 equiv if X = aryl group (room temperature, 4 h).
(9) H. Mayr and R. Huisgen, *Angew. Chem.*, **87**, 491 (1975).
(10) Compare, e.g., (a) E. Patton and R. West, *J. Am. Chem. Soc.*, **95**, 8703 (1973); (b) A. J. Fatiadi, *ibid.*, **100**, 2586 (1978).
(11) **1** (X = CH=CCl₂) (bp 48–54 °C (11 mm)) was prepared from the readily available (D. Borrmann and R. Wengler (to Bayer AG), German Patent 1 214 211 (1962); H. Ohse, R. Palm, and H. Cherdron, *Monatsh. Chem.*, **98**, 2138 (1967)) ketene chloral [2 + 2] cycloadduct i in 90% overall yield as shown.
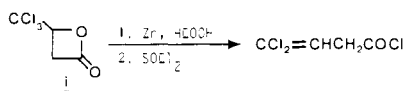
(12) E.g., chlorides of **9** with X = cyclohexyl, bp 100 °C (0.1 mm); with X = CH=CCl₂, mp 90.5–91 °C; with X = 4-CH₃OC₆H₄, mp 122–123 °C; and with X = 4-ClC₆H₄, mp 142–142.5 °C.
(13) Similar ¹³C NMR signal averaging was observed for squaric acid (**9**, X = OH) (W. Städeli, R. Hollenstein, and W. von Philipsborn, *Helv. Chim. Acta*, **60**, 948 (1977)), as well as for moniliformin (**9**, X = H) (H.-D. Scharf, H. Frauenrath, and W. Pinske, *Chem. Ber.*, **111**, 168 (1978)).

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Hypovalent Radicals. 3.[1] Chemical Reductions of Certain Diazo Compounds to Carbene Anion Radicals— Formation of (Fluorenylidene) disodium, a Carbene Dianion
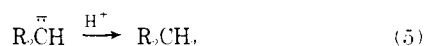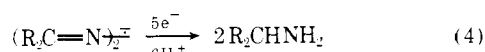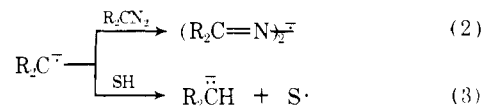
Sir:

We wish to report preliminary results of chemical reductions of diphenyldiazomethane (Ph_2CN_2) and 9-diazofluorene (FlN_2) which demonstrate that coupling of diaryl carbene anion radicals occurs under certain conditions. Other results

establish that the 9-fluorenyl anion (FlH^-) nucleophilically adds to the terminal nitrogen of FlN_2. This suggests that a similar addition of the carbene anion radical to the diazo compound is involved in azine anion radical formation, a principal reaction channel for Ar_2C^-· produced in these and electrochemical experiments.[1,2] The further reduction of fluorenylidene anion radical (Fl^-·) by sodium naphthalene (Na^+Naph^-·) in THF to the carbene dianion,(fluorenylidene)-disodium ($Fl^{-2}2Na^+$), is proposed to account for acid quenching studies on these reductions of FlN_2.

We have examined the reductions of Ph_2CN_2 and FlN_2 with Na^+Naph^-· in THF by slow (1 h) dropwise addition and rapid (~5-s addition time) syringe injection of the diazo compounds to excess reducing agent. The reactions were quenched by adding water shortly after the additions were complete. The conditions and products of these chemical reductions are listed in Table I. Benzophenone (($Ph_2C=N+_2$) and fluorenone azines (($Fl=N+_2$) are reduced by excess Na^+Naph^-· in THF quantitatively to the corresponding primary amines.[3]

In expt 1 and 2 (Table I) involving slow additions of Ph_2CN_2 to the reducing medium (Na^+Naph^-·, THF), we observed a small increase in the amount of diphenylmethane (Ph_2CH_2) produced by increasing the $[Na^+Naph^-·]/[Ph_2CN_2]$ ratio from 4 to 10. The low yield (17%) of Ph_2CH_2 (expt 2) was in contrast to the reduction FlN_2 under the same conditions (expt 4) where 40% fluorene (FlH_2) was obtained. The yields of the hydrocarbon products, Ph_2CH_2 and FlH_2, were attenuated when the THF solution of the diazo compound was syringe injected (addition time ~10 s) into the reducing medium (expt 3 and 5, Table I). The sequence of reactions considered to be in accord with this data is shown as eq 1–5.

$$R_2CN_2 \xrightarrow{e^-} [R_2CN_2^-] \longrightarrow R_2C^- + N_2 \quad\quad (1)$$

$$(R_2C=N+_2)^= \quad\quad (2)$$
$$R_2\ddot{C}H + S· \quad\quad (3)$$

$$(R_2C=N+_2)^= \xrightarrow[6H^+]{5e^-} 2R_2CHNH_2 \quad\quad (4)$$

$$R_2\ddot{C}H \xrightarrow{H^+} R_2CH_2 \quad\quad (5)$$

The variations in the product yields of both the hydrocarbon and amine as a function of the method of addition of the diazo compound to the reduction medium show that one of the reaction channels of the carbene anion radical involves coupling with the diazo compound. That this reaction *could* occur on the terminal nitrogen of the diazo compound was demonstrated in the following way. One equivalent of FlN_2 in THF was syringe injected into a THF solution of the 9-fluorenyl anion

Table I. Conditions and Products for the Chemical Reductions of Diazo Compounds Ph_2CN_2 and FlN_2

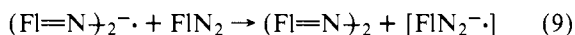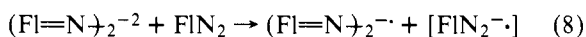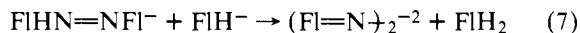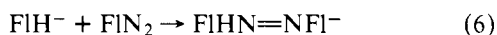| expt no.	substrate (mmol)	rate of addition	solvent	reducing agent (mmol)	products (% yields)[a,b]
1	Ph_2CN_2 (15.7)	slow[c]	THF[d]	Na^+Naph^-· (62.8)	PH_2CH_2 (13), Ph_2CHNH_2 (84)
2	Ph_2CN_2 (15.8)	slow[c]	THF[d]	Na^+Naph^-· (159)	Ph_2CH_2 (17), Ph_2CHNH_2 (85)
3	Ph_2CN_2 (10.4)	fast[e]	THF[f]	Na^+Naph^-· (52.2)	Ph_2CH_2 (4), Ph_2CHNH_2 (92)
4	FlN_2 (15.6)	slow[c]	THF[d]	Na^+Naph^-· (157)	FlH_2 (40), $FlHNH_2$ (53)
5	FlN_2 (11.3)	fast[e]	THF[f]	Na^+Naph^-· (112)	FlH_2 (12), $FlHNH_2$ (88)
6	FlN_2 (10.2)	fast[e]	NH_3[g]	Na (10.2)	($Fl=N+_2$ (79), $Fl=O$ (6), $Fl=Fl$ (4), $FlH—HFl$ (4)

[a] % yields are generally better than ±2% in duplicate experiments.   Yields of amines are corrected for known losses in the workup procedures.
[c] Slow, dropwise addition of R_2CN_2 to reducing solution.   [d] Na^+Naph^-· in 400 mL of THF (−10 °C), R_2CN_2 in 100 mL of THF; H_2O quench.
[e] Rapid syringe injection of R_2CN_2 to reducing solution.   [f] Na^+Naph^-· in 200 mL of THF (−10 °C), R_2CN_2 in 10 mL of THF; H_2O quench.
[g] 100 mL of $NH_3(l)$, FlN_2 in 10 mL of THF; reaction quenched with NH_4Cl.

(FlH⁻) (prepared from 1.2FlH₂ + C₆H₅Li in THF). Correcting for the excess of FlH₂ introduced, the products are (Fl=N+₂ and FlH₂ in a 2:1 ratio with 98% material balance. The steps which are considered to be involved are

$$FlH^- + FlN_2 \rightarrow FlHN{=}NFl^- \tag{6}$$

$$FlHN{=}NFl^- + FlH^- \rightarrow (Fl{=}N{+}_2{}^{-2} + FlH_2 \tag{7}$$

$$(Fl{=}N{+}_2{}^{-2} + FlN_2 \rightarrow (Fl{=}N{+}_2{}^{-\cdot} + [FlN_2{}^{-\cdot}] \tag{8}$$

$$(Fl{=}N{+}_2{}^{-\cdot} + FlN_2 \rightarrow (Fl{=}N{+}_2 + [FlN_2{}^{-\cdot}] \tag{9}$$

$$[FlN_2{}^{-\cdot}] \rightarrow N_2 + Fl^-{\cdot} \rightarrow products \tag{10}$$
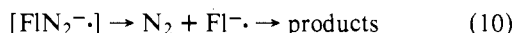
We believe that this result demonstrates nucleophilic attack by FlH⁻ on the terminal nitrogen of FlN₂ to give the conjugate acid of (Fl=N+₂⁻² (eq 6).[4] A second FlH⁻ is consumed to deprotonate FlHN=NFl⁻ (eq 7). Both (Fl=N+₂⁻² and (Fl=N+₂⁻· may reduce FlN₂ (eq 8 and 9), and Fl⁻· will produce azine and FlH₂ in a ratio dependent on the concentrate of FlN₂ available.
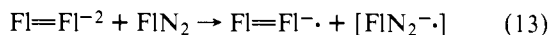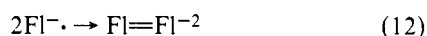
This result is also important in that it establishes a second pathway for azine formation in the reduction of diazo compounds. This sequence would involve reactions 3 and 6–10, and means that the yield of FlH₂ from the reduction of FlN₂ represents only a fraction of the carbene anion radicals partitioned via reactions 3 and 2. This point is significant in potential studies of reactions of carbene anion radicals with other reactant molecules.

In an effort to verify that the sequence of reactions from Fl⁻· → FlH₂ involved reactions 3 *followed* by 5,[1] FlN₂ was reduced by solvated electrons in liquid NH₃ (a poor H· donor). Owing to the poor solubility of FlN₂ in liquid NH₃, the diazo compound was dissolved in a minimum amount of THF and syringe injected into the reducing medium (1 equiv of electrons).[5] The products were (Fl=N+₂ (79%), fluorenone (Fl=O, 6%), and the dimers, 9,9'-bifluorenylidene (Fl=Fl, 4%) and 9,9'-bifluorenyl (FlH—HFl, 4%).

The presence of 9 vol. % of THF in this reduction allows for some H· abstraction by Fl⁻· (reaction 3) to occur. This may have been the source of the ketone, Fl=O, by the known reaction (eq 11),[6] if O₂ was present in the NH₄Cl quench of the reduction mixture.

$$FlH^- + O_2 \rightarrow Fl{=}O \tag{11}$$
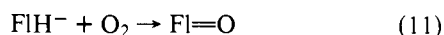
However, we believe that isolation of quantities of the two hydrocarbon dimers, Fl=Fl and FlH—HFl, is the result of a marked attenuation of reaction 3 in the medium allowing for the radical dimerization of Fl⁻· (reaction 12). Since the reduction potentials of Fl=Fl are essentially the same as those of (Fl=N+₂, electron transfer between Fl=Fl⁻² and FlN₂ (reaction 13) should occur readily. The equal amounts of the dimeric hydrocarbons could then be produced by reactions 14–16, or certain other reactions.

$$2Fl^-{\cdot} \rightarrow Fl{=}Fl^{-2} \tag{12}$$

$$Fl{=}Fl^{-2} + FlN_2 \rightarrow Fl{=}Fl^-{\cdot} + [FlN_2{}^{-\cdot}] \tag{13}$$

$$Fl{=}Fl^-{\cdot} + H^+ \rightarrow FlH{-}Fl{\cdot} \tag{14}$$

$$FlH{-}Fl{\cdot} + Fl{=}Fl^-{\cdot} \rightarrow FlH{-}Fl^- + Fl{=}Fl \tag{15}$$

$$FlH{-}Fl^- + H^+ \rightarrow FlH{-}HFl \tag{16}$$

In a further attempt to establish that Fl⁻· → FlH₂ involved the sequence of H· abstraction (eq 3) followed by protonation (eq 5), a reduction of FlN₂ with Na⁺Naph⁻· was carried out according to expt 4, Table I. Shortly after the addition was complete, D₂O (Merck, 99.5% *d*) was syringe injected into the reduction mixture followed by acidification by HCl–H₂O. After workup and sublimation of naphthalene and dihydro-
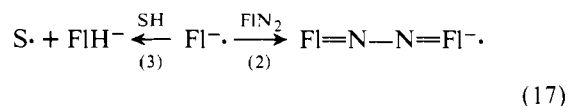
naphthalene, the purified fluorene (40% yield) was found to contain a large excess of deuterium at C-9 (5% FlH₂, 35% FlHD, and 60% FlD₂ by ¹H NMR, and 5% FlH₂, 38% FlHD, and 57% FlD₂ by ¹³C NMR).[8] Since it was possible that H–D exchange may have occurred during the D₂O quench and H⁺ acidification of the reduction mixture, the reduction was rerun and quenched by syringe injection (~10 s) with D₂O–CF₃CO₂D (large excess of acid). The analyses of fluorene showed its composition to be 5% FlH₂, 25% FlHD, and 70% FlD₂ by ¹H and 5% FlH₂, 33% FlHD, and 62% FlD₂ by ¹³C NMR spectroscopy.[8]

Reaction of FlH₂ with 6 equiv of Na⁺Naph⁻· in THF, followed by the D₂OCF₃CO₂D quench, gave a much smaller amount of excess deuterium in the fluorene (8% FlH₂, 72% FlHD, and 20% FlD₂ by ¹H NMR and 8% FlH₂, 72% FlHD, and 20% FlD₂ by ¹³C NMR).[8] To better approximate the concentrations and types of bases present compared with those of the FlN₂ reduction, 0.5 equiv each of FlH₂ and (Fl=N+₂ were added stepwise to 10 equiv of Na⁺Naph⁻· in THF. After the D₂O–CF₃CO₂D quench and workup, the ¹H and ¹³C NMR analyses of the recovered fluorene were the same as those above.[9]

If we assume in the reaction of FlH₂ + Na⁺Naph⁻· that only FlH⁻ was produced,[10] the 20% of FlD₂ generated serves as a reference for the amount of H–D exchange occurring in the D₂O–CF₃CO₂D quench of FlH⁻. This requires that we must still account for the 40–50% excess FlD₂ produced in the similar quench of the reduction products from FlN₂ + 10Na⁺Naph⁻·. Since a dibasic intermediate is required, we propose that this intermediate is the carbene dianion, Fl⁻²,

Fl⁻²
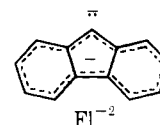
which is produced by further reduction of the carbene anion radical Fl⁻·.[11] Such requires that a third reaction channel (eq 17) for Fl⁻· be added to the two (eq 2 and 3) previously given, e.g.,

$$S{\cdot} + FlH^- \overset{SH}{\underset{(3)}{\longleftarrow}} Fl^-{\cdot} \overset{FlN_2}{\underset{(2)}{\longrightarrow}} Fl{=}N{-}N{=}Fl^-{\cdot}$$

$$\tag{17}$$

Using Sargent's suggestion that carbene anion radicals may be formed by Na⁺Naph⁻· reduction of geminate dihalides,[12] 9,9-dibromofluorene (FlBr₂) was reduced with 10 equiv of Na⁺Naph⁻· in THF. Quenching the reduction mixture with D₂O–CF₃CO₂D and isolation of the products gave a 90% yield of fluorene containing excess deuterium (4% FlH₂, 73% FlHD, and 23% FlD₂ by ¹H and 4% FlH₂, 67% FlHD, and 29% FlD₂ by ¹³C NMR spectroscopy).[8] While the ¹H NMR results showed no excess deuterium in the fluorene compared with that from FlH₂ + Na⁺Naph⁻·, the ¹³C NMR results indicated that ~9% of the starting FlBr₂ may have been trapped as Fl⁻². Using the latter results and a branching ratio of 1.0 for reactions 3 and 17 suggests that up to 18% of Fl⁻· was produced in this reaction. Thus, the preparation of Fl⁻· by reduction of FlBr₂ is relatively poor at best. This is not too surprising when we consider the number and types of reactive intermediates probable in the reduction of FlBr₂. Under these chemical reduction conditions, bimolecular dimer formation was obviously not a significant reaction channel.[12,13]

The variety of reactions (H· abstraction, addition to R₂CN₂, dimerization, and reduction) observed for Fl⁻· suggests to us that this carbene anion radical has a reasonable lifetime under these solution conditions. This supports our previous proposal

that the Fl⁻·/Fl: reversible redox couple was observed in the cyclic voltammetric reduction of FlN_2.[2] The chemical reductions of FlN_2 and $FlBr_2$ lead us to conclude that reduction of diazo compounds is the only efficient method presently available for producing these aryl carbene anion radicals in solution. As to the question of whether the reduction of carbene anion radicals → carbene dianions will be observed generally or will be strongly structure dependent, the answer must await the results of studies in progress.

References and Notes

(1) R. N. McDonald, J. R. January, K. J. Borhani, and M. D. Hawley, *J. Am. Chem. Soc.*, **99**, 1268 (1977).
(2) R. N. McDonald, K. J. Borhani, and M. D. Hawley, *J. Am. Chem. Soc.*, **100**, 995 (1978).
(3) Lithium metal reductively cleaves (Ph₂C=N+)₂ to Ph₂CHNH₂ (E. J. MacPherson and J. C. Smith, *Can. J. Chem.*, **48**, 1915 (1970)), while sodium and potassium give adducts which on hydrolysis yield *N*-benzhydrylbenzophenone hydrazone (*ibid.*, **48**, 1904 (1970)). See also H. Lund, *Acta Chem. Scand.*, **13**, 249 (1959), for the electrochemical reduction of benzalazine to the corresponding primary amines.
(4) The attack of FlH⁻ and Fl⁻· on the terminal N of FlN₂ supports the view that ethylidene anion radical reacts on the terminal N of N₂O in the gas phase: J. H. J. Dawson and N. M. M. Nibbering, *J. Am. Chem. Soc.*, **100**, 1928 (1978). Diazo compounds and N₂O are isoelectronic structures.
(5) The use of excess solvated electrons in the reduction of FlN₂ produced some azine reduction along with considerable saturated C–H's in the ¹H NMR spectrum of the product. This was probably the result of Birch reduction of the fluorene nucleus.
(6) (a) G. A. Russell, A. J. Bemis, E. J. Geels, E. G. Janzen, and A. J. Moye, *Adv. Chem. Ser.*, No. **75**, 174–202 (1968); (b) G. A. Russell, *IUPAC Int. Symp. Org. Chem. 1966*, 185–206 (1967).
(7) Both of these hydrocarbon dimers were indicated to be present as trace products by GLC in other reductions of FlN₂.
(8) Percent compositions from ¹H NMR use the value of FlH₂ determined for this species by ¹³C NMR using relative integrals of two different aryl C's and C₉–H₂ of authentic FlH₂ and of the deuterated sample. In the ¹³C NMR analysis known relative integrals of these aryl C's to the triplet of authentic FlHD were used to determine the percent of this species. The amount of FlD₂ was by difference.
(9) We thank Mr. Kevin Reid for this result.
(10) A. Lagu, H. B. Mark, and J. R. Jezorek, *J. Org. Chem.*, **42**, 1063 (1977), and references therein.
(11) In our gas-phase studies of related compounds in a flowing afterflow apparatus, we find no evidence for the parent molecular anion either by thermal electron attachment in the flow or at very low ionization energy (nominal 3.3 eV) directly in the mass spectrometer chamber. Thus, the process appears to be dissociative electron attachment in the gas phase with such reactants, and the same is indicated to be true in solution.[1,2]
(12) G. D. Sargent, C. M. Tatum, and S. M. Kastner, *J. Am. Chem. Soc.*, **94**, 7174 (1972). (b) G. D. Sargent, C. M. Tatum, and R. P. Scott, *ibid.*, **96**, 1602 (1974).
(13) See Y.-J. Lee and W. D. Closson, *Tetrahedron Lett.*, 1395 (1974), for similar reductions of benzhydryl and benzyl halides.

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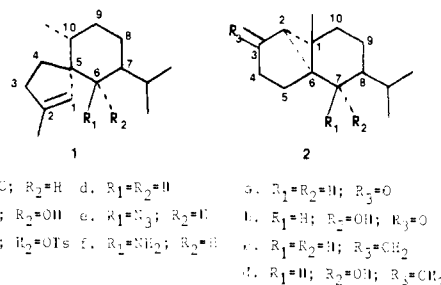*Manhattan, Kansas 66506*
Received June 5, 1978

Total Synthesis of (−)-Axisonitrile-3. An Application of the Reductive Ring Opening of Vinylcyclopropanes

Sir:

Recently, Sica and co-workers isolated the isonitrile sesquiterpene (+)-axisonitrile-3 from the marine sponge *Axinella cannabina* and determined that it has a novel spiro[4.5]decane ring system by X-ray crystallography.[1] We report the total synthesis of (−)-axisonitrile-3 (**1a**) from (+)-dihydrocarvone. This synthesis establishes that the absolute configuration of the natural product is opposite to that shown in structure **1a**.

It is well known that reductive cleavage of 1-methyltricyclo[4.4.0.0²,⁶]decan-3-ones provides a general method of

a. R₁=NC; R₂=H   d. R₁=R₂=H
b. R₁=H; R₂=OH   e. R₁=N₃; R₂=H
c. R₁=H; R₂=OTs   f. R₁=NH₂; R₂=H

a. R₁=R₂=H; R₃=O
b. R₁=H; R₂=OH; R₃=O
c. R₁=R₂=H; R₃=CH₂
d. R₁=H; R₂=OH; R₃=CH₂

synthesis of spiro[4.5]decanone derivatives.[2] Our recent work on the lithium/liquid ammonia cleavage of the tricyclodecanone **2a** demonstrated that opening of the cyclopropane ring to the corresponding spiro ketone occurred exclusively with inversion of configuration at the β carbon (C-1).[2c] We have now found that the related vinylcyclopropanes (cf. **2c,d**) undergo reductive ring opening with lithium in ethylamine to produce spiro[4.5]decenes such as **1b,d**. Again, exclusive inversion of configuration at C-1 was observed. This suggested that an *exo*-methylene compound of the type **2** having a substituent at C-7 which would allow elaboration to an isonitrile group would serve as a useful precursor of **1a**. From a number of possibilities, we selected a route which utilized the 7α-hydroxy compound **2d**.

The known ketol **3**,[3] which was prepared in 50% yield by annulation of (+)-dihydrocarvone[4] with methyl vinyl ketone followed by catalytic hydrogenation of the double bond of the isopropenyl group, was the starting material for the synthesis.

a. 1,2-Single Bond
b. 1,2-Double Bond
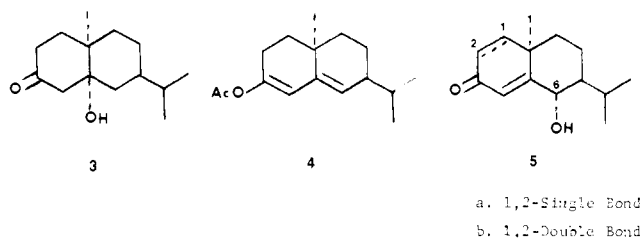
Treatment of **3** with acetic anhydride containing a catalytic amount of sulfuric acid (12 h, 25 °C) gave the dienol acetate **4** (NMR δ_{Me_4Si} (CCl₄) 0.88 (d, J = 6 Hz, 3 H), 0.91 (d, J = 6 Hz, 3 H), 1.02 (s, 3 H), 2.03 (s, 3 H), 5.33 (d, J = 3 Hz, 1 H), 5.62 (d, J = 2 Hz, 1 H)) in 80% yield. Oxidation of **4** with *m*-chloroperbenzoic acid in 20:1 isopropyl alcohol–water[5] (4 h, 25 °C) gave a mixture of products containing 42% of the enone derived from dehydration of the ketol **3** and 56% (96% based upon unrecovered enone) of an ~6:1 mixture of the hydroxy enone **5a** and its 6β epimer. Hydroxy enone **5a**[6] (mp 116.0–118.0 °C (from benzene–hexane); NMR δ_{Me_4Si} (CCl₄) 0.93 (br m, 6 H), 1.40 (s, 3 H), 3.75 (s, 1 H), 4.20 (br s, 1 H), 5.67 (s, 1 H)) was isolated by chromatography by Florisil. The 6β epimer was not obtained completely pure, but the crude material showed NMR δ_{Me_4Si} (CCl₄) 0.92 (br m, 6 H), 1.25 (s, 3 H), 4.53 (br s, 1 H), 6.05 (d, J = 1.5 Hz, 1 H).

Conversion of **5a** to its MIP (methoxyisopropylidene) derivative,[7] followed by the introduction of a 1,2 double bond using the phenylselenenylation–selenoxide elimination procedure,[8] gave **5b**[6] (mp 92.5–93.5 °C (from benzene–hexane); NMR δ_{Me_4Si} (CCl₄) 0.83 (d, J = 5 Hz, 3 H), 0.93 (d, J = 5 Hz, 3 H), 1.41 (s, 3 H), 4.38 (br s, 1 H), 5.93 (dd, J = 1.6, 10 Hz, 1 H), 5.97 (d, J = 1.6 Hz, 1 H), 6.57 (d, J = 10 Hz, 1 H)) in 85% yield. Irradiation of a 0.04 M solution of **5b** in anhydrous dioxane at room temperature gave a single crude tricyclodecenone[9] (NMR δ_{Me_4Si} (CCl₄) 0.81 (d, J = 6 Hz, 3 H), 0.93 (d, J = 6 Hz, 3 H), 1.17 (s, 3 H), 4.03 (d, J = 7 Hz, 1 H), 5.73 (d, J = 6 Hz, 1 H), 7.33 (d, J = 6 Hz, 1 H)) which was catalytically reduced (Pd/C, ethanol) to the hydroxy ketone **2b**[6] (mp 70.5–72.0 °C (from hexane); NMR δ_{Me_4Si} (CCl₄) 0.78 (d, J