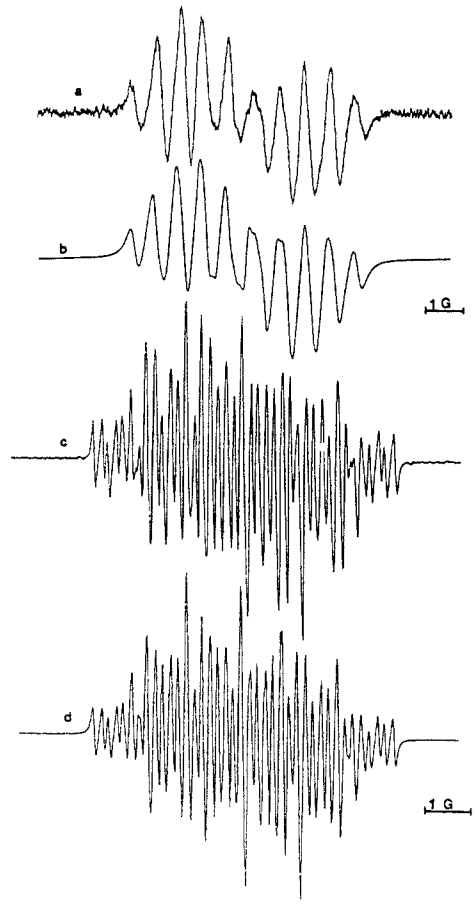


Figure 3. Experimental (a) and simulated (b) ESR spectra for $1^{\bullet-}$ in CH_2Cl_2 solution. (c) and (d) are the corresponding experimental and simulated spectra in the presence of a 1 M aqueous $LiClO_4$.

Transport was monitored for the unreduced neutral ligand for a period of 2 h, during which no appreciable Li^+ was detected in the receiving phase, see segment a in Figure 2. At that point a potential of −1.0 V (vs. a Ag wire reference, r in Figure 1) was applied at the working electrode (w) while the auxiliary electrode (a) was kept in the compartment separated by the low-porosity fritted-glass filter (5 in Figure 1). The initial current observed was $\simeq$1 mA and increased as a function of time to $\simeq$1.5 mA, where it remained constant throughout the experiment. During this period reduction at the working electrode resulted in the development of a very intense red color, which was quickly distributed exclusively over the organic phase. Oxidation at the auxiliary electrode did not produce a color change; the pale yellow color of the original solution persisted.

As indicated by segment a in Figure 2, transport by the neutral carrier is negligible in the time interval studied. As the electrolysis progressed and the intensity of the red color increased so did the amount of Li^+ detected until, after 1.5 h, the time dependence was approximately linear, segment c in Figure 2. The calculated transport rate from the slope of this segment is 2.2×10^{-7} mol/h. These results indicate an "all-or-nothing" situation where *no* transport is observed for the neutral ligand and significant transport when reduced.

Some observations deserve mention. If electrolysis is stopped, the red color slowly fades, initially to an intense orange and, eventually, after several hours, to pale yellow. Figure 2 shows a second set of data points (d and e) obtained for the same solution after allowing it to remain overnight in the transport cell without nitrogen or stirring. All the points except the first were obtained during a second electrolysis of the solution during which the intense red color returned to the organic phase. Note again that after an induction period the Li^+ concentration increases until it changes almost linearly with time. The transport rate determined from this limiting slope is 1.8×10^{-7} mol/h. This value coincides well with the previous one, the small difference probably due to some overnight decomposition.

In order to establish if the red and orange colors observed could be identified with the Li^+-$1^{\bullet-}$ ion pair, ESR measurements were conducted under identical conditions as those used for the transport experiments. The same CH_2Cl_2 solution used above was placed in an electrolytic ESR cell with Hg as the working electrode. Electrolysis was conducted directly in the ESR cavity as described previously.[3] The resulting spectrum, exhibiting relatively broad lines, is shown in Figure 3a. The simulation shown in Figure 3b was obtained by using the parameters $a_{2H} = 0.53$, $a_{1H} = 0.66$, $a_{1H} = 1.07$, $a_{1H} = 1.19$, and $a_{1H} = 1.40$ G and a line width of 0.22 G. Addition of a 1 M $LiClO_4$ water solution on top of the CH_2Cl_2 phase directly in the ESR cell resulted in the appearance of the spectrum in Figure 3c, with a concomitant color change from red to orange. The simulation for Figure 3c is given as Figure 3d and was obtained using the following parameters: $a_{2H} = 1.19$, $a_{1H} = 0.21$, $a_{1H} = 0.71$, $a_{1H} = 0.87$, $a_{1H} = 1.43$, and $a_{Li^+} = 0.33$ G and a line width of 0.07 G. The observed metal splitting is clear proof of strong ionic association between the anion radical and the cation.

These results indicate that $1^{\bullet-}$ is infinitely better as a transporter for Li^+ than **1**, an expected result based on the previously reported binding enhancement factor measured in acetonitrile solution by cyclic voltammetry (10^5).[2c] Estimating a binding constant of $\simeq$10 for **1** with Li^+, binding by the reduced ligand should be in the optimum range for transport as reported by Izatt ($\simeq 10^6$).[4]

Attempts are currently under way to improve the transport efficiency by not only enhancing the binding strength of the ligand upon reduction at the donor interphase but by returning to the low binding neutral state at the receiving interphase using electrochemical oxidation.

Acknowledgment. We warmly thank the National Institutes of Health, GM 33940, for support of this work.

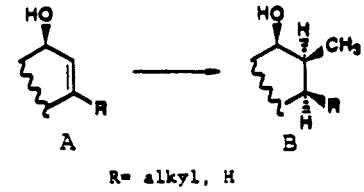
(3) Delgado, M.; Echegoyen, L.; Gatto, V. J.; Gustkowski, D. A.; Gokel, G. W. *J. Am. Chem. Soc.* **1986**, *108*, 4135.
(4) Lamb, J. D.; Christensen, J. J.; Oscarson, J. L.; Nielsen, B. L.; Asay, B. W.; Izatt, R. N. *J. Am. Chem. Soc.* **1980**, *102*, 6820.

Stereospecific Reductive Methylation via a Radical Cyclization-Desilylation Process

Gilbert Stork* and Michael J. Sofia

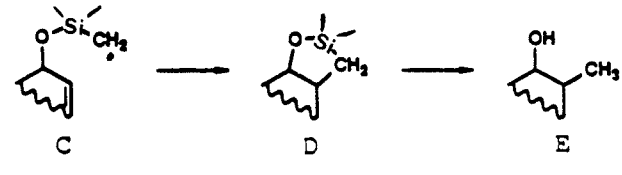
Department of Chemistry, Columbia University
New York, New York 10027
Received April 28, 1986

We wish to report a method, schematized in A → B, for the addition of the elements of methane to the double bond of an allyl alcohol.

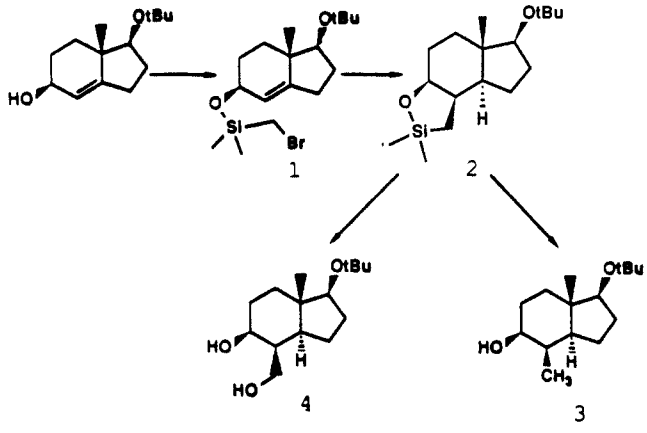


R= alkyl, H

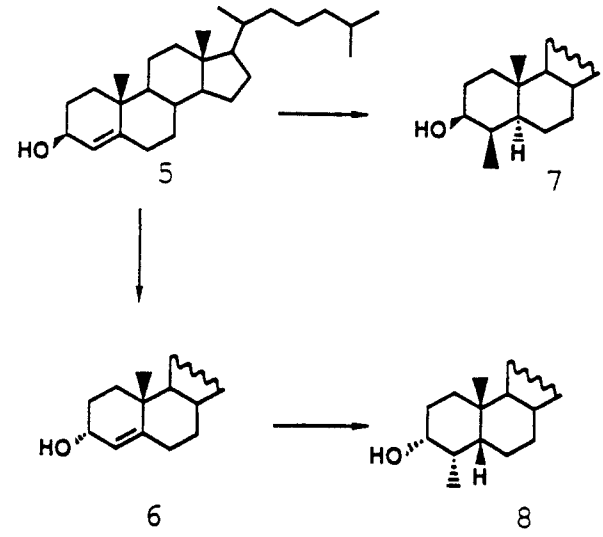
The importance of the process is that it leads to the introduction of a methyl group regiospecifically next to the allylic hydroxyl and stereospecifically cis to it. This is illustrated by C → D → E.



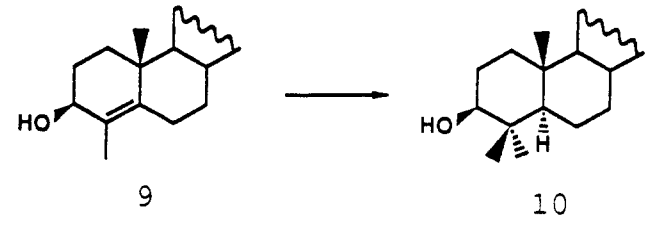
We have already described the transformation 1 → 2 in connection with the control of ring junction stereochemistry.[1a] The present report is prompted by two developments which considerably expand the scope of the method: First, we have now shown that the yield of the radical cyclization of bromide **1** to the cyclic siloxane **2**[1a] must be at least 90% because the yield of crystalline diol **4** obtained by direct oxidation of the mixture from the cyclization of **1**[1b] is actually 88% overall from **1**.[2,3] Second, we have now found that it is possible to do the transformation D → E (cf. 2 → 3) directly: Removal of solvent after the completion of the radical cyclization step (1 → 2), followed by treatment with potassium *tert*-butoxide (5 equiv) in dimethyl sulfoxide at room temperature,[4] produced the methylindanol **3**, mp 93.5–94 °C, in an overall yield of 60% from the silyl ether **1**.[5]



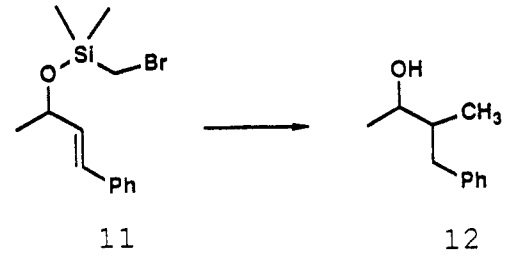
Similarly, very good overall yields of methylation[6] were achieved from 4-cholesten-3β-ol (**5**) as well as from its 3α-isomer **6**.[7] The known 4β-methyl-5α-cholestan-3β-ol (**7**)[8,9] and the so far unknown 4α-methyl-5β-cholestan-3α-ol (**8**), mp 45–46 °C,[10,11] were thus obtained respectively in 75% and 80% overall yields for the cyclization–hydrolysis process.



Under stoichiometric tin hydride conditions, cyclization of **6** to **8** led to recovery of some uncyclized starting material, after the eventual hydrolysis (cyclized/uncyclized 2.3:1). This problem, presumably a result of less favorable geometry of approach of the intermediate radical to the 4,5-double bond in the 3α- than in the 3β-epimer, was essentially solved by slowing down hydrogen transfer to the initial radical (cf. C) either by using the catalytic tin hydride process[13] (9:1 cyclized to uncyclized) or (of more theoretical than practical interest) even further (24:1) by the use of triphenylgermane.[14] The addition of a methyl to form a quaternary center was more difficult but still gave 4,4-dimethyl-5α-cholestan-3β-ol (**10**)[8] from 4-methyl-4-cholesten-3β-ol (**9**) in >40% yield.



The method can also be used, although less dramatically, in acyclic systems: the silyl ether **11**[15] was thus converted to the alcohol **12** (anti/syn >4:1).



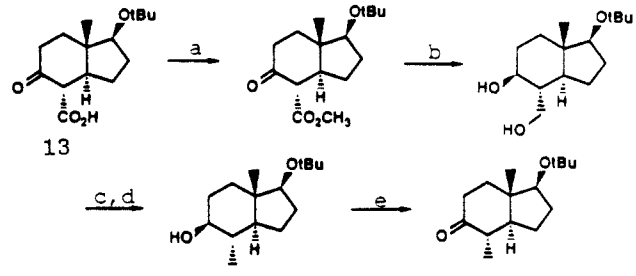
(1) (a) Stork, G.; Kahn, M. *J. Am. Chem. Soc.* **1985**, *107*, 500. (b) The radical cyclizations in the present paper were effected by either the stoichiometric or catalytic[13] process.

(2) By treatment by the method of Tamao et al. (Tamao, K.; Ishida, N.; Kumada, M. *J. Org. Chem.* **1983**, *48*, 2120) using KF/DMF/30% H_2O_2 on the crude cyclization (AIBN PhH, 80 °C) product from **1**.

(3) The cyclic silyl ether **2** can be purified by flash chromatography on silica gel; however, because of severe streaking (possible decomposition), the pure substance could be obtained, at best, in only 40–45% yield.

(4) This appears to be the first example of the protiodesilylation of a γ-hydroxysilane (the presumed intermediate from a cyclic siloxane such as **2**). It has been shown previously that α- and certain β-hydroxysilanes can be readily protiodesilylated: Hudrlik, P. F.; Hudrlik, A. M.; Kulkarni, A. K. *J. Am. Chem. Soc.* **1982**, *104*, 6809 and references cited therein.

(5) The stereochemistry of alcohol **3** was confirmed by oxidation (NaOCl/AcOH) and epimerization (NaOMe/MeOH) to the corresponding 4α-methylhydrindan-3-one. This proved identical with a sample prepared independently from the keto acid **13** (Hajos, Z. G.; Parrish, D. R. *J. Org. Chem.* **1973**, *38*, 3239) as follows: (a) CH_2N_2; (b) $NaBH_4$–CH_3OH; (c)



Bu_3P,Ph_2S_2 in CH_3CN; (d) Raney Ni, ethanol, reflux; (e) NaOCl, acetic acid.

(6) In the steroid cases, desilylation was carried out at 100 °C.

(7) Made from the 3β-isomer via the Mitsunobu inversion (Mitsunobu, O. *Synthesis* **1981**, *13*, 1).

(8) (a) Iida, T.; Tamura, T.; Miura, N.; Matsumoto, T. *Steroids* **1977**, *29*, 453. (b) Tamura, T.; Wainai, T.; Mashimo, K.; Matsumoto, T. *Chem. Phys. Lipids* **1977**, *19*, 169. (c) Iida, T.; Mitsuko, K.; Ishikawa, T.; Tamura, T.; Matsumoto, T. *Org. Magn. Reson.* **1982**, *19*, 228.

(9) The corresponding 1,3-diol, the previously unknown 4β-hydroxymethyl-5α-cholestan-3β-ol, mp 209–210 °C, HRMS, calcd 418.3810, found 418.3797, was obtained in 78% yield from the (bromomethyl)dimethylsilyl ether of **5** (cf. **1** → **4**).

(10) HRMS, calcd 402.3862, found 402.3879. NMR ($CDCl_3$) δ 1.05 (J = 7.3 Hz, C_4-methyl). The structure was rigorously established by oxidation to the ketone, followed by epimerization (KO-*t*-Bu/THF/reflux) to the known[12] 4β-methyl-5β-cholestanone.

(11) In the preparation of 4α-methyl-5β-cholestan-3α-ol a 6% yield of 4α-methyl-5α-cholestan-3α-ol[12] was also obtained.

(12) Mazur, Y.; Sondheimer, F. *J. Am. Chem. Soc.* **1958**, *80*, 5220. See also ref 8a,b.

(13) Stork, G.; Sher, P. M. *J. Am. Chem. Soc.* **1986**, *108*, 303.

(14) Johnston, L. J.; Lusztyk, J.; Wayner, D. D. M.; Abeywickreyma, A. N.; Beckwith, A. L. J.; Scaiano, J. C.; Ingold, K. U. *J. Am. Chem. Soc.* **1985**, *107*, 4594.

(15) Nishiyama, H.; Kitajama, T.; Matsumoto, M.; Itoh, K. *J. Org. Chem.* **1984**, *49*, 2298.

In conclusion, we draw attention to the fact that our (hydro)methylation method can, in favorable cases, produce any of the four possible arrangements of a methyl and a hydrogen adjacent to the original carbinol center. This is illustrated by considering the ketones derived from **7** and **8**, respectively: It is a consequence of their mode of formation that they both have an axial 4-methyl group. Equilibration via the ketone thus makes available the other two (equatorial) epimers. It follows that in systems related to **1**, **5**, and **6**, in which the unsaturated β-center is part of a ring junction, control of the ring junction stereochemistry[1a] can be achieved independently of that of the stereochemistry at the center adjacent to the hydroxyl group.

Acknowledgment. We thank the National Institutes of Health and the National Science Foundation for financial support of this work.

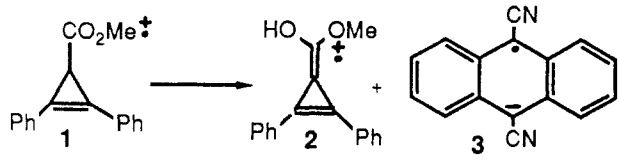
Electron Transfer Photochemistry of Aromatic Imides and Phenylcyclopropane. Radical Anion–Radical Cation Cycloaddition

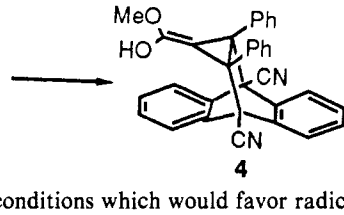
Paul H. Mazzocchi,* Cathleen Somich, Michael Edwards, Tina Morgan, and Herman L. Ammon

Department of Chemistry and Biochemistry University of Maryland, College Park, Maryland 20742

Received June 16, 1986

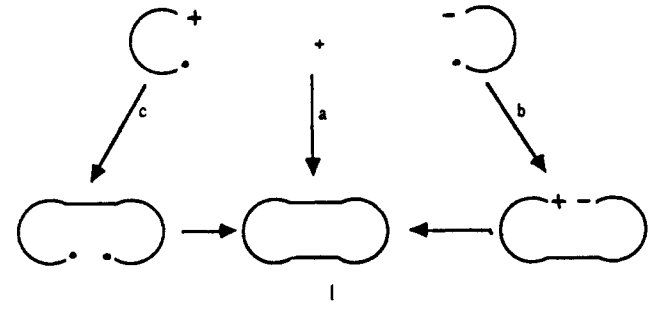
The most obvious reaction of a photochemical electron transfer generated radical anion–radical cation pair is cycloaddition which could occur concertedly (path a) or by the two-step processes outlined in Scheme I (paths b, c). However, there are no clear examples of this cycloaddition[1] presumably because competing processes such as reverse electron transfer and proton transfer from the radical cation to the radical anion[2] dominate the cycloaddition process. Perhaps the closest example of this reaction is the formation of **4** by the addition of the methyldiphenylcyclopropene carboxylate radical cation (**1**), after preliminary enolization (**2**), to the dicyanoanthracene radical anion (**3**).[3]



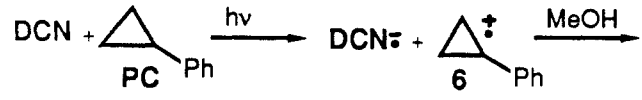


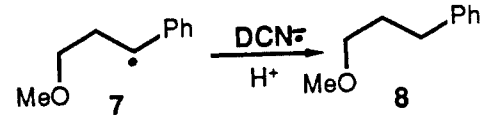
We desired to establish conditions which would favor radical cycloaddition; however, it appeared that it would be difficult to design factors that would affect a concerted process and that the process initiated by radical coupling to a zwitterion (path a) would probably result in intramolecular proton transfer as it has in other cases.[2d-f] However, nucleophilic addition of the radical anion to the radical cation (path c) would afford a biradical which should undergo the desired coupling analogous to the Paterno–Buchi and related reactions.[4] We chose *N*-methylphthalimide (NMP) as the electron acceptor since previous investigations[5] indicated that its reactions were localized to the carbonyl group and that the carbonyl oxygen was likely to have nucleophilic properties.

Scheme I

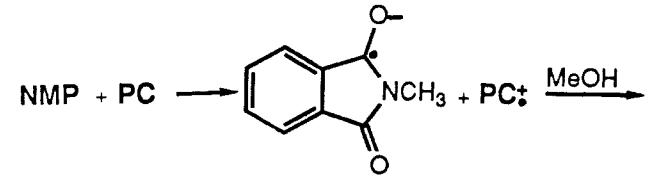


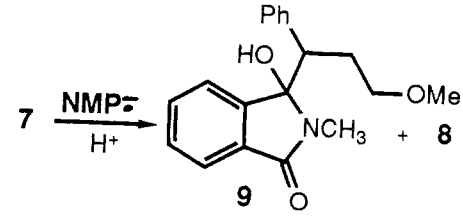
Phenylcyclopropanes are effective donors in photochemical electron transfer reactions[6-9] and evidence indicates that the cyclopropane bond remains intact in the radical cation.[6-10] The susceptibility of phenylcyclopropane (PC) radical cations to nucleophilic attack has been demonstrated[6,7] by the addition of methanol to **6** with subsequent cleavage to **7** which is then reduced by **3** and protonated to give **8**.





Irradiation of NMP and PC in methanol afforded the ether **8** and the hydroxy lactam **9**, establishing that an electron transfer process has taken place and that NMP cannot compete as a nucleophile with methanol.





(1) Mattes, S. L.; Farid, S. *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, **1983**; Vol. 6, p 233.
(2) (a) Hub, W.; Schneider, S.; Dorr, F.; Oxman, J. D.; Lewis, F. D. *J. Am. Chem. Soc.* **1984**, *106*, 708. (b) Lewis, F. D. *Acc. Chem. Res.* **1979**, *12*, 152. (c) Lewis, F. D.; Ho, T.-I. *J. Am. Chem. Soc.* **1977**, *99*, 7991. (d) Maroulis, A. I.; Arnold, D. R. *J. Chem. Soc., Chem. Commun.* **1979**, 351. (e) Arnold, D. R.; Wong, P. C.; Maroulis, A. J.; Cameron, T. S. *Pure Appl. Chem.* **1980**, *52*, 2609. (f) Mazzocchi, P. H.; Klingler, L. *J. Am. Chem. Soc.* **1984**, *106*, 7567.
(3) Farid, S.; Brown, K. A. *J. Chem. Soc., Chem. Commun.* **1976**, 564. Brown-Wensley, K. A.; Mattes, S. L.; Farid, S. *J. Am. Chem. Soc.* **1978**, *100*, 4162.
(4) For reviews, see: Arnold, D. R. *Adv. Photochem.* **1968**, *6*, 301. Wilson, R. M. *Org. Photochem.* **1985**, *7*, 339.
(5) Mazzocchi, P. H.; Khachik, F. *Tetrahedron Lett.* **1983**, 1879. Mazzocchi, P. H.; Khachik, F. *Tetrahedron Lett.* **1981**, 4186.
(6) Rao, V. R.; Hixson, S. S. *J. Am. Chem. Soc.* **1979**, *101*, 6458.
(7) Mizuno, K.; Ogawa, J.; Otsuji, Y. *Chem. Lett.* **1981**, 741.
(8) Mizuno, K.; Ogawa, J.; Kogano, H.; Otsuji, Y. *Chem. Lett.* **1981**, 437.
(9) Wong, P. C.; Arnold, D. R. *Tetrahedron Lett.* **1979**, 2101.
(10) Roth, H. D.; Schilling, M. L. M.; Schilling, F. C. *J. Am. Chem. Soc.* **1985**, *107*, 4152. Roth, H. D.; Schilling, M. L. M. *J. Am. Chem. Soc.* **1981**, *103*, 7210. Roth, H. D.; Schilling, M. L. M. *J. Am. Chem. Soc.* **1980**, *102*, 7958.

0002-7863/86/1508-6828$01.50/0