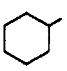
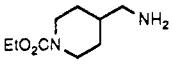
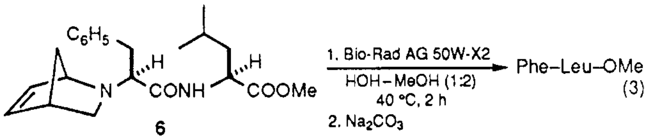
Table II. Acid-Catalyzed Retro Aza Diels–Alder Reactions[a]

amine	time, h	temp, °C	% yield[b]
$CH_3(CH_2)_4CH_2NH_2$	5.0	73	97[e]
	7.5	73	94[e]
$H_2NCH_2(CH_2)_4CH_2NHCO_2Et$	3.5	73	87
	1.25	71	91
Leu-OMe	1.0	73	98[e]
Phe-OMe[c]	1.5	45	93
Ser-OMe	1.5	73	87[e]
Ala-Leu-OMe	1.0	73	82
Leu-Leu-Leu-OMe[d]	2.0	70	82
Phe-Phe-Phe-OMe[d]	1.5	45	86

[a] All reactions were conducted 0.17 M in methanol-water (2:1) employing 3.0 wt equiv of Bio-Rad AG 50W-X2, 200–400 mesh, unless stated otherwise. [b] Isolated yields. [c] 2.5 wt equiv of ion-exchange resin were employed. [d] 2.0 wt equiv of ion-exchange resin were employed. [e] Isolated as the hydrochloride salt.

200–400 mesh, ion-exchange[3] resin at 40 °C. After cooling to ambient temperature, the resin was washed with hexanes and neutralized with 10% aqueous sodium carbonate solution. Extraction with ethyl acetate provided L-phenylalanyl-L-leucine methyl ester in 80% yield without any racemization.[4] It is important to note that the success of this heterocycloreversion process is highly dependent upon the percentage of crosslinking in the resin. In our initial study conducted with an 8% crosslinked resin (Dowex 50X8-200), results were disappointing. For example, exposure of 6 to 2 wt equiv of Dowex 50X8-200 using the conditions cited above in eq 3 gave rise after 5 h to only a 47% yield of Phe-Leu-OMe.



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(3)

We anticipate that the mildness and efficiency of the procedures detailed above for the unmasking of primary amines will render the 2-azanorbornene structural unit as a useful new protecting group for primary amines.[5]

Acknowledgment. This investigation was supported by a grant from the National Science Foundation. We thank Heidi Berven for experimental assistance during the early stage of this work.

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[3] The resin was washed sequentially with 1.0 N hydrochloric acid, deionized water (until pH 7.0), and methanol followed by air-drying prior to use.

[4] Any racemization is less than the detection limit which is estimated at 0.06–0.07% (Dewey, R. S.; Schoenewaldt, E. F.; Joshua, H.; Paleveda, W. J., Jr.; Schwam, H.; Barkemeyer, H.; Arison, B. H.; Veber, D. F.; Denkewalter, R. G.; Hirschmann, R. *J. Am. Chem. Soc.* **1968**, *90*, 3254.

[5] For the protection of primary amines, see: Greene, T. W. *Protective Groups in Organic Synthesis*; John Wiley and Sons: New York, 1981. Djuric, S.; Venit, J.; Magnus, P. *Tetrahedron Lett.* **1981**, *22*, 1787. Weinreb, S. M.; Demko, D. M.; Lessen, T. A.; Demers, J. P. *Ibid.* **1986**, *27*, 2099. Overman, L. E.; Okazaki, M. E.; Mishra, P. *Ibid.* **1986**, *27*, 4391.

Photochemical 1,3-Oxygen-to-Carbon Migrations. An Efficient, High-Yield Route to Protected Spirodienones

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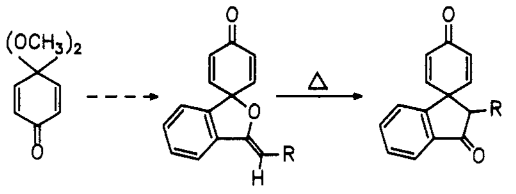
Summary: Irradiation of ethylene ketals of spiro *p*-quinol vinyl ethers in the presence of piperylene affords protected 2,5-cyclohexadienones in high quantum and chemical yields via a 1,3-oxygen-to-carbon migration.

Many standard methods for carbon–carbon bond formation are not applicable to the construction of quaternary centers in complex organic molecules. The thermal 1,3-oxygen-to-carbon rearrangement of *p*-quinol vinyl ethers is the key step in a carbonyl-to-quaternary carbon transformation described earlier, e.g., 1 → 3.[1] However, selective chemical transformations of the carbonyl groups in 3 could be difficult. In addition, molecules having sensitive functionality may not be stable at the temperature (130–160 °C) required for rearrangement.[1] We report herein that the photochemical 1,3-oxygen-to-carbon migration in these systems at room temperature gives spirocyclic dienone ketals having differentiated carbonyl groups with high chemical and quantum yields.

The photochemistry of the vinyl ether moiety has not been extensively studied. Two primary photochemical processes of ethyl vinyl ether are[2] (1) formation of ethylene and acetaldehyde and (2) formation of ethyl and vinyloxy radicals. No products resulting from a 1,3-oxygen-to-carbon rearrangement were reported.[2] The results from the irradiation of substituted α-(benzyloxy)styrenes with a low-pressure mercury lamp were somewhat more encouraging: β-phenylpropiophenones were formed with quantum yields in the range 0.04–0.11.[3] A triplet excited



1 2 3

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[1] Wang, S.; Morrow, G. W.; Swenton, J. S. *J. Org. Chem.* **1989**, *54*, 5364–5371.

[2] Murad, E. *J. Am. Chem. Soc.* **1961**, *83*, 1327.

[3] Izawa, Y.; Ogata, Y. *J. Org. Chem.* **1970**, *35*, 3192.

[4] A representative irradiation is described below. These reactions can be performed in either methylene chloride or benzene. Comparable results were obtained in several systems using either a 450-W Hanovia medium-pressure source (Corex filter) or the reactor described below as light sources. A solution of **4b** (1.0 g, 4 mmol) and piperylene (16 mL) in benzene (60 mL) was placed in eight Pyrex test tubes. After nitrogen was bubbled through the tubes for 5 min, they were sealed with a neoprene stopper and irradiated for 2.5 h with 12 RPR-3000 Å lamps in a Rayonet photochemical reactor at room temperature. The combined irradiation mixture was concentrated, and the crude product was filtered through silica gel (1 × 12 cm column, 20% Et_2O/petroleum ether as eluant). The product **5b** (0.97 g, 97%) was obtained as a clear oil, showing spectroscopic properties identical to those reported previously.[1]

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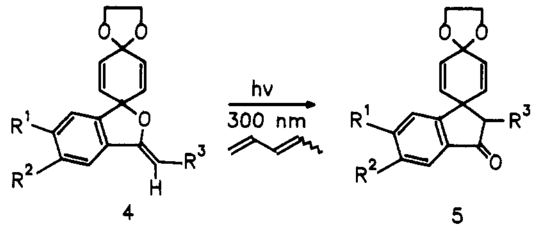
Table I. The Photochemical Conversion 4 → 5[4]



4	5, % yield
a: R^1, R^2 = R^3 = H	82
b: R^1, R^2 = H; R^3 = CH_3	96
c: R^1, R^2 = H; R^3 = C_6H_5	96
d: R^1, R^2 = H; R^3 = 4-CH_3-C_6H_4	87
e: R^1, R^2 = H; R^3 = 4-CH_3O-C_6H_4	98
f: R^1, R^2 = OCH_2O; R^3 = H	72

state was suggested as being responsible for the rearrangement on the basis of quenching of the reaction by oxygen. However, the isolated yield (20%) from preparative irradiation of the material—40% when corrected for recovered starting material—made the process of little value in synthesis.

Our preliminary irradiation studies of **4a** using 2537-Å light were also discouraging: a complicated reaction mixture resulted with no major product. However, since product **5a** also has ultraviolet absorption at 2537 Å, secondary photoreactions of **5a** could have been responsible for the complex product mixture under these conditions. Photoactivated aryl ketones cross rapidly from the singlet to the triplet state, suggesting that the secondary photochemistry of **5a** was occurring from the triplet state. If the **4a** → **5a** conversion were occurring in the singlet excited state, addition of a triplet quencher to the reaction mixture would reduce the problem of further photochemistry of **5a**. Indeed, irradiation of **4a** in the presence of 0.4 M piperylene gave a much cleaner reaction mixture and allowed isolation of **5a** in 50% yield. A final improvement, using a 3000-Å source for excitation and piperylene to function as a triplet quencher led to **5a** in 82% isolated yield. The conditions optimized for the **4a** → **5a** transformation allowed the related transformations outlined in Table I to be effected in excellent isolated yields. The structures of **5a**–**e** were confirmed by acid-catalyzed hydrolysis to the known dienones[1] in high yield.

The potential of this photochemistry in forming quaternary carbon–carbon bonds in highly functionalized systems is illustrated by the **4g** → **5g** transformation. Thus, irradiation of **4g** in the presence of piperylene afforded the expected β-methoxy ketone which was not purified, but rather was converted to **5g** via elimination of methanol on florisil.[5]

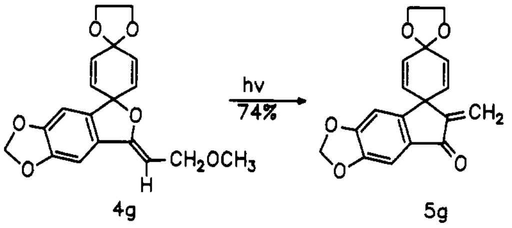


Table II. Quantum Yields[7] **for 4b → 5b and 2b → 3b in Methylene Chloride**

reaction	irradiation	quantum yield[a]
4b → **5b**	direct (300 nm)	0.40[b]
4b → **5b**	sensitized (350 nm)	<0.05[c]
4b → **5b**	quencher (0.44 M piperylene)	0.49[d]
2b → **3b**	direct (300 nm)	0.98[e]
2b → **3b**	sensitized	<0.02[f]

[a] Average of two determinations for appearance of product at <10% conversion of starting material; estimated error ± 10%. [b] [**4b**] = (3–4) × 10^{-3} M. [c] [**4b**] = 5.4 × 10^{-3} M; [Ph_2CO] = 1.8 × 10^{-2} M. [d] [**4b**] = 4.5 × 10^{-3} M; [piperylene] = 0.42 M. [e] [**2b**] = (3–5) × 10^{-3} M. [f] [**2b**] = 5.4 × 10^{-3} M; acetone (276 nm), acetophenone (320 nm), and Michler's ketone (350 nm) were employed as sensitizers using the indicated excitation wavelength.

The results from quantum yield determinations (Table II) show that the **4** → **5** reaction occurs with high efficiency. In addition, the quantum yield for the benzophenone triplet (E_T = 68.6 kcal/mol) sensitization of **4b** → **5b** is <0.05,[6] establishing that the triplet state of **4b** rearranges very inefficiently to **5b**. Attempts to conduct the **4b** → **5b** conversion preparatively using benzophenone as sensitizer resulted in low conversion to product, even on extended irradiation. Furthermore, 0.44 M piperylene (E_T = 59 kcal/mol) did not quench the **4b** → **5b** reaction, although this experiment is less meaningful since the rate constant for triplet decay of **4b** is not known. In contrast to the suggestion that α-(benzyloxy)styrenes undergo rearrangement in the triplet state, these systems rearrange primarily via singlet states. Thus, the high yield of product **5** at complete conversion of **4** under the conditions noted above results primarily from piperylene quenching the photochemical reactions of **5** with little effect on the **4** → **5** process. The photochemistry described above allows an efficient high-yield preparation of spirodienone ketals **5**.

An interesting and unexpected result was obtained from irradiation of the unprotected 2,5-cyclohexadienone, **2b**. Irradiation of 2,5-cyclohexadienones usually results in rapid, efficient (Φ = 0.5–0.85)[9] rearrangement to bicyclo[3.1.0]hex-3-en-2-ones. Thus, we expected minimal preparative value of irradiations akin to the **2b** → **3b** reaction due to problems associated with the secondary reactions of **3b**.[10] Preparative irradiation of **2b** gave **3b** in high yield (82%), despite the fact that **3b** absorbed appreciable amounts of irradiation during the reaction. Indeed, irradiation of **3b** at 3500 Å[11] showed that it was remarkably stable to irradiation,[12] establishing the reason for the high yield in the **2b** → **3b** transformation. The results of quantum yield determinations collected in Table II indicate that this reaction occurs primarily in the singlet state with near unit efficiency.

The results presented herein establish a high-yield procedure for conversion of a quinone monoketal to a protected 2,5-cyclohexadienone under extremely mild

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(5) The elimination was effected by stirring an ethyl acetate solution of the crude β-methoxy compound with 10 times its weight of florosil for 24 h at 45 °C.

(6) At these concentrations of benzophenone and **4b**, the benzophenone captured >95% of the incident irradiation, and energy transfer from benzophenone triplet to **4b** was calculated to be >90% efficient. Triplet energies are taken from: Murov, S. L. *Handbook of Photochemistry*; Marcel Decker Inc.: New York, 1973; pp 3–27.

(7) Quantum yield measurements were performed using a Bausch and Lomb Monochrometer as described earlier.[8]

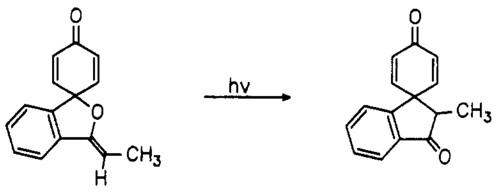
(8) Burdett, K. A.; Shenton, F. L.; Yates, D. H.; Swenton, J. S. *Tetrahedron* **1974**, *30*, 2057.

(9) For a recent investigation of 2,5-cyclohexadienone photochemistry and a listing of quantum yields and rate constants for rearrangement of these compounds, see: Zimmerman, H. E.; Lamers, P. H. *J. Org. Chem.* **1989**, *54*, 5788.

(10) For 2,5-cyclohexadienone rearrangements of preparative value and references to related work, see: Schultz, A. G.; Lavieri, F. P.; Macielag, M.; Plummer, M. *J. Am. Chem. Soc.* **1987**, *109*, 3991.

(11) A Rayonet photochemical reactor using RPR-3500 Å lamps was used as the light source.

(12) The dienone **3b** does react to give products upon extended irradiation. However, the efficiency of this reaction is substantially lower than the **2b** → **3b** conversion.



2b 3b

conditions. Since the dienone carbonyl group of **3** is protected as a ketal, selective chemistry of the indanone portion of the molecule should be facilitated. The success of the **4** → **5** reaction derives from selective quenching of the secondary photochemistry of the product by piperylene. In contrast, the unexpected photochemical stability of the 2,5-cyclohexadienone product accounts for the high-yield **2b** → **3b** reaction. We defer discussion on the relatively high photochemical stability of **3b** relative to other simple 2,5-cyclohexadienones. However, reactions analogous to **2b** → **3b** would complement the earlier described thermal route to spirodienones since the photochemical reaction can be effected at room temperature.[13]

Acknowledgment. We acknowledge partial support from the National Science Foundation.

Supplementary Material Available: ^{1}H NMR spectra of **5a–g** and **3b** and the ^{13}C NMR spectrum of **5g** (9 pages). Ordering information is given on any current masthead page.

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(13) All compounds showed IR and ^{1}H NMR spectra in agreement with the assigned structures and showed exact mass measurements within 3 millimass units of calculated values. Compounds **5a,b** were colorless oils, and the remaining products showed the following melting points: **5c**, 111–112 °C; **5d**, 97–99 °C; **5e**, 113–116 °C; **5f**, 191–191.5 °C; **5g**, 188–189 °C.

Hydroboration with Boron Halides and Trialkylsilanes

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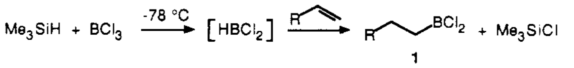
Received January 26, 1990

Summary: Mixtures of alkenes and trialkylsilanes added to boron trichloride at –78 °C result in quantitative hydroboration, presumably via dichloroborane, to alkyldichloroboranes, which with trialkylsilanes at 25 °C hydroborate alkenes to dialkylchloroboranes.

Dichloroborane was prepared from boron trichloride and hydrogen and shown to be an effective hydroborating agent 30 years ago,[1] though the high-temperature reaction and rapid quench required would be cumbersome for laboratory use. More recently dichloroborane has been prepared as etherate or dimethyl sulfide complexes, which can be dissociated with boron trichloride to hydroborate olefins, though the reactions are slow.[2] Direct reaction of methylnaphthylphenylsilane with boron trichloride has yielded diborane and the halosilane with retention of configuration at silicon,[3] and other reactions of haloboranes with silanes have yielded diborane,[4] but no hydrohaloborane products have ever been noted.

We have now found that mixing trialkylsilanes, boron trichloride, and alkenes neat or in pentane results in rapid, quantitative hydroboration of the alkene to the corresponding alkyldichloroborane (1), presumably via dichloroborane as an intermediate. Results are summarized in Table I.



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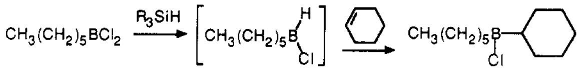
Trimethylsilane was added to 1-hexene and boron trichloride at –78 °C, the mixture was transferred via cannula to an NMR tube kept at –78 °C, and the 64-MHz ^{11}B NMR spectrum was taken within 5 min. The formation of 1-hexyldichloroborane (**1a**) (δ 62.0)[5] [lit.[6] RBCl$_2$ δ 61–64] was already complete.[7] Triethylsilane and tributylsilane are similarly effective, but the trialkylsilyl chlorides have high enough boiling points to complicate separation from **1**. Boron tribromide can be used in place of boron trichloride to generate alkyldibromoboranes.

Trialkylsilanes reduce **1** at 25 °C to alkylchloroboranes. For example, **1a** with cyclohexene and trimethylsilane in a few minutes (or tributylsilane more slowly) shows a few percent conversion to **2** (^{11}B NMR δ 42, broad), which disappears as 1-hexylcyclohexylchloroborane (**3**) forms during ~2 h.[8]



1a 2 3

With 2 mol of trialkylsilane, cyclohexyldichloroborane is converted to cyclohexylborane dimer, ^{11}B NMR δ 23.7 [lit.[9] (RBH$_2$)$_2$ δ 22–24],[5] ^{1}H coupled: broad d (J = 105 Hz), bridge H couplings not resolved.

The preferred procedure for reaction of acid-sensitive alkenes with dichloroborane or dibromoborane is to mix the silane and alkene first. Addition of an equimolar mixture of 1-hexyne and trimethylsilane to boron trichloride at –78 °C yielded only 1-hexenyldichloroborane (**4**) and no detectable 1,1-bis(dichloroboryl)hexane (**5**).

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(5) External boron trifluoride etherate reference.

(6) Brown, H. C.; Sikorski, J. A. *Organometallics* **1982**, *1*, 28–37.

(7) The rapidity was further demonstrated by layering diethylsilane on top of 1-hexene/BCl$_3$ in a 5-mm NMR tube encased in a 14-mm tube at –98 °C. After 5 min the reactants remained unmixed, BCl$_3$ δ 47, but after one inversion of the tube and return to the –98 °C bath in 2–3 s, the ^{11}B NMR within 1 min showed only **1a**, δ 62.

(8) Generation of **2** in the absence of alkene yielded R$_2$BCl (^{11}B δ 78.3), B$_2$H$_5$Cl (for NMR data see ref 12), B$_2$H$_6$, and other unidentified products. However, **1a** + cyclohexene led to **3** [50-MHz ^{13}C NMR δ 14.1, 22.7, 24.6, 26.8, 27.4, 28.1, ~28 (broad, obscured by sharp peaks, B*C*), 31.8, 32.1, 37.7 (broad, B*C*')], which may have contained ≤5% di-*n*-hexylchloroborane [δ 14.1, 22.7, 24.6, 29.4 (broad, B*C*), 31.9, 32.0] and ≤5% dicyclohexylchloroborane [δ 26.7, 27.2, 27.8, 36.4 (broad, B*C*)].

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