Graduate School of the University of Minnesota for financial support.

Registry No. 1, 117310-05-1; 1·DCHA, 117310-06-2; 2, 45234-12-6; 2·DCHA, 40044-22-2; 3, 19746-37-3; 4A, 117310-03-9; 4B, 117310-04-0; 5, 117310-07-3; ClC(O)SCl, 2757-23-5; MeNHPh, 100-61-8; MeOC(O)SCl, 26555-40-8; BOC-Val-OH, 13734-41-3; H-Cys-OH, 52-90-4; 2-mercaptopyridine, 2637-34-5.

Pressure Effect on the Product Distribution in Competing Reactions: Formation of a Bis Diels–Alder Adduct via an Aromatizable Intermediate

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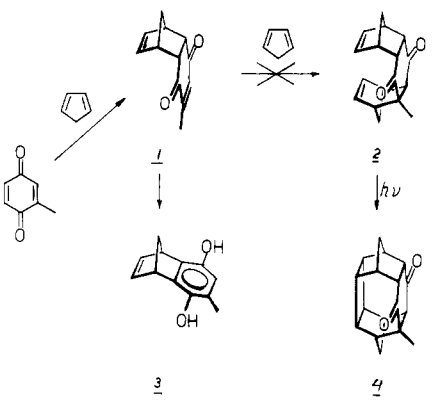
Received June 30, 1988

The exceptionally large accelerating effect of pressure on the Diels–Alder reaction has long been known,[2] and this phenomenon has been exploited both for mechanistic[3] and for synthetic[4] purposes. While the availability of very extensive listings of activation volumes[5] makes the choice of further such applications of pressure a simple matter indeed, it is often less obvious what the effect of compression will be in the case of competing reactions, and we begin to address that concern here: any additional tools in the manipulation of the relative rates of desired conversions and side reactions are of obvious value to the synthetic chemists.

In the construction of many polycyclic cage compounds such as **4**, a 2-fold Diels–Alder reaction can be an indispensable tool; however, side reactions may intervene after the first step. In the sequence shown in Scheme I, for example, aromatization of **1** to give **3** may interfere with the formation of **2**. This side reaction has been shown to be promoted by either acidic or basic impurities.[6] It can be avoided by the use of well-purified **1**, however, even then, no **2** is formed.

We reasoned that the second-stage cycloadditions would be accelerated more by compression than by the proton transfers required for enolization, *and* that the relative rates of these two reactions under ambient conditions should be sufficiently similar that the former might, if needs be, overtake the latter at high pressure.

Scheme I

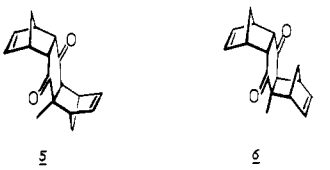


Results and Discussion

The experimental results confirm this assessment. Compression of a solution of methyl-*p*-benzoquinone and excess cyclopentadiene in toluene at 75–80 °C to 700–800 MPa leads to an excellent yield of bisadducts. The conversion is low (20%) because the competing diene dimerization is also accelerated; we therefore use a procedure of several cycles of compression, pressure release, and diene replenishment. After the conversion has reached about 60%, the reaction is stopped as the growing dimer concentration begins to pose purification problems.

HPLC analysis showed the presence of two products in a 4:1 ratio with very similar R_f values; ^{13}C NMR spectra of this mixture confirmed that both were stereoisomeric bisadducts, but the configurations could not immediately be assigned. In the hope of obtaining solid derivatives, we attempted to prepare semicarbazone derivatives, but no reaction occurred under the usual conditions.[7] Once again, the application of high pressure was expected to be helpful as the activation volumes for the related acyl transfer reactions are large and negative, particularly for hindered reactions;[5] indeed, both isomers did form semicarbazones at 800 MPa. The crystals obtained were not suitable for X-ray diffraction purposes, however.

The search for separation procedures was eventually rewarded with substantial quantities of both isomers. Irradiation experiments failed to produce any evidence for the formation of cage ketone **4**, leading us to doubt that isomer **2** was formed at all. Indeed, the configurations of the major and minor products were proved to be *endo-anti-endo* (**5**) and *endo-anti-exo* (**6**), respectively. The steric factor is evidently decisive in directing the second molecule to the convex face of **1**. The proofs proceeded as follows.



Reduction of the major and minor isomers by means of sodium borohydride–cerium(III) chloride[8,9] gave a hydroxy ketone in each case in which the hydroxyl groups originated from the less hindered carbonyl groups. Oxidation

(1) (a) At Stony Brook (S.S. present address: E. R. Squibb and Sons, P.O. Box 191, New Brunswick, NJ 08903-0191). (b) At Denton. (c) At Washington. (d) At Krakow.

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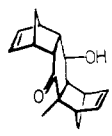
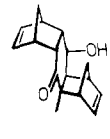
with pyridium chlorochromate regenerated the original bisadducts, hence the structural integrity of the diketones was preserved in the reduction. Both products 7 and 8 yielded crystals suitable for diffraction purposes.



7



8

In conclusion, while our hopes to generate compound 2 were not fulfilled, our study shows that high pressure can be used to alter the competition between two chemical processes at a branching point decisively.

Experimental Section

2-Methylpentacyclo[10.2.1.1^{5,8}.0^{2,11}.0^{4,9}]hexadeca-6,13-diene-3,10-dione (5). A 20-mL syringe (open plunger, sealed needle) containing 2 g of *endo*-4-methyltricyclo[6.2.1.0^{2,7}]undeca-4,9-diene-3,6-dione[10] (1) and 4 mL of freshly distilled cyclopentadiene dissolved in 9 mL of toluene was suspended in a high-pressure vessel[11] at 75 °C and pressurized to 800 MPa. After 3 h, the pressure was released and 2 mL of additional diene was drawn into the syringe; after mixing, it was repressurized. This procedure was repeated once more, and the mixture was left under pressure overnight. After removal of solvent, the residue was chromatographed (36 mm vs 40 cm column, silica gel, petroleum ether–ethyl acetate) to give, in succession, the diene dimer, an unidentified yellow impurity, the bisadducts (1.2 g, 60%), and 1. The bisadduct mixture was dissolved in 6 mL of ether and kept cold overnight to give 0.9 g of white crystals consisting of 96% 5; crystallization from ether gave an analytical sample with mp 104–5 °C. ^{1}H NMR[12] ($CDCl_3$): δ 1.20 (m, 4 H), 1.30 (d, 1 H), 1.50 (d, 1 H), 1.70 (d, 1 H), 2.50 (s, 1 H), 2.85 (m, 3 H), 3.25 (br s, 1 H), 3.40 (br d, 2 H), 6.08 (t, 1 H), 6.16 (m, 1 H), 6.25 (t, 2 H). ^{13}C NMR: ($CDCl_3$) δ 25.8 (q), 47.0 (d), 47.6 (d), 47.9 (t), 49.1 (t), 50.8 (d), 52.0 (d), 53.6 (d), 55.5 (s), 56.2 (d), 60.0 (d), 134.9 (d), 136.5 (d), 137.3 (d), 137.6 (d), 213.3 (s), 215.2 (s). Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.37; H, 7.50.

Hydroquinone 3 was obtained as the principal product at high pressure if impure 1 was used. ^{1}H NMR ($CDCl_3$): δ 2.07 (s, 3 H), 2.89 (m, 2 H), 4.08 (s, 1 H), 4.16 (s, 1 H), 6.70 (m, 2 H), 7.02 (s, 1 H), 7.31 (s, 1 H). ^{13}C NMR ($CDCl_3$): δ 16.27 (q), 47.12 (d), 47.38 (d), 69.14 (t), 115.65 (d), 123.63 (d), 134.43, 137.48, 142.69, 143.19, 143.49, 144.88.

Semicarbazone of Bisadduct. The mixture of 5 and 6 (200 mg) was heated to 75 °C overnight in solution in 6 mL of ethanol together with 1 g of semicarbazide hydrochloride and 1.1 g of sodium acetate in 10 mL of water at 800 MPa. A solid product was obtained. ^{1}H NMR spectroscopy showed that both isomers had been converted, and mass spectra showed that both derivatives were monosemicarbazones. The use of pure 5 gave the corresponding semicarbazone in 80% yield; it was crystallized from ethanol, mp 153–4 °C.

Reduction of 5 with $NaBH_4$–$CeCl_3$. A solution of 5 (51 mg, 0.20 mmol) in ethanol (2 mL) was cooled to 0 °C and cerium(III) chloride heptahydrate[8,9] (100 mg) and sodium borohydride (10 mg, 0.25 mmol) were added. The resulting mixture was stirred for 30 min. The reaction was quenched with 10% aqueous sodium carbonate (0.2 mL). After filtration, extraction with ethyl acetate (2 × 10 mL), drying (anhydrous sodium sulfate), and evaporation, the residue obtained was crystallized from ethyl acetate–hexane; pure 7 (48 mg, 92%) was obtained as a colorless solid, mp 126–128 °C. IR (KBr): 3400 (br, s), 1675 cm^{-1} (s). ^{1}H NMR ($CDCl_3$): δ 1.20 (s, 3 H), 1.30 (m, 4 H), 1.60 (m, 2 H), 2.00 (dt, J_1 = 3.0 Hz, J_2 = 11.0 Hz, 1 H), 2.50 (m, 2 H), 2.95 (m, 1 H), 3.15 (br s, 2 H), 3.35 (dd, J_1 = 6.0 Hz, J_2 = 11.0 Hz, 1 H), 6.10 (m, 4 H). ^{13}C NMR ($CDCl_3$): δ 24.65 (q), 44.55 (d), 45.00 (d), 45.14 (d), 46.95 (d), 48.39 (d), 51.38 (t), 53.72 (t), 54.17 (s), 54.50 (d), 71.73 (d), 134.49 (d), 134.68 (d), 135.53 (d), 137.15 (d), 217.30 (s). Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.71; H, 7.84.

Reduction of a ca. 1:1 Mixture of 5 and 6 with $NaBH_4$–$CeCl_3$. A sample of material containing roughly equal quantities of 5 and 6 (100 mg, 0.40 mmol) in methanol (4 mL) was reduced as above with cerous chloride heptahydrate (200 mg) and sodium borohydride (19 mg, 0.50 mmol) to give a mixture of keto alcohols 7 and 8 (90 mg, 89%). This mixture was further purified via column chromatograph [silica gel (60 g), dimensions 2.5 × 50 cm]; the column was eluted sequentially with hexane (1 L) and with 30:1 hexane–ethyl acetate (600 mL) to give 8 (40 mg). Further elution with the 30:1 mixture (300 mL) afforded a mixture of 7 and 8 (35 mg); subsequent use of 10:1 mixed solvent (200 mL) afforded pure 7. Recrystallization of 8 (ethyl acetate–hexane) afforded a colorless solid, mp 124 °C. IR (KBr) 3330 (br, s), 1685 cm^{-1} (s). ^{1}H NMR ($CDCl_3$): δ 0.8 (s, 3 H), 1.3 (m, 6 H), 1.75 (br s, 1 H), 2.1 (m, 1 H), 2.5 (m, 1 H), 3.0 (m, 2 H), 3.2 (br s, 1 H), 3.45 (dd, J_1 = 6.0 Hz, J_2 = 11.0 Hz, 1 H), 6.2 (m, 4 H). ^{13}C NMR ($CDCl_3$): δ 22.77 (q), 40.91 (d), 44.75 (d), 45.27 (d), 45.40 (d), 45.98 (d), 48.45 (t), 52.87 (t), 53.98 (d), 54.43 (d), 56.52 (s), 71.67 (d), 134.94 (d), 136.11 (d), 136.95 (d), 139.36 (d), 217.92 (s). Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.69; H, 7.81. Found: C, 79.68; H, 8.17.

Oxidation of 8. To a solution of keto alcohol 8 (10 mg, 39 mmol) in methylene chloride (2 mL) was added pyridinium chlorochromate (PCC, 30 mg, 139 mmol). The mixture was stirred at room temperature for 5 h and then diluted with ether (50 mL). The reaction mixture was passed through a 4-cm silica gel column. The eluant was concentrated in vacuo to afford pure 6 (80%) as a colorless microcrystalline solid, mp 96–97 °C. ^{1}H NMR: δ 0.85 (s, 3 H), 1.37 (br s, 1 H), 1.45 (m, 1 H), 1.77 (m, 1 H), 1.84 (d, 1 H), 2.94 (s, 1 H), 3.08 (s, 1 H), 3.25 (m, 2 H), 3.35 (m, 2 H), 3.51 (s, 1 H), 6.05 (br s, 1 H), 6.15 (br s, 1 H), 6.22 (br s, 1 H), 6.36 (br s, 1 H). ^{13}C NMR ($CDCl_3$): δ 24.19, 46.18, 47.20, 47.95, 48.06, 51.65, 52.28, 53.25, 55.44, 55.67, 60.67, 135.98, 136.19, 137.45, 138.77, 212.56, 215.37. Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.31; H, 7.09. Found: C, 80.68; H, 7.19.

Oxidation of 7. Oxidation of keto alcohol 7 with PCC as described above afforded material (85%) that was identical in all respects with 5.

X-ray Experiment. Compound 7, $C_{17}H_{20}O_2 \cdot {}^1/_2H_2O$ crystallizes in the monoclinic space group $P2_1/a$ with a = 13.215 (2) Å, b = 17.587 (2) Å, c = 13.393 (2) Å, β = 118.86 (9)°, and z = 8 (two molecules per asymmetric unit). The calculated crystal density is 1.29 g/cm^3. Compound 8, $C_{17}H_{20}O_2$, crystallizes in the trigonal space group $R3$, with $a = b$ = 17.150 (2) Å, c = 24.995 (3) Å, γ = 120.00°, and z = 18 for a calculated crystal density of 1.20 g/cm^3. Data for both materials were collected at room temperature on a Nicolet R3m/v diffractometer with Cu Kα (λ 1.541 84 Å) radiation with an incident beam graphite monochromator. The structures were solved by direct methods and refined by full-matrix least-squares methods.[13] For 7, refinement of 464 parameters (carbon and oxygen atoms anisotropic, hydrogen coordinates) by using the 2645 observed reflections ($F_o > 3\sigma|F_o|$) from a set of 3719 unique data points gave a final R factor of 0.070 (R_w = 0.069). For 8, refinement of 180 parameters (carbon and oxygen atoms anisotropic, hydrogens riding) by using 1613 observed reflections (from a set of 1850 unique data points) gave a final R factor of 0.046 (R_w = 0.056).

Acknowledgment. The Stony Brook portion of this work was supported by Geocenters (Contact Number DAAA21-86-C-0101, Subcontract GC-1686-86-003). A.P.M. thanks the Air Force Office of Scientific Research (Grant AFOSR-84-0085), the Robert A. Welch Foundation (Grant B-963), and the North Texas State University Faculty Research Committee for financial suupport.

Registry No. 1, 117604-59-8; 5, 117527-62-5; 5 (monosemicarbazone deriv), 117527-64-7; 6, 117604-60-1; 6 (monosemi-

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(12) NT-300 and QE-300 instruments were used for all NMR experiments.
(13) Tables of atomic coordinates and bond lengths and angles are available from the Cambridge Crystallographic Data Base: Crystallographic Data Centre, Cambridge University, University Chemical Lab., Cambridge, CB2 1EW, England.

carbazone deriv), 117604-62-3; 7, 117527-63-6; 8, 117604-61-2; cyclopentadiene, 542-92-7.

Supplementary Material Available: Computer-drawn structures of 7 and 8 and tables of atomic coordinates, bond lengths and angles, and displacement parameters (11 pages). Ordering information is given on any current masthead page.

Preparation of Hindered Styrenes and Arylacetylenes

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Received June 14, 1988

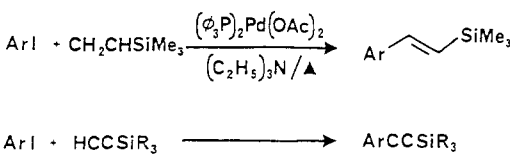
In connection with an approach to the synthesis of colchicine,[2] we required hindered, electron-rich styrenes and arylacetylenes such as **2**, **3**, and **5**. Recent reports by Karabelas and Hallberg[4] and by Stille et al.[5] prompt us to report our observations during the preparation of **2**, **3**, and **5**.

The preparation of simple styrenes and arylacetylenes is fraught with potential difficulties that have been previously discussed.[3-6] Furthermore, metal-catalyzed coupling reactions are often prevented by steric hinderance. These problems can be avoided by treatment of an aryl iodide[6] with vinyltrimethylsilane, catalytic palladium diacetate, and triphenylphosphine in refluxing triethylamine (Scheme I). From **1**, styrene **2** was formed in 93% isolated yield. This procedure is essentially that reported by Lau et al.[6] for the preparation of arylacetylenes. Iodide **1** was also converted into acetylenes **3a–c** with these conditions. (**3a**, >90% yield; **3b**, 92% yield; and **3c**, 95% yield, Table I).

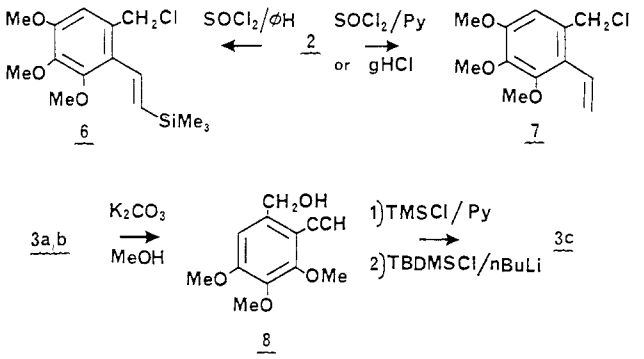
Conversion of malonate **4**[8] into styrene **5** (69% yield) required added cuprous iodide and reflux for 10 days. All TMS styrenes were exclusively the *E* isomer. Purification was effected by removal of the salts by filtration, by evaporation of the solvent, and by distillation of the residue in a Kugelrohr apparatus or filtration of the residue through silica gel. Unfortunately, the bromide corresponding to iodide **1** did not react with vinyltrimethylsilane under a variety of conditions with palladium(II) catalysts.

Removal of the silyl groups proceeded as expected to provide unsubstituted styrenes and acetylenes. The transformation of **2** into **6** could be accomplished by treatment with HCl gas (Scheme II). Exposure of **2** to thionyl chloride/pyridine also gave chloride **6**, while omission of pyridine afforded the benzyl chloride **7**. The silyl group of **3a,b** was readily cleaved with K_2CO_3 in methanol to yield **8**, which in turn could be transformed into **3c**.

Scheme I



Scheme II



This procedure for aryl substitution offers advantages over the recently published ones.[3-6] The aryl halide can be hindered and still yield the desired product, albeit slowly. This process can be used to prepare styrenes containing electron-donating groups. This procedure uses stable, readily available palladium(II) catalysts and does not require additional oxidants, such as silver. All reagents except the aryl iodide are commercially available. The byproducts of the reaction mixture are easy to remove. The requirement for an aryl iodide rather than a bromide may be a disadvantage in certain instances, but could permit selectivity. This method is an alternative to Stille's styrene synthesis,[5] which effects net direct displacement of tin in a vinyltin reagent. We believe this procedure offers a reasonable alternative for the preparation of certain hindered styrenes and arylacetylenes.

Experimental Section[9]

(*E*)-3,4,5-Trimethoxy-2-[2-(trimethylsilyl)ethenyl]-benzenemethanol (2a). Palladium acetate, 0.0538 g (2.40×10^{-4} mol, 2.2 M %), was added to a room-temperature solution containing 2.40 g (2.40×10^{-2} mol, 220 M %) of vinyltrimethylsilane, 0.1164 g (4.44×10^{-4} mol, 4.1 M %) of triphenylphosphine, and 3.55 g (1.10×10^{-2} mol, 100 M %) of the iodide **1a**[7] in 25 mL of deaereated triethylamine. The reaction was then heated at reflux under argon for 3 days. The reaction yielded 3.01 g of 93% yield of (*E*)-styrene (**2a**) after workup: IR 3600–3200, 2950, 1590, 1490, 1400, 1330, 1245, and 1120 cm^{-1}; NMR δ 0.18 (s, 9 H), 3.68 (s, 3 H), 3.78 (s, 6 H), 4.67 (2, 2 H), 6.13 (d, $J \sim 20$ Hz, 1 H), 6.83 (s, 1 H), and 7.92 (d, $J \sim 20$ Hz, 1 H); mass spectrum, *m/z* 296 (M^+).

The styrene **2a** converted to bis(β,β,β-trichloroethyl) [(2-ethenyl-3,4,5-trimethoxyphenyl)methyl]propanedioate by sequential treatment with thionyl chloride to provide **3b**, which was reacted with bis(β,β,β-trichloroethyl) propanedioate. This compound was identical with material prepared by an alternate route.[10]

The silyl ether **1b** was converted into the silyl ether **2b**. From 0.113 g (5.05×10^{-5} mol, 2 M %) of palladium(II) acetate, 1.00 g (2.53×10^{-3} mol, 100 M %) of the aryl iodide **1b**, 0.38 g (3.79×10^{-3} mol, 150 M %) of vinyltrimethylsilane, and 0.0245 g (9.34×10^{-5} mol, 3.7 M %) of triphenylphosphine in 6 mL of triethylamine, at reflux for 2 days, 0.86 g (93% yield) of the (*E*)-styrene **2b** was isolated: NMR δ 2.00 (s, 18 H), 3.79 (s, 3 H), 3.85 (s, 3 H), 3.89 (s, 3 H), 4.67 (s, 2 H), 6.14 (d, $J \sim 20$ Hz, 1 H), 6.86

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(2) (a) Taken from the Ph.D. Thesis of Bill J. McBride, University of California, San Diego, 1984. (b) Garst, M. E.; McBride, B. J. Abstract no. 49, Organic Division; 192nd American Chemical Society Meeting, Anaheim, CA, 1986.

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(8) Prepared from iodide **4** by sequential treatment with thionyl chloride and di-*tert*-butyl malonate (see ref 2a).

(9) See: Garst, M. E.; Frazier, J. D. *J. Org. Chem.* **1987**, *52*, 446–448 for general experimental details.

(10) Prepared from bis(β,β,β-trichloroethyl) 3,4,5-trimethoxybenzylpropanedioate by formylation with dichloromethyl methyl ether and stannic chloride followed by Wittig olefination (see ref 2a).

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