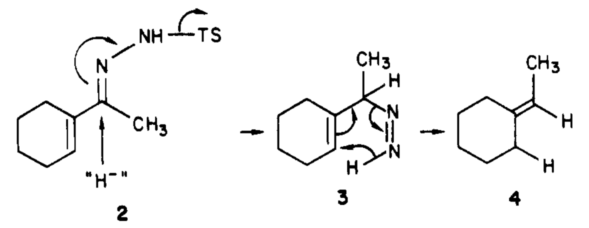
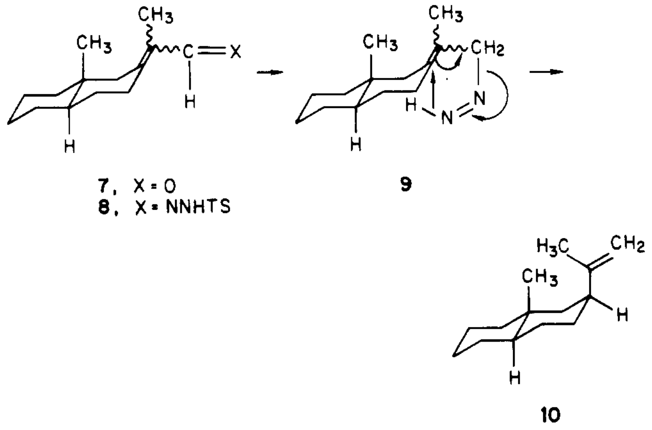
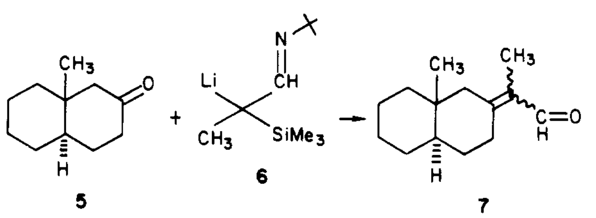


suggests that hydride reacts via 1,2 addition to the tosylhydrazone to produce a diazene intermediate which collapses with a 1,5-sigmatropic shift of hydrogen to produce an olefin with a transposed double bond. We recognized that a stereocenter could be formed by application of this reaction to a suitably substituted α,β-unsaturated aldehyde but also questioned whether the steric bulk in the molecule would direct the decomposition of the diazene intermediate.

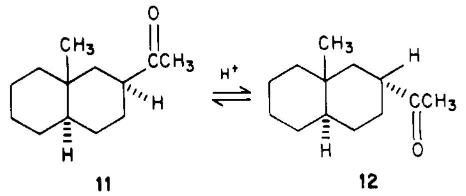
To test this hypothesis, the α,β-unsaturated aldehyde **7** was chosen as a model. We envisioned that the corresponding *p*-tosylhydrazone **8** would react with hydride to produce the diazene intermediate **9**, which would decompose with the delivery of hydrogen to the equatorial face of the ring. The delivery of hydrogen to the less hindered side of the molecule would thus push the newly forming isopropenyl group into the desired axial orientation of the olefin **10**.



trans-9-Methyl-2-decalone (**5**)[6] was treated with 1.1 equiv of α-(trimethylsilyl)propionaldehyde *tert*-butylimine **6**, under the influence of LDA/THF, according to the procedure of Corey et al.[7] Quenching with tartaric acid and purification on silica gel (5% EtOAc/petroleum ether) produced the α,β-unsaturated aldehyde **7**, as a 2:1 mixture of *E*/*Z* isomers: mass spectrum, *m*/*e* 206 (M^+); IR ($CDCl_3$) 1670, 1625 cm^{-1}; NMR ($CDCl_3$) δ 10.30 and 10.20 (two singlets, 1 H), 1.75 (s, 3 H), 0.73 (s, 3 H); 80% yield. Treatment of the aldehydes **7** with (*p*-tolylsulfonyl)hydazide in EtOH yielded the *p*-tosylhydrazones **8**: purification on silica gel (20% EtOAc/petroleum ether), 75% yield; mp 65–110 °C; NMR ($CDCl_3$) δ 7.80 (d, 2 H), 7.30 (d, 2 H), 2.40 (s, 3 H), 0.60 and 0.55 (two singlets, 3 H each). Hydrazones **8** were treated with 4 molar equiv of $NaBH_3CN$ in a 1:1 sulfolane/DMF solvent at pH <3 which gave the olefinic product **10** as a 3:1 mixture of isomers:[5] silica gel chromatography (cyclohexane), 80% yield; mass spectrum, *m*/*e* 194 (M^+); NMR ($CDCl_3$) δ 4.82 and 4.70 (two multiplets, 2 H), 1.80 and 1.70 (two singlets, 3 H each), 0.86 (s, 3 H).



To show that the major isopropenyl product was the axial isomer, the olefinic mixture **10** was subjected to ozonolysis. The resultant methyl ketones **11** and **12** were allowed to equilibrate in deuteriochloroform with a catalytic amount of concentrated HCl. Inspection of the proton NMR revealed that the mixture rapidly equilibrated to the more stable trans-axial, equatorial isomer **12**: cis isomer **11**, mass spectrum, *m*/*e* 194 (M^+); IR ($CHCl_3$) 1700 cm^{-1}; NMR ($CDCl_3$) δ 2.18 (s, 3 H), 0.68 (s, 3 H); trans isomer **12**, mass spectrum, *m*/*e* 194 (M^+); IR ($CHCl_3$) 1700 cm^{-1}; NMR ($CDCl_3$) δ 2.10 (s, 3 H), 0.82 (s, 3 H).



The generality of this procedure is further being explored on other substituted ring systems and terpene synthesis. We are also investigating some of the interesting mechanistic questions that have been raised in the discovery of this reaction.

Registry No. **5**, 1197-95-1; **6**, 96791-23-0; **7** (isomer 1), 96791-24-1; **7** (isomer 2), 96791-25-2; **8** (isomer 1), 96791-26-3; **8** (isomer 2), 96791-27-4; **10** (isomer 1), 96791-28-5; **10** (isomer 2), 96791-29-6; **11**, 96791-30-9; **12**, 96791-31-0; (*p*-tolylsulfonyl)hydrazide, 1576-35-8.

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(6) Nagata, W.; Kikkawa, I. *Chem. Pharm. Bull.* **1963**, *11*, 289.

(7) Corey, E. J.; Endres, D.; Bock, M. G. *Tetrahedron Lett.* **1976**, 7.

Oxidation of 2,2′-Dihydroxy-1,1′-binaphthyl by Periodic Acid. Structure of the Product

Summary: Oxidation of 2,2′-dihydroxy-1,1′-binaphthyl with periodic acid gives a new nine-membered keto lactone. The implication of this result on the mechanism of oxidation of phenols by periodic acid has been pointed out.

Sir: Oxidation of aromatic substrates like hydrocarbons, phenols, etc., by periodic acid presents a confused mechanistic picture,[1-4] None of the published mechanistic proposals are consistent with a large body of facts and observations. In connection with an extended study of an

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(1) Adler, E.; Anderson, G.; Edman, E. *Acta Chem. Scand., Ser. B* **1975**, *29*, 909.

(2) Fatiadi, A. J. *J. Res. Natl. Bur. Stand., Sect. A* **1968**, *72a*, 341.

(3) Becker, H. D.; Gustafson, K. *J. Org. Chem.* **1979**, *46*, 428.

(4) Fatiadi, A. J. *Synthesis* **1974**, 229.

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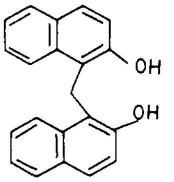
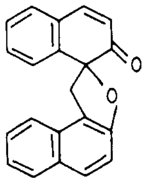
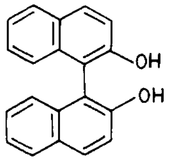
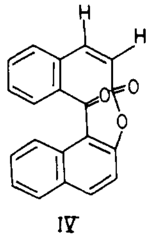
the pathways of aromatic oxidation, we became interested in this topic.[5,6]

Bis(2-hydroxyl-1-naphthyl)methane (I) is oxidized effeciently by a molar proportion of periodic acid in aqueous acetonitrile at 25 °C to furnish the expected product—the spirolactone II in 73% yield.[7] 2,2′-Dihydroxy-1,1′-binaphthyl (III) under similar conditions produced a product (IV), mp 194 °C in 41.7% yield, with a 1 molar proportion of periodic acid. With a 2 molar proportion of periodic acid, however, the same product was obtained in 80% yield. Clearly, 2,2′-dihydroxy-1,1′-binaphthyl is undergoing oxidation to a greater extent than its analogue I, through the involvement of an intermediate which is more readily oxidized than the starting material.

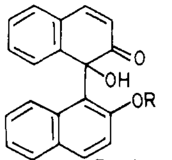

I

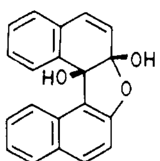

II


III


IV

It was found[8] that periodic acid or iodic acid does not oxidize Va, obtainable from 2-hydroxy-2′-methoxy-1,1′-binaphthyl through lead tetraacetate oxidation in two steps. Apparently the free hydroxyl group of the naphthol VI is playing a role in mediating the increased oxidation.


V a, R = CH$_3$
b, R = H


VI

The product of mp 194 °C (IV) analyzed for $C_{20}H_{12}O_3$ and showed two carbonyl bands in the IR—at 1735 and 1685 cm^{-1}—and gave an M$^+$ peak at *m/e* 300. The carbon-13 NMR spectrum confirmed the two carbonyl peaks at δ 165.6 and 198.7. Its ^{13}C and ^{1}H NMR chemical shift values are as follows. ^{13}C NMR ($CDCl_3$ + $CHCl_3$): 121.3 (d, 3), 122.6 (d, 4), 124.3 (dd, 3′), 125.7 (dd, 5), 126.4 (dd, 6′), 128.6 (dd, 7,7′), 128.7 (dd, 5′), 129.6 (s, 10′), 129.9 (dd, 8′), 130.5 (s, 1′), 131.0 (dd, 4′), 132.0 (s, 9′), 132.3 (s, 9), 132.5 (dd, 6), 142.1 (dd, 8), 142.5 (s, 10), 150.8 (s, 2′), 165.6 (s, 2), 198.7 (s, 1). ^{1}H NMR ($CDCl_3$): δ 6.1 (d, J = 12 Hz, 1 H), 7.1–8.0 (m, 11 H).

Crystals of IV suitable for single-crytstal X-ray diffraction studies were grown from chloroform. The compound crystallizes in the space group $P2_1/n$ with lattice constants a = 12.417 (1) Å, b = 7.043 (4) Å, c = 17.243 (2) Å, and β = 101.48 (1)° with V = 1477.8 Å^3 and with Z = 4. Intensity data were collected on an Enraf-Nonius CAD-4 diffractometer using graphite monochromated Mo K_α radiation by the $\omega/2\theta$ mode to a limit of θ = 23.5°. A total of 2046 unique reflexions were measured, and after correction for Lorentz, polarization, and background effects 813 were judged observed [$I \geq 3\sigma(I)$]. The structure was determined by using the SHELX program system.[9] Least-squares refinement of the non-hydrogen atoms anisotropically and hydrogen atoms isotropically led to the final R factor of 0.025 for the observed reflextions (R = 0.061 for the complete data). Figure 1 depicts a computer-generated perspective drawing of the final X-ray structure.

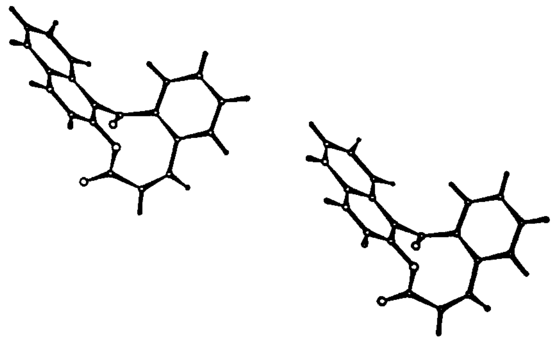
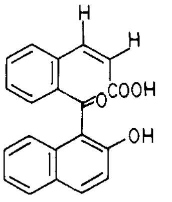


Figure 1.

The structure contains a nine-membered keto lactone, having a cisoid double bond formed by overoxidation of one of the naphthol moieties and with the other naphthol moiety remaining unaffected by periodic acid.

Although a nine-membered ring can accommodate a transoid double bond, in the present structure it is clearly cisoid. Basic hydrolysis of IV, produced the keto acid VII on acidification, which did not cyclize to the keto lactone IV in aqueous acetonitrile. A comparison of the ^{1}H NMR spectrum of the lactone and the keto acid established that the stereochemistry of the acid is the same as in the keto lactone, i.e., cisoid. These experiments lead to the following conclusions. (a) The primary product of the oxidation is the keto lactone and not the acid. (b) It is unlikely that the keto lactone could have been formed by the involvement of a species having an electron-deficient center or a radical at the carboxyl carbon, because this species could have produced a thermodynamically equilibrated trans acid.


VII

One possibility is that the elusive intermediate is the cis glycol VI formed from the keto alcohol V, which could get cleaved to the keto lactone by the well-known pathway involving V, VI, and IV.

An interesting question that remains unanswered is why does the keto alcohol V give only the cis glycol and not a mixture of cis and trans isomers? Then there are the important questions: Do phenols get oxidized through the involvement of periodate esters? And do aromatic hydrocarbons and phenolic derivatives have similar pathways of oxidation? We hope to answer these questions.

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(5) Perumal, P. T.; Bhatt, M. V. *Synthesis* **1979**, 205.

(6) Bhatt, M. V., Gopinathan, M. B. *Ind. J. Chem.* **1981**, *20B*, 72.

(7) Hewitt, D. G. *J. Chem. Soc. C* **1971**, 1750.

(8) Hosur, B. M.; Bhatt, M. V. manuscript in preparation.

(9) Sheldric, G. M. X-ray System Report, University of Cambridge, England, 1976.

Registry No. III, 602-09-5; IV, 96728-47-1.

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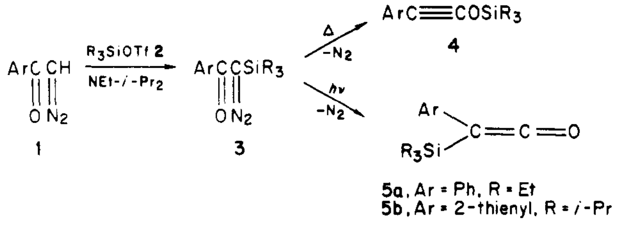
Preparation of 1-Aryl-2-siloxyalkynes from Silylated α-Diazo Carbonyl Compounds

Summary: Silylated α-diazo carbonyl compounds $R_3SiC(N_2)C(O)Ar$, prepared from a monosubstituted α-diazo carbonyl compound with trialkylsilyl triflates, rearrange to 1-aryl-2-siloxyalkynes with loss of N_2 at or above room temperature; this novel transformation is thought to be initiated by a C → O silyl shift yielding a diazoethene intermediate.

Sir: Silylated α-diazo carbonyl compounds are usually obtained by electrophilic diazoalkane substitution of monosubstituted α-diazo carbonyl compounds with a chlorosilane.[1] Recently, trimethylsilyl triflate (Me_3SiOTf), already known for its superior silylating power,[2] has been introduced for a smooth and effective trimethylsilylation of diazomethane, ethyl diazoacetate, and diazomethylphosphoryl compounds.[3,4] However, in our hands no clean reaction took place in the case of α-diazoacetophenone and Me_3SiOTf; the initially formed silylated diazo compound decomposed on workup.

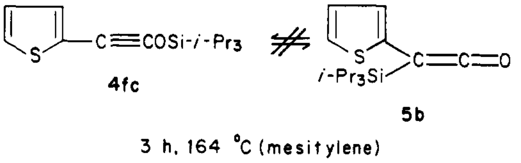
As we have now found, 1-aryl(or heteroaryl)-2-diazo-1-ethanones **1** can be silylated smoothly with triethylsilyl triflate, *tert*-butyldimethylsilyl triflate, or triisopropyl triflate in the presence of a tertiary amine (see Table I). The formation of the silylated diazo compound **3** followed from the appearance of a new diazo stretching vibration in the IR spectrum. Simultaneously, a more or less intense band indicating a $\nu(C{\equiv}C)$ vibration was observed. It turned out that a thermal rearrangement of **3** with loss of N_2 was taking place, leading to a siloxyacetylene **4**. In most cases, this rearrangement occurs already at room temperature, and no effort was then made to isolate **3**. Compounds **3aA**, **3cA**, **3cC**, and **3fC**, being sufficiently stable, could be isolated and then rearranged to the siloxyacetylene in boiling benzene.

Typically, the following procedure for the synthesis of **4** was applied: The solution of silyl triflate **3** (10 mmol) in ether (5 mL) was added dropwise to a solution of diazo carbonyl compound **1**[1] (10 mmol) and diisopropylethylamine (1.74 mL, 10 mmol) in ether (60 mL), kept at 0 °C. The mixture was then allowed to assume room temperature and was stirred for another 20 h. The precipitated ammonium triflate was filtered off and washed with ether. The filtrate was concentrated and benzene (50 mL) was added. After 2 h at reflux, the solvent was evaporated and the residue was separated by column chromatography (Merck Lobar column, LiChroprep Si60, 40–63 μm, eluent $CHCl_3$). The siloxyacetylenes **4** were further purified by Kugelrohr distillation.

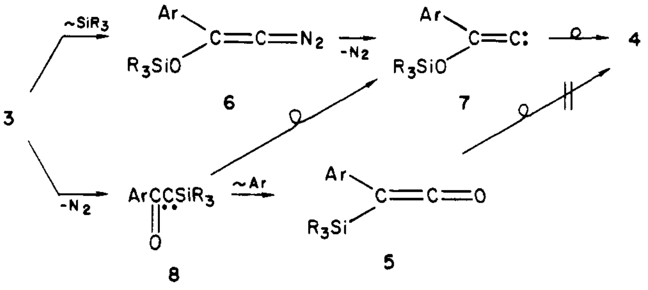


5a, Ar = Ph, R = Et
5b, Ar = 2-thienyl, R = *i*-Pr

Scheme I



Scheme II



The silylated diazo compounds **3** suffer protodesilylation extremely easily (e.g., **3cC** in CH_3OH gave **1c** in 86% isolated yield). Thus, with the trialkylammonium triflate around, it is understandable why the silylation reaction **1** → **3** could never be driven to completion.

To our knowledge, siloxyalkynes have been mentioned only once in the literature,[5] but their reactivity is not yet known. Compounds **4** with Si-*i*-Pr_3 or $SiMe_2$-*t*-Bu are thermally stable oils which were distilled without decomposition. The $SiEt_3$ derivatives, on the other hand, decomposed partly on column chromatography and extensively on attempted distillation. The possible interconversion siloxyacetylene/silyl ketene could not be observed, as was checked for the isomeric pair **4fC** and **5b** (Scheme I).

The siloxyalkynes are solvolyzed at room temperature by water–acetone or alcohols to give arylacetic acids or their esters, respectively. The C≡C stretching frequency of siloxyalkynes **4** compares well with that of alkynyl tosylates[6] (e.g., PhC≡COTs, 2260 cm^{-1}) but is distinctly different from isomeric yne ethers, e.g., PhOC≡CSi-*i*-Pr_3[7] (2190 cm^{-1}).

A preliminary picture of the rearrangement **3** → **4** is given in Scheme II. We think that the sequence is initiated by a C → O 1,3-silyl shift, for which there is much precedent.[8,9] The activation barrier for **3** is, however,

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[1] Regitz, M. "Diazoalkane"; Thieme; Stuttgart, 1977.

[2] Hergott, H. H.; Simchen, G. *Liebigs Ann. Chem.* **1980**, 1781.

[3] Martin, M. *Synth. Commun.* **1983**, *13*, 809.

[4] Regitz, M.; Allspach, T.; Gümbel, H. *J. Organomet. Chem.*, in press.

[5] Pirrung, M. C.; Hwu, J. R. *Tetrahedron Lett.* **1983**, *24*, 565.

[6] Stang, P. J.; Surber, B. W. *J. Am. Chem. Soc.* **1985**, *107*, 1452.

[7] Prepared according to: Himbert, G.; Henn, L. *Liebigs Ann. Chem.* **1984**, 1358. This compound is an oil which decomposed on attempted distillation.

[8] (a) Brook, A. G.; Bassindale, A. R.; "Molecular Rearrangements in Ground and Excited States"; De Mayo, P., Ed.; p 193; Academic Press: New York, 1980; Vol. 2. (b) Brook, A. G. *Acc. Chem. Res.* **1974**, *7*, 77.

[9] Colvin, E. "Silicon in Organic Synthesis"; Butterworths; London, 1981; p 33.

0022-3263/85/1950-2801$01.50/0