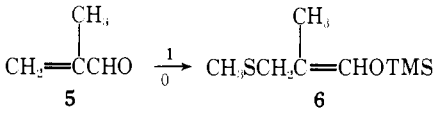
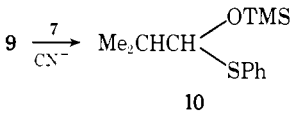
The reactions of thiosilanes such as **1** with α,β-unsaturated aldehydes and ketones depart from the traditional path that is normally observed in thioketalization. For example, **1** spontaneously reacts with methacrolein (**5**) without catalysis at 0° in methylene chloride to give the 1,4-adduct **6** in 82% yield (bp 82–83°, 3 mm) as a 2:1 mixture



5 **6**

of *E* and *Z* isomers. This uncatalyzed mode of addition has been observed for a wide variety of unsaturated carbonyl compounds, and in no instance was 1,2-addition detected.

In contrast to TMS-SMe (**1**), other silanes such as phenylthiotrimethylsilane (**7**)[4c] react only sluggishly at elevated temperatures (100–150°, 2–4 days) with carbonyl derivatives. However, in the presence of anionic initiators such as potassium cyanide-18-crown-6 (0.01 equiv) or potassium ethylthiolate-crown complex,[8] stoichiometric amounts of **7** and isobutyraldehyde (**9**) (25°, neat, 20 hr) react to give the adduct **10** (bp 71°, 0.05 mm) in 81% yield. Under similar conditions, unsaturated aldehydes **11a** and **11b** reacted exothermically to give adducts **12a** (86%, bp 87–89°, 0.02 mm) and **12b** (90%, bp 90–92°, 0.02 mm) as a mixture of *E* and *Z* isomers.[9] The catalyzed addition of **7** to methyl vinyl ketone (**11c**) and cyclohexenone (**13**) proceeds with equal facility to give **12c** (86%, bp 85–86°, 0.03 mm) and **14** (88%, bp 117–119°, 0.16 mm), respectively.



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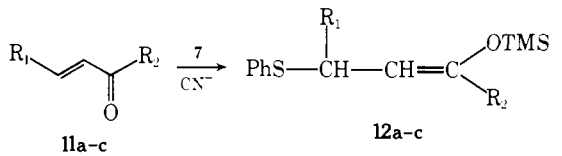
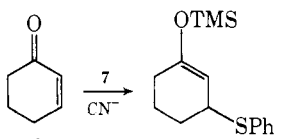


11a–c **12a–c**

a, $R_1 = H$; $R_2 = H$
b, $R_1 = CH_3$; $R_2 = H$
c, $R_1 = H$; $R_2 = CH_3$



13 **14**

In conclusion, the high reactivity of TMS-SMe (**1**) is quite surprising. Other silanes such as **7** and even ethylthiotrimethylsilane, TMS-SEt, are quite unreactive by comparison. The mechanistic details of these interesting transformations must await further study.

Acknowledgment. We wish to thank the Upjohn Company for a sample of PGE_2 and the National Institutes of Health and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

References and Notes

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(2) For a comprehensive review of the synthesis and properties of organosulfur derivatives of the group 4 atoms see E. W. Abel and D. A. Armitage, *Adv. Organomet. Chem.*, **5**, 2 (1967).
(3) (a) I. Ojima and Y. Nagai, *J. Organomet. Chem.*, **57**, C42 (1973); (b) T. Mukaiyama, T. Takeda, and K. Atsumi, *Chem. Lett.*, 1013 (1974); (c) *ibid.*, 187 (1974); (d) E. W. Abel, D. J. Walker, and J. N. Wingfield, *J. Chem. Soc. A*, 1814 (1968); (e) E. W. Abel and D. J. Walker, *ibid.*, 2338 (1968); (f) K. Itoh, K. Matsuzaki, and Y. Ishii, *J. Chem. Soc. C*, 2709 (1968).
(4) (a) K. A. Hooten and A. L. Allred, *Inorg. Chem.*, **4**, 671 (1965); (b) E. W. Abel, D. A. Armitage, and D. B. Brady, *J. Organomet. Chem.*, **5**, 130 (1966); (c) I. Ojima, M. Nihonyangi, and T. Nagai, *ibid.*, **50**, C26 (1973); (d) R. S. Glass, *ibid.*, **61**, 83 (1973).
(5) TMS-SMe may either be prepared according to ref 4a or more conveniently as follows. To a mechanically stirred suspension of 125 mmol of $LiAlH_4$ in 500 ml of anhydrous ether was added dropwise 250 mmol of dimethyl disulfide. After heating at reflux for 1 hr, a solution of 68 g of Me_3SiCl (distilled from CaH_2) in 50 ml of ether was added dropwise. The resulting gelatinous precipitated aluminum salts may be transformed into a granular solid by heating for several hours followed by stirring at 25° (12 hr). Filtration of the inorganic salts under an inert atmosphere followed by fractional distillation of the filtrate afforded the desired **1**, bp 110–111° in 65–70% yield. TMS-SMe is exceptionally moisture sensitive and should be handled accordingly.
(6) The mass spectrum (70 eV) of **4b** revealed fragment ions at *m/e* 426 (P-18), 408 (P − 36) and 99. The fragment ion at 426 exhibited an exact mass of 426.2263 (calcd for $C_{23}H_{38}O_3S_2$: 426.2262). All other spectral data are consistent with the assigned structure.
(7) E. W. Yankee, C. H. Lin, and J. Fried, *J. Chem. Soc., Chem. Commun.*, 1120 (1972).
(8) D. A. Evans and L. K. Truesdale, *Tetrahedron Lett.*, 4929 (1973); see footnote 9 for catalyst preparation.
(9) Triphenylphosphine is also an excellent initiator for thiosilane addition to α,β-unsaturated ketones and aldehydes.
(10) Camille and Henry Dreyfus Teacher-Scholar Recipient (1971–1976); Alfred P. Sloan Fellow (1972–1974).

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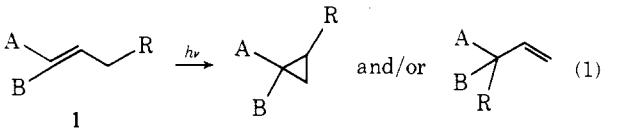
An Unusual Mechanism for 1,3-Hydrogen Migration in the Photochemistry of 4-Methyl-1,1,4-triphenyl-1-pentene

Sir:

Upon irradiation many systems of the type **1**, in which R = H, alkyl, benzyl, or allyl and the olefinic group is either a simple olefin or part of a diene, styrene, or diphenylethylene system, undergo a 1,2- and/or 1,3-shift of the group R (eq 1).[1] As a start in determining the influence of various types

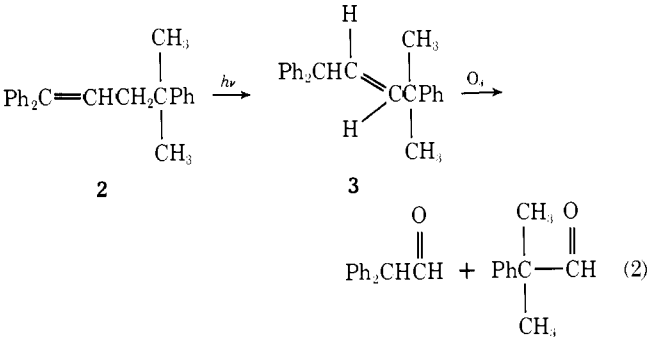


1 (1)

of substitution on the course of rearrangement of such systems we chose to study the photochemistry of the diphenylethylene derivative **2**. Our findings, which proved most unusual and interesting, are presented here.

Irradiation[2] of a cyclohexane solution of **2** provided, slowly, one major product isolated in 36% yield at 69% conversion of **2**. The formation of other minor products in quantities too small to allow identification as well as high molecular weight material was also noted. Spectral data on the major product indicated it had the structure **3**. The NMR spectrum showed a singlet for the geminal methyls at τ 8.58, a doublet ($J_{1,2}$ = 7.0 Hz) for the benzhydryl hydrogen at 5.24, a doublet ($J_{2,3}$ = 15.0 Hz) for the C-3 vinyl hydrogen at 4.28, and a doublet of doublets for the C-2 vinyl hydrogen at 4.05. The magnitude of $J_{2,3}$ is indicative of a trans arrangement of hydrogens on the double bond. This stereochemistry is supported by the strong band at 974 cm^{-1} in the infrared spectrum of **3**. Confirmation of the structure of **3** was provided by its ozonolysis to approxi-

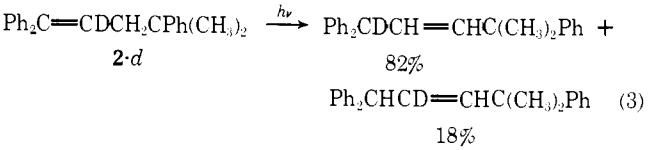
mately equal amounts of diphenylacetaldehyde and dimethylphenylacetaldehyde.



2 3

Benzophenone sensitization of **2** gave no detectable reaction, indicating the observed process proceeds via the singlet state of **2.**

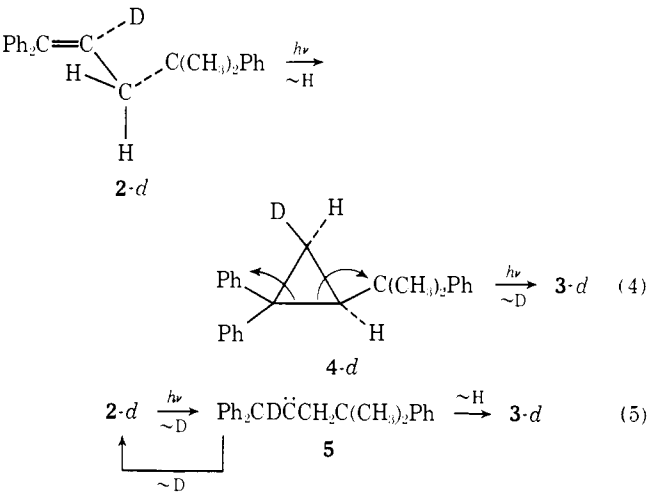
Although nonconjugated olefin **3** appears to be the product of a simple 1,3-hydrogen migration in **2,** several other plausible routes for its formation were considered a priori as likely alternatives.[3] To aid in distinguishing among these pathways **2**-*d* (>95% *d*) was prepared and irradiated until GC analysis showed the presence of approximately equal amounts of **2**-*d* and **3**-*d*. The **2**-*d* and **3**-*d* were then separated and subjected to NMR analysis. Most surprisingly, the **3**-*d* isolated consisted mainly (82 ± 5%) of C-1 deuterated material. The remainder (18 ± 5%) of the **3**-*d* possessed deuterium at C-2 (eq 3). No (<6%) C-3 deuteration could be detected. Importantly, recovered starting material **2**-*d* showed no detectable scrambling of the deuterium.



(3)

These results eliminate as major contributors to the **2** → **3** transformation both a simple 1,3-hydrogen mechanism or a mechanism involving initial 1,2-cumyl migration to form a cyclopropane followed by a 1,2-hydrogen shift in the cyclopropane to form **3,** for these pathways would result respectively in deuterium incorporation at C-2 and C-3 of **3.** We can see two reasonable rationalizations for the preference for net deuterium migration: (1) a mechanism involving two consecutive hydrogen shifts via cyclopropane intermediate **4** (**4**-*d*) predominates, and for stereoelectronic reasons[4] deuterium migration from C-2 to C-1 is favored in the second step; (2) deuterium migration is favored because it is the hydrogen (deuterium) at C-2 of **2** (**2**-*d*) which migrates first, giving a carbene. These possibilities are illustrated in eq 4 and 5.

Consider the first possibility (eq 4). If one assumes (a) that the migrating hydrogen in the first step must initially be parallel to the π orbital of the olefinic double bond, (b) that **2** reacts predominantly from the lowest energy conformation (satisfying a) with the cumyl group "anti" to the diphenylmethylene moiety, and (c) that the migration follows $_2\pi_a + _2\sigma_a$ stereochemistry,[5] then the formation of cyclopropane **4**-*d* with the deuterium and cumyl groups cis is predicted. A preferential migration of the hydrogen (deuterium) cis to the cumyl group in **4** (**4**-*d*) to the benzhydryl position in the second step forming **3** would then explain the results. (In eq 4 we have assumed the sterically most favorable disrotatory mode of ring opening occurs.) The assumptions concerning the first migration step seem reasonable;



2-*d* 4-*d*

(4)

(5)

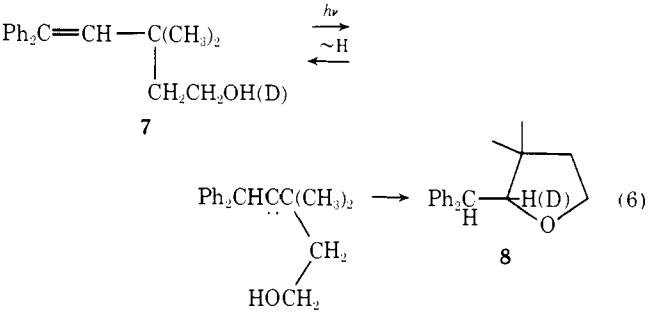
5

however, while migration of the hydrogens cis and trans to the cumyl group in **4** are clearly different processes, we are unable to provide a reason as to why migration of the cis hydrogen should be preferred over the trans. Indeed, one might predict the opposite. One would also expect some deuterium scrambling in **2** to occur should **4**-*d* be the intermediate, whereas none was observed. One may assume other preferred modes of ring opening or of hydrogen migration stereochemistries in eq 4. However, this does not eliminate the seemingly arbitrary nature of the basic mechanism.

The carbene pathway (eq 5) must then be considered a strong possibility for the predominant reaction pathway of **2** in view of both the restrictions to which a two-photochemical-step (cyclopropane) mechanism must conform and the very recent evidence for similar carbene-forming processes in other olefinic systems,[6-8] notably the closely related β-*tert*-butyl-1,1-diphenylethylene (**6**).[8] Such a mechanism nicely rationalizes the observed preference for deuterium migration. Likewise the lack of scrambling of deuterium in recovered **2**-*d* is understandable, for although carbene **5** would undoubtedly revert to the conjugated olefin **2** faster than it would proceed onward to **3,** this would not interchange hydrogens and would simply be a nonobservable deactivation mechanism for photoexcited **2.**

Strong evidence for the intermediacy of carbene **5** would be provided by trapping it with an external reagent, for instance the O-H bond of an alcohol.[9] Such a process, however, would be expected to compete but poorly with the facile intramolecular C-H insertions. We have therefore synthesized and irradiated olefin **7,** another hindered diphenylethylene derivative similar to **2** (and **6**) which has an intramolecular O-H group favorably positioned for trapping a carbene at C-2 should one, in fact, be generated.

Indeed, irradiation[2] of **7** in cyclohexane provided as the major product in 26% yield the substituted tetrahydrofuran derivative **8,**[12] the product expected from insertion of a carbene at C-2 into the O-H bond (eq 6). That the mechanism



7

(6)

8

illustrated in eq 6 is operative was demonstrated by irradiating **7**-*O*-*d*. NMR and mass spectral analysis of the resulting **8** showed that the deuterium was located almost entirely, if not exclusively, at C-2 of **8** (eq 6). Thus the a priori possible nucleophilic addition mechanism[13] for formation of **8** is ruled out as a major process.

The evidence that carbene formation does occur in certain 3-alkyl-1,1-diphenylpropenes is conclusive. It is, therefore, highly likely that the carbene mechanism for net 1,3-hydrogen migration in **2** is the one operative,[14] and that carbene formation from 3-alkyl-1,1-diphenylpropenes may well be a general process. The mechanisms of previously observed 1,3-hydrogen migrations[1a] deserve further scrutiny.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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(2) Vycor-filtered light from a 450-W medium-pressure mercury arc was used. Progress of the reaction was monitored closely by gas chromatography.
(3) Griffin[1a] has suggested two consecutive 1,2-hydrogen shifts as a likely mechanism for the conversion of 1,1-diphenylpropene to 3,3-diphenylpropene.
(4) We assume a normal isotope effect would be operative in the migration.
(5) This is the preferred stereochemistry in the analogous 1,2-migration of vinyl substituents (the di-π-methane rearrangement). See H. E. Zimmerman, J. D. Robbins, R. D. McKelvey, C. J. Samuel, and L. R. Sousa, *J. Am. Chem. Soc.*, **96**, 4630 (1974), and references therein.
(6) S. J. Cristol and C. S. Ilenda, Abstracts of the 167th National Meeting of the American Chemical Society, Los Angeles, Calif., April 1974, ORGN 113.
(7) T. R. Fields and P. J. Kropp, *J. Am. Chem. Soc.*, **96**, 7559 (1974).
(8) S. S. Hixson, *J. Am. Chem. Soc.* **97**, 1981 (1975).
(9) The insertion of carbenes into the O–H bond of alcohols has been frequenctly observed, both with methylene itself and with more stabilized carbenes.[10] Intramolecular OH insertion of a carbene has also been noted.[11]
(10) W. Kirmse, "Carbene Chemistry", Academic Press, New York, N.Y., 1971, p 423 ff.
(11) A. C. Day and M. C. Whiting, *J. Chem. Soc. C*, 1719 (1966).
(12) (a) NMR ($CDCl_3$) δ 0.59 (s, 3), 1.03 (s, 3), 1.66–2.10 (m, 2), 3.62–3.93 (m, 2), 4.13 (AB quartet, 2, J = 10 Hz), 7.14–7.55 (m, 10); mass spectrum (80 eV) *m/e* 266 (M^+, 0.5%), 264 (0.5), 167 (7.6), 165 (5.5), 152 (2.7), 99 (100). (b) Small amounts of other unidentified products as well as polymeric material were also formed.
(13) See, e.g., S. S. Hixson, *Tetrahedron Lett.*, 4211 (1972).
(14) A minor amount of another pathway, either a 1,3-hydrogen shift or two consecutive 1,2-hydrogen shifts, must also be followed.

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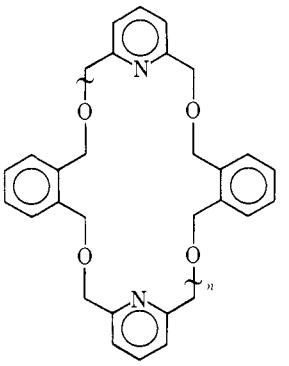
Chemistry of Heterocyclic Compounds. 20. Multidentate Chelating Agents. Pyridine Macrocyclic Ether Synthesis

Sir:

In view of the current interest in the design and construction of specific metal ion ligands,[1] we wish to report convenient direct nucleophilic displacement by alkoxide of pyridine 2,6-dihalides to prepare several new pyridine-containing macrocyclic ethers in which the oxygen is attached *directly* to the hetero ring. Recently, we described the facile preparation of 22-, 33-, 44-, and 55-membered macrocyclic azaethers (**1**) that contained the 2,6-pyridino moiety;[2] however, in this series the pyridine rings were isolated from the ether linkage by a $-CH_2-$ group. Further examples of this latter type of pyridine-containing multiheteromacrocycle have been described by Vögtle and Weber[3] and Cram et al.[4] (**2a**[5] and **2b**, respectively).



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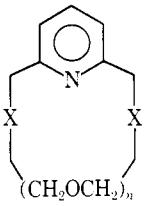

2a (X = S)
2b (X = O)

During our ketalization studies of substituted di(2-pyridyl) ketones[6] as well as attempted synthesis of different pyridylacetylenes,[7] several minor products were isolated that had resulted from nucleophilic displacement of a 2-pyridyl substituent. In practice, application of this substitution reaction has resulted in a convenient selective 2-pyridone synthesis[8] as well as the herein reported new route to heteromacrocyclic ethers.

Treatment of diethylene glycol (**3b**) with sodium hydride in anhydrous diethylene glycol diethyl ether (DEE) smoothly generated diethylene glycol dianion in near quantitative yield. 2-Bromopyridine (**4a**) was added and the mixture warmed to 140° for 24 hr. After removal of solvent and unreacted starting materials, the major products were the monoether **5a**[9] and diether **6a** isolated in 27 and 35% yields, respectively, along with traces (<3%) of **7a** and **8a.** These latter trace products and ethylene oxide resulted from thermal fragmentation of polyethylene glycols under reaction conditions; both fragmentation and oligomerization are precedented reactions of ethylene glycols.[10] Side reactions are minimized by maintaining the reaction temperatures below 150°. Substantiation of the oligomerization process was demonstrated when **4a** was subjected to ethylene glycol dianion under identical conditions: the major products were 2-(2-pyridinoxy)ethanol (**7a**) and 1,2-di(2-pyridinoxy)-ethane (**8a**), along with traces of **5a** and **6a.**

When 2,6-dibromopyridine (**4b**) was subjected to dianion **3b** in DEE at 140°, the desired cyclized ethers **9** (mp 111–112°; 18%; NMR ($CDCl_3$) δ 3.86 (t, β-CH_2O, J = 5 Hz), 4.48 (t, α-CH_2O, J = 5 Hz), 6.23 (d, 3,5-PyrH, J = 8 Hz), 7.45 (t, 4-PyrH, J = 8 Hz)), **10** (mp 120.5–121.5°; 3%; identical NMR), and **11** (mp 94.5–95.5°; 5%; NMR ($CDCl_3$) δ 3.81 (dd, β-CH_2-O, J = 6 Hz), 4.50 (dd, α-CH_2O, J = 6 Hz), 4.64 (s, OCH_2CH_2O), 6.38 (dd, 3,5-PyrH, J = 8.8 Hz), 7.48 (t, 4-PyrH, J = 8 Hz)) were isolated along with several intermediates **5b** (ca. 25%), **6b, 8b, 12,** and **13.**[11] The structure of unsymmetrical ether **11** was substantiated by successful cyclization of 1,2-di(6-bromo-2-pyridinoxy)ethane (**8b**) with dianion **3b;** however, **6b** could not be cyclized with dianion **3a** under diverse reaction conditions. An identical mixture of heteromacrocyclic ethers (**9, 10,** and **11**) were obtained when ether **5b** in DEE was treated with 1 equiv of sodium hydride, then the reaction mixture heated to 140°.

When triethylene glycol (**3c**) is utilized in this synthesis with 2,6-dibromopyridine (**4b**), the 1:1 cyclic ether **14a** was isolated. Pure **14a** was obtained by preparative thick layer