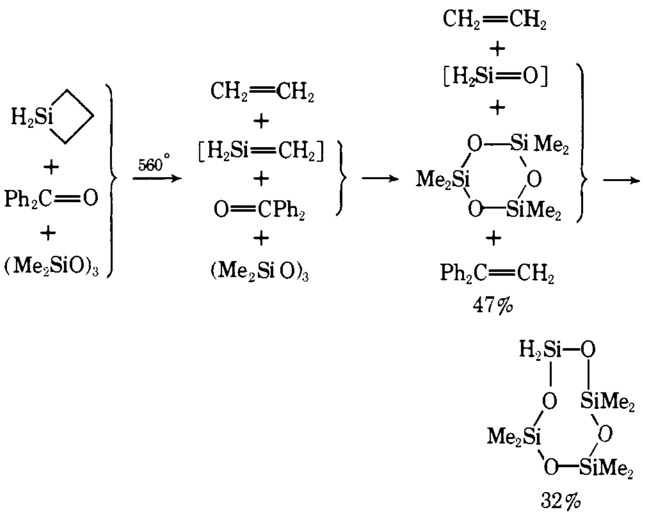
Scheme III



(silanone) is provided by the following experiment. Pyrolysis of a benzene solution of silacyclobutane (2.2 mmol), benzophenone (4.0 mmol), and hexamethylcyclotrisiloxane (10.0 mmol), followed by resolution by preparative GLPC, afforded 1,1,3,3,5,5-hexamethylcyclotetrasiloxane (32%) and 1,1-diphenylethylene (47%) as the only major reaction products[15] (Scheme III).

The products reported in Schemes II and III, the facile insertion of [$Me_2Si{=}O$] into the Si-O bond of $(Me_2SiO)_3$ under similar reaction conditions,[16] and the observation that $(Me_2SiO)_3$ is stable under the reaction conditions constitute convincing evidence for the existence of [$H_2Si{=}O$] as a transient intermediate.

We are currently attempting to verify the intermediacy of an [O=Si=O] species by means of chemical trapping experiments.

Acknowledgments. We thank the National Science Foundation for generous support of this research and Mr. Kei Miyano for mass spectral studies.

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(4) J. Laane, *J. Am. Chem. Soc.*, **89**, 1144 (1967).

(5) All new compounds reported were fully characterized by an exact mass determination and their ir, NMR, and mass spectra. This information will be reported in detail in the full paper.

(6) The observed substrate reactivity order toward [$Me_2Si{=}CH_2$] is: $Ph_2C{=}O > (Me_2SiO)_3 > CH_3CN, SiCl_4$.[1f,7]

(7) C. M. Golino and R. D. Bush, unpublished results.

(8) Elemental analysis of this yellow solid (Anal. Calcd for CH_4Si: C, 27.2; H, 9.13; Si, 63.6. Found: C, 25.41; H, 4.86; Si, 55.28.) indicates a considerable loss of hydrogen, probably due to the fact thet this material condensed at the relatively warm (ca. 200°) ends of the pyrolysis tube. The observed carbon:silicon mole ratio of 1.08:1.0 supports the proposed decomposition reaction given in eq 1. The infrared spectrum (KBr) of this material showed only a very strong band at ~2080 cm^{-1} (Si–H stretch) and a weak band at 1248 cm^{-1} (Si–Me stretch). The *insolubility* of this material has prevented further investigation of its structure.

(9) 1,1-Dimethyl-1,3-disilacyclobutane has been obtained in 30% yield from a pyrolysis carried out at 500°;[10] 1,3-dimethyl-1,3-disilacyclobutane undergoes only minor (< 15%) decomposition under our reaction conditions.

(10) D. N. Roark and G. J. D. Peddle, *J. Am. Chem. Soc.*, **94**, 5837 (1972).

(11) H. J. Campbell-Ferguson, *J. Inorg. Nucl. Chem.*, **27**, 212 (1965).

(12) Ph_2CD_2[13] did not undergo observable H–D exchange when copyrolyzed with $Ph_2C{=}O$, $Ph_2C{=}CH_2$, and benzene at 560°. In pyrolyses which produce Ph_2CD_2, the $Ph_2C{=}CH_2$ which was also formed contained less then 10% deuterium at the 2-positions. The isotopic impurity of the Ph_2CD_2 is likely due to prior Si–H formation via an unknown pathway which is currently under investigation.

(13) K. B. Wiberg and R. J. Evans, *Tetrahedron*, **8**, 313 (1960).

(14) A dihydro (p_π–p_π) multiply bonded silicon species ([$H_2Si{=}X$], X = CH_2 or O) appears to be necessary for the occurrence of this reduction. The reaction between $Ph_2C{=}O$ and [$CH_2{=}Si(H)Me$] at 611° afforded a 74% yield of $Ph_2C{=}CH_2$, but did not produce detectable quantities of Ph_2CH_2.[7]

(15) Diphenylmethene (0.18 mmol, 8%), benzophenone (1.4 mmol), and $(Me_2SiO)_3$ (8.4 mmol) were also recovered from the pyrolysate.

(16) (a) L. E. Gusel'nikov, N. S. Nametkin, T. H. Islamov, A. A. Sobtsov, and V. M. Vdovin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 84 (1971); (b) I. M. T. Davidson and J. F. Thompson, *Chem. Commun.*, 251 (1971); (c) C. M. Golino, R. D. Bush, and L. H. Sommer, Abstracts, 167th National Meeting of The American Chemical Society, Los Angeles, Calif., April 1975, No. ORGN 005.

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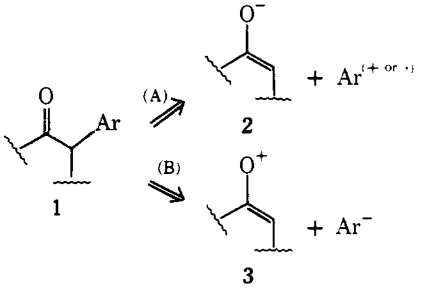
α-Arylation of Carbonyl Groups. Utilization of the *p*-Toluenesulfonylazo Olefin Functional Group as an Enolonium Synthon

Sir:

In connection with a synthetic study, we required substrates bearing an α-aryl ketone moiety (**1**). Methodology involving the α-arylation of ketones is one conceptual approach for the synthesis of such systems. Analysis of this problem suggests two primary modes of synthesis: (A) the combination of an enolate **2** (or its equivalent) with some electron-deficient aryl species or (B) reaction of an enolonium (α-keto cation) synthon **3** with an electron-rich aryl species.

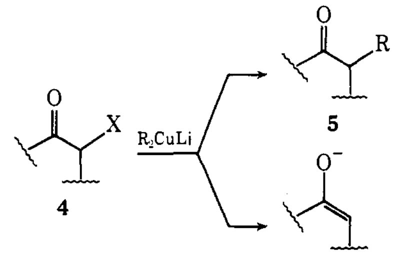


Although the reaction of enolates and enamines with strongly activated arenes, diphenyliodonium chloride, or benzyne has been shown to produce α-arylated ketones,[1-9] it appears that a more promising approach to enolate arylation is the method of Rossi and Bunnett involving the reaction of enolates with photogenerated aryl radicals.[10-12] An intramolecular variant of this latter procedure has recently been used to great advantage by Semmelhack et al. in their total synthesis of cephalotaxine.[13,14]

In assessing the enolate method for natural product synthesis, complications can be anticipated in those cases where intramolecular condensations (aldol, Claisen) or β-eliminations can occur. Additionally, it has yet to be conclusively demonstrated that a kinetically generated enolate can be regiospecifically arylated.[11,15]

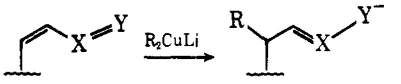
Whereas, a priori, methodology based on mode (B) might avoid some of these difficulties, there has been essentially no effort to utilize such a strategy.[16,17]

Superficial consideration of this problem suggests that the reaction of α-halo ketones with lithium diarylcuprate might provide a method of α-aryl ketone synthesis; however, since the reaction of α-halo ketones **4** with lithium *dialkyl* cuprates has been shown to produce both α-alkylated ketones **5** and reduction product **6**, it was anticipated that similar difficulties would also occur with lithium diarylcuprate.[18-24] This is indeed the case.[25,26]

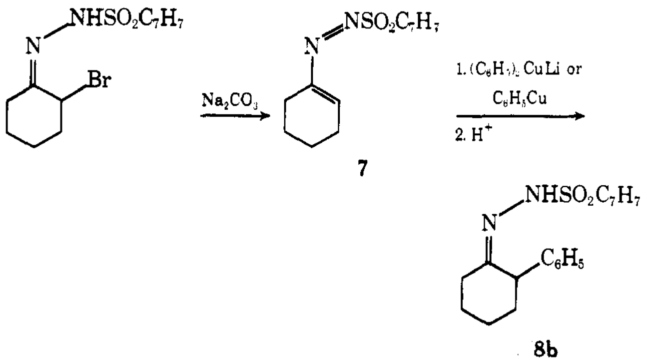


4 **5** **6**

In contrast to the difficulties associated with reaction of α-halo ketones with cuprates, the conjugate addition of cuprates to α,β-unsaturated carbonyl systems is known to be an exceptionally facile reaction.[27] In simplest terms (detailed mechanism notwithstanding), this reaction may be visualized as a formal Michael-type addition of an alkyl (vinyl, aryl) group to the terminus of a four-atom array with concomitant generation of a stabilized anion (X = C, Y = O). These considerations suggest that the *p*-toluenesulfonylazo olefin system (X = N, Y = $NSO_2C_7H_7$) should be an excellent substrate for conjugate addition reactions.[28,29]



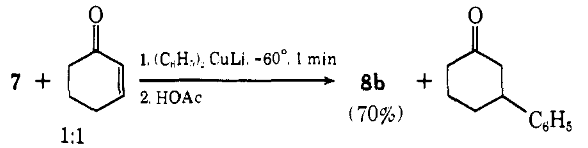
Specifically, reaction of *p*-toluenesulfonylazocyclohex-1-ene (**7**) (prepared from the tosylhydrazone of α-bromocyclohexanone by the method of Caglioti[30]) with lithium diphenylcuprate or phenylcopper leads to complete consumption of starting material within 1 min (−60°, THF-ether) concurrent with the production of pure α-phenyltosylhydrazone **8b** (70–75%).[31-35]



7

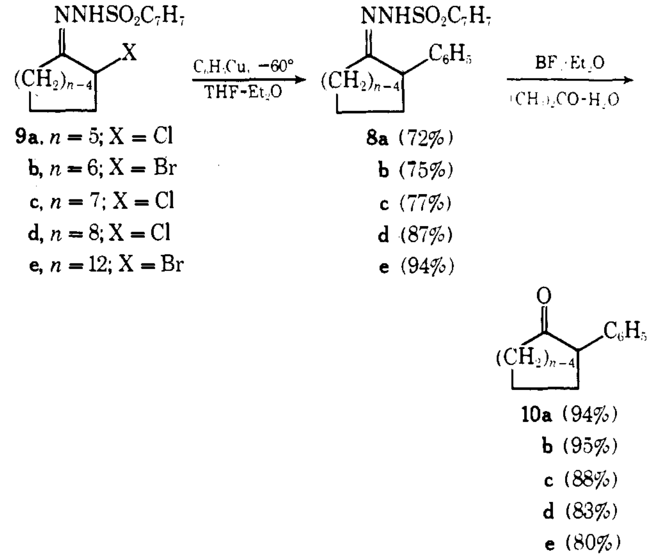
8b

The considerable reactivity of azo-ene **7** can be further demonstrated in a competition experiment. Addition of a 1:1 mixture of **7** and cyclohexenone to 1 equiv of $(C_6H_5)_2CuLi$ in THF-ether at −60°, followed by quenching with acetic acid after 1 min, yields product only resulting from reaction of azoene **7**, the enone being recovered unchanged.



In attempting to generalize this reaction, it became increasingly more obvious that in many cases the labile tosylazoenes could not be obtained in sufficient yield and purity to be synthetically useful.[36,37]

Since azoenes may be generated in situ, there is fortunately no need to isolate them. For example, reaction[38] (−60°, THF-ether, 5 min) of a series of α-halotosylhydrazones (**9a–e**)[32,33] (prepared[30b] from the corresponding α-halo ketone,[39] average yield 78%) with an excess (2.5–3.0 equiv) of phenylcopper (1 equiv serving as base for azoene generation) smoothly produces the α-phenyltosylhydrazones **8a–e**,[32,33] which may be converted in high yield via carbonyl exchange[40] to the corresponding α-phenyl ketones **10a–e**.[32,33]

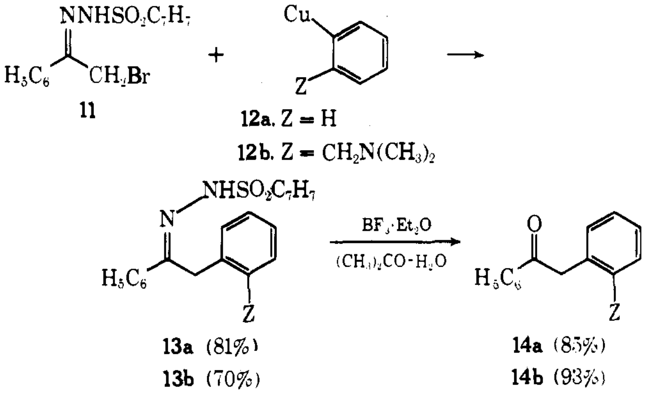


9a, $n = 5$; X = Cl
b, $n = 6$; X = Br
c, $n = 7$; X = Cl
d, $n = 8$; X = Cl
e, $n = 12$; X = Br

8a (72%)
b (75%)
c (77%)
d (87%)
e (94%)

10a (94%)
b (95%)
c (88%)
d (83%)
e (80%)

Although reaction of the tosylhydrazone of phenacyl bromide **11** with phenylcopper still proceeds rapidly under the standard conditions,[38] similar reaction with the more stable *o*-(dimethylaminomethyl)phenylcopper (**12b**)[41,42] requires more forcing conditions (−20°, 0.5 hr).



11

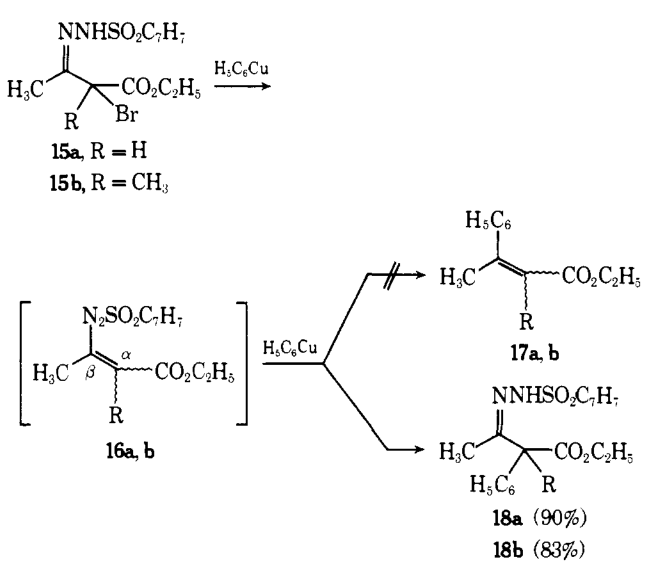
12a, Z = H
12b, Z = $CH_2N(CH_3)_2$

13a (81%)
13b (70%)

14a (85%)
14b (93%)

The further utility of the tosylazo olefin group as an enolonium synthon is demonstrated in the reaction of α-bromo-β-keto ester tosylhydrazones **15a,b**[43] with phenylcopper. Conceptually, intermediates **16a,b** could either produce cinnimate esters **17a,b** via β-phenyl addition (followed by extrusion of nitrogen and *p*-toluenesulfinic acid)[44] or tosylhydrazones **18a,b** via α-addition. Examination of the product mixture by VPC revealed no detectable amounts of esters **17a,b**.[45] Hydrolysis of tosylhydrazones **18a,b** by the usual method[40] produced the corresponding α-phenyl-β-keto esters in high yield.

Although the primary goal of this investigation was to provide methodology (in combination with the excellent regiospecific procedures available for the synthesis of α-halo carbonyl compounds[46]) for the α-arylation (alkylation[34]) of



carbonyl groups,[47] the α-aryl (alkyl[34]) tosylhydrazones produced via the azoene route should serve equally well as precursors for previously established tosylhydrazone (carbene, olefin, methylene, etc.) transformations.[48]

Acknowledgment. We wish to thank Research Corporation for their generous support of this research.

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(14) An additional approach to nucleophilic aromatic substitution has been investigated by the Cornell group which utilizes chromium tricarbonyl complexes for arene activation. Although these reagents serve well as phenyl cation synthons when used in combination with relatively basic anions, as yet they have not proven effective for phenylation of ketone enolates: M. F. Semmelhack and H. T. Hall, *J. Am. Chem. Soc.*, **96**, 7091 (1974); M. F. Semmelhack, H. T. Hall, M. Yoshifuji, and G. Clark, *ibid.*, **97**, 1247 (1975).

(15) A further complication with the SRN1 reaction[10-13] is that secondary alkyl enolates such as that from diisopropyl ketone give only poor yields of α-aryl ketones: personal communication, M. F. Semmelhack, Cornell University.

(16) The reaction of cyclic α-chloro ketones with aryl Grignard reagents, followed by isomerization of the initially formed chlorohydrin allows synthesis of several simple α-aryl ketones. Clearly this procedure is limited to those ketones which do not bear additional carbonyl functionality: A. S. Hussey and R. R. Herr, *J. Org. Chem.*, **24**, 843 (1959).

(17) Another method (which can be considered to be a hybrid of modes (A) and (B)) for the synthesis of α-aryl ketones is the reaction of α-bromo enolates with aryl boranes: H. C. Brown and M. M. Rogić, *J. Am. Chem. Soc.*, **91**, 4304 (1969); H. C. Brown, H. Nambu, and M. M. Rogić, *ibid.*, **91**, 6852 (1969).

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(25) Our specific experience is that reaction of α-halocyclohexanone 4 (X = Cl, Br) with lithium diphenylcuprate (Et_2O–THF, −60°, 4 hr) yields predominantly reduction product **6** (66%, 80%) with only minor amounts of α-phenyl ketone **5** (9%, 4%). Similar reaction with phenacyl bromide produces only the reduced product, acetophenone (67%). Reaction of chlorocyclohexanone with phenylcopper (Et_2O–THF, −20°, 5 hr) gives 94% recovered starting material, 4% phenylation, and 2% reduction; bromocyclohexanone gives 23% phenylation and 76% reduction; and phenacyl bromide yields 68% recovered starting material, 5% reduction, and no detectable phenylation product.

(26) Methods based on the reaction of Ar_2CuLi with α,α′-dibromo ketones (similar to their reaction with R_2CuLi; see ref 18, 22, C. Lion and J. E. Dubois, *Tetrahedron*, **31**, 1223 (1975); and G. H. Posner, J. J. Sterling, C. E. Whitten, and D. J. Brunelle, *J. Am. Chem. Soc.*, **97**, 107 (1975) were not pursued because of the anticipated lack of regiochemical control in the case of unsymmetrical dihalo ketones.

(27) G. H. Posner, *Org. React.*, **19**, 1 (1972).

(28) Simple pK_a comparison of the product anions (tosylhydrazone, pK_a ~10; enolate, pK_a ~ 16) leads to the prediction that the azoene should be superior to enone as an acceptor on conjugate-addition reactions.

(29) The 1,4-addition of β-dicarbonyl compounds to azoenes has previously been reported: S. Brodka and H. Simon, *Justus Liebigs Ann. Chem.*, **745**, 193 (1971); L. Bernardi, P. Masi, and G. Rosini, *Ann. Chim. (Rome)*, **63**, 601 (1973).

(30) L. Caglioti, P. Grasselli, F. Morlacchi, and G. Rosini, *Chem. Ind. (London)*, 25 (1968); A. Dondoni, G. Rosini, G. Mossa, and L. Caglioti, *J. Chem. Soc. B*, 1404 (1968).

(31) Identical in all respects with an authentic sample.

(32) This material exhibits spectra (ir, NMR, MS, and exact mass) in accord with its assigned structure.

(33) All reactions are run on a 1-5 mmol scale, and no attempt has yet been made to maximize the yields.

(34) This reaction is not limited to the arylcopper reagent. Reaction of **7** with $(CH_3)_2CuLi$ or $[(CH_3)_3C]_2CuLi$ also smoothly produces the tosylhydrazones of α-methyl (85%) and α-*tert*-butyl (70%) cyclohexanone, respectively.[31-33] The full scope and limitations of this polarity-inversion alkylation reaction will be reported in due course.

(35) Reaction of **7** with phenyllithium (−78°) leads to a complicated product mixture.

(36) Several of the pathways for azoene decomposition have been enumerated: ref 30; G. Rosini and R. Ranza, *J. Org. Chem.*, **36**, 1915 (1971); G. Rosini and S. Cacchi, *ibid.*, **37**, 1856 (1972); L. Caglioti, F. Gasparrini, and G. Paolucci, *ibid.*, **38**, 920 (1973).

(37) Samples of azoenes should be stored in the freezer in vented containers. In one instance a sample of **7** which had warmed to room temperature developed sufficient pressure to blow the lid off a snap-cap vial.

(38) Phenyllithium (3.0 mmol in benzene) is added to an ether (5 ml) suspension of purified (*Inorg. Synth.*, **7**, 9 (1963)) CuI (3.3 mmol) and the reaction is stirred (−5°) until a negative Gilman test (*J. Am. Chem. Soc.*, **47**, 2002 (1925)) results (~5 min). To this suspension is added THF (5 ml) and the mixture is cooled to −60°. α-Halotosylhydrazone (1.0 mmol, 5 ml of THF) is added via syringe with maintenance of the reaction temperature at −60°. Analysis by TLC (SiO_2) indicates the reaction to be complete within 5 min. The reaction is quenched by addition of HOAc (5 mmol) and warmed to room temperature. The reaction mixture is added to an NH_4Cl–NH_4OH solution (*Org. React.*, **19**, 1 (1972)) and extracted twice with THF and once with ether. Drying over $MgSO_4$, removal of the solvent, and washing the crude solid with hexane (to remove biphenyl from commercial phenyllithum) produces pure tosylhydrazones in the isolated yields indicated.

(39) **9a,c**, and **d** are commercially available. **9b** was prepared according to the method of Brown: *J. Am. Chem. Soc.*, **90**, 6218 (1968). **9e** was prepared according to the method of Bauer: *J. Org. Chem.*, **40**, 1990 (1975).

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(42) In this instance the copper compound was not isolated but simply formed by addition of CuI (in diisopropyl sulfide) to the corresponding organolithium compound prepared by the method of Hauser (*J. Org. Chem.*, **32**, 1479 (1967)).

(43) Bromides were prepared by the method of Brühl (*Chem. Ber.*, **36**, 1722 (1903)).

(44) Addition–elimination reactions of *cuprates* with β (OR and SR) substituted α,β-unsaturated esters have been reported: C. P. Casey, D. F. Martin, and R. A. Boggs, *Tetrahedron Lett.*, 2071 (1973); G. H. Posner and D. J. Brunelle, *J. Chem. Soc., Chem. Commun.*, 907 (1973).

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(47) The standard procedure also serves well for the synthesis of an α-phenylaldehyde: α-bromohydrocinnamaldehyde (prepared from the silyl enol ether[46]) can be converted to the tosylhydrazone (90%), phenylated (88%), and hydrolyzed[40] (65%) to give 2,3-diphenylpropionaldehyde.

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