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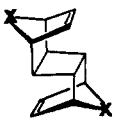
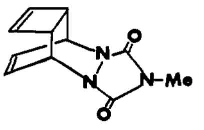


6: X = C(OMe)$_2$

7: X = C$_2$(CO$_2$Me)$_2$

melting point and by comparison of ir and nmr spectra with those of an authentic sample kindly supplied by Professor Schröder. Observation of the course of this reaction by nmr spectroscopy provides evidence that diadduct formation occurs by generation and entrapment of first one and then the other of the cyclohexadiene moieties. This suggests that in the absence of dienophile a similar stepwise decarbonylation may occur and that the resulting monoketone may decompose without ever forming **1a**.

The alternative route avoids this difficulty by the use of two different masking groups, the second of which can be removed under very mild conditions. Debromination of the cyclooctatetraene[8] dibromide–*N*-methyltriazolinedione adduct with zinc gives **8**.[7,9] The cyclobutene double bond of this intermediate can be made to function selectively as a dienophile toward α-pyrone,[10] and the resulting lactonic adduct[7] suffers smooth decarboxylation at 160° in *o*-dichlorobenzene to give the singly-masked precursor **9**.[7]



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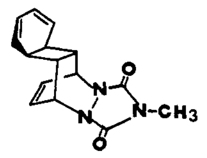
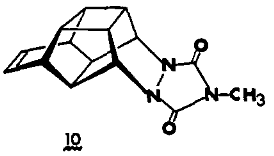


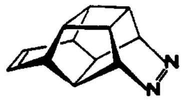
9

Hydrolysis of **9** with boiling KOH–*i*-PrOH gives the corresponding semicarbazide, which can but need not be isolated. Direct treatment of the neutralized hydrolysis mixture with CuCl$_2$[11] under N$_2$ at 0° gives (presumably *via* the unstable azo compound) the dibenzene **1a** in 35% yield.

A hypothetical rearrangement scheme for effecting a face-to-face juxtaposition of the two cyclohexadiene moieties would involve reversible ring opening of the tricyclic system of the anti isomer **1a** to a bicyclo[6.4.0]-dodecapentaene and recyclization in the syn form **1b**. This is impractical in the hydrocarbon system because of the instability of **1a**, but a related anti → syn rearrangement can be effected in the protected compound **9**. Prolonged heating of **9** at 160° results in gradual conversion to the hexacyclic derivative **10**.[7] The nmr spectrum of this substance shows an N-Me singlet (3 H, δ 3.05) and six two-proton absorptions at δ 6.24, 4.28, 2.93, 2.69, 2.34, and 2.17. Its mass spectrum shows a strong parent peak at *m*/*e* 269 (base peak of the spectrum), in contrast to that of **9**, which shows a relatively weak parent peak and a base peak at *m*/*e* 78, corresponding to C$_6$H$_6^+$. This rearrangement must involve a bicyclooctadiene → cyclooctatriene valency tautomerism in the anti compound **9**, reclosure in the syn stereochemistry, and intramolecular entrapment of the cyclohexadiene by a Diels–Alder reaction. Hydrolysis and oxidation of **10** give the pentacyclic azo compound **11**.[7] Although efforts to eliminate N$_2$ from **11** so far have been unsuccessful, methods for converting this azo compound or similar substances with other masking groups to **1b** (and/or **2**, which is related hypothetically to **1b** by Cope rearrangement) or to other (CH)$_{12}$ compounds are under investigation.



10



11

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[8] We are grateful to Dr. H. Pommer and the Badische Anilin und Soda Fabrik, Ludwigshafen, for a generous sample of cyclooctatetraene.

[9] For the *N*-phenyl analog, see D. G. Farnum and J. P. Snyder, *Tetrahedron Lett.*, 3861 (1965).

[10] Prepared according to H. E. Zimmerman, G. L. Grunewald, and R. M. Paufler, *Org. Syn.*, **46**, 101 (1966).

[11] *Cf.* M. Heyman, V. T. Bandurco, and J. P. Snyder, *J. Chem. Soc.*, *D*, 297 (1971). We are indebted to these authors for personal communication of further details of their method of azoalkane synthesis.

[12] Supported by a Predoctoral Fellowship (GM-40, 824), sponsored by the National Institute of General Medical Sciences, 1968–1971.

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Silane Reductions in Acidic Media. I. Reduction of Aldehydes and Ketones in Alcoholic Acidic Media. A General Synthesis of Ethers

Sir:

Acetals and ketals,[1] aldehydes and ketones,[2] and esters and lactones[3] have been reduced to ethers using a variety of reducing agents. Of these methods the catalytic hydrogenation of aldehydes and ketones in alcoholic acidic media (eq 1) appears to provide the most

$$R_2C{=}O + H_2 + R'OH \xrightarrow[H^-]{Pt} R_2CH{-}OR' + H_2O \qquad (1)$$

general and convenient route to symmetrical and unsymmetrical ethers.[2] However, hydrocarbon formation competes with ether production, and yields are low when aldehydes are reduced or when the alcohol used is larger than propyl.[2a] We wish to report that trialkylsilanes reduce aldehydes and ketones in alcoholic acidic media to ethers. In a reaction analogous to that given in eq 1, the use of alcohols directs product formation to the ethers and trialkylsilanol (eq 2).

$$R_2C{=}O + R'_3SiH + R''OH \xrightarrow{H^-} R_2CHOR'' + R'_3SiOH \qquad (2)$$

In a typical experiment 1.0 ml of 97% sulfuric acid was added dropwise to a stirred solution of methanol (2.5 ml) containing benzaldehyde (5.0 mmol) and triethylsilane (5.5 mmol) at 0°. The resulting heterogeneous[4] solution was warmed to room temperature

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[1] (a) W. L. Howard and J. H. Brown, Jr., *J. Org. Chem.*, **26**, 1026 (1961); (b) E. L. Eliel, V. G. Badding, and M. N. Rerick, *J. Amer. Chem. Soc.*, **84**, 2371 (1962); (c) I. A. Kaye and I. C. Kogon, *ibid.*, **73**, 4893 (1951); (d) E. Frainnet and C. Esclamadon, *C. R. Acad. Sci.*, **254**, 1814 (1962).

[2] (a) M. Verzele, M. Acke, and M. Anteunis, *J. Chem. Soc.*, 5598 (1963); (b) M. Acke and M. Anteunis, *Bull. Soc. Chim. Belges*, **74**, 41 (1965).

[3] G. R. Pettit and D. M. Piatak, *J. Org. Chem.*, **27**, 2127 (1962), and previous articles in this series.

[4] Silane and silanol are only partially soluble in the reaction medium.

and stirred for 1 hr. The work-up procedure involved addition of pentane and a saturated solution of sodium chloride, separation of the resulting liquid phases, and washing of the aqueous solution with pentane; the combined pentane extracts were dried and the pentane distilled. Benzyl methyl ether and benzyl alcohol (and dibenzyl ether) were isolated in 87 and 4% yields, respectively. Triethylsilanol was the only silane product. Pmr analysis both before and after work-up showed the same relative amounts of products, indicating that there was no selectivity in product loss during product isolation.

When trifluoroacetic acid or trichloroacetic acid was used in place of sulfuric acid, the reaction medium was homogeneous. The progress of reduction was followed by pmr spectroscopy, and absolute yields were obtained by using an internal standard. In this manner the triethylsilane reduction of benzaldehyde in methanol–trifluoroacetic acid was observed to give benzyl methyl ether (97%) and dibenzyl ether (3%). The isolated yield of benzyl methyl ether was 87%.

Table I. Reduction of Aldehydes and Ketones by Triethylsilane in Alcoholic Acidic Media[a]

$R_2C{=}O$	R''OH	Acid	Mol of acid/ mol of R''OH	Isolated yield, % R_2CHOR''[b]
Benzaldehyde	Methanol	H_2SO_4	0.29	87[c]
	Methanol	CF_3CO_2H	2.2	87[c]
	Methanol	CCl_3CO_2H	1.5	85[c]
	Ethanol	H_2SO_4	0.42	87[c]
	1-Propanol	H_2SO_4	0.34	68[c]
	2-Propanol	H_2SO_4	0.54	69[c]
	1-Heptanol	CF_3CO_2H	2.0	81[c]
	2-Methyl-2-propanol	CF_3CO_2H	1.2	26
	2-Methyl-2-propanol	H_2SO_4	0.30	45
Heptanal	Methanol	H_2SO_4	0.30	87[d]
	Benzyl alcohol	CF_3CO_2H	2.0	49[d]
Cyclohexanone	Methanol	CF_3CO_2H	3.0	88[d]
	Ethanol	CF_3CO_2H	3.0	68[e]
	Ethanol	H_2SO_4	0.45	44[f]
Benzophenone	Methanol	H_2SO_4	0.23	43[g]

[a] Reactions were run at room temperature (28 ± 3°). Reactants were commercially available; 5.0 mmol of carbonyl compound and 5.5 mmol of triethylsilane were used. [b] Based on carbonyl compound treated and obtained by pmr analyses using an internal standard. Products were analyzed by adding an internal standard and using glpc and pmr analyses. Isolated yields refer to products recovered after extraction as described in the text. Due to the small amount of reactants, distillation was not feasible. [c] Less than 10% yields of other reduction products are formed. [d] Only product isolated; no other product observed. [e] 21% cyclohexyl trifluoroacetate also produced. [f] 46% cyclohexanol also obtained. [g] Diphenylmethane also formed.

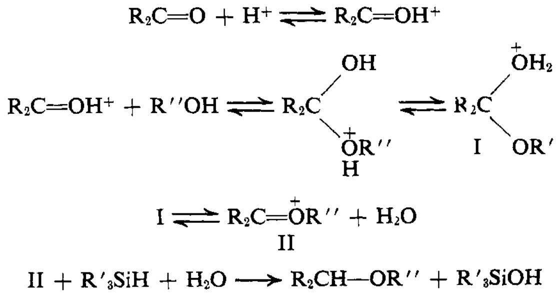
Results from the reductions of representative aldehydes and ketones in a variety of alcoholic solutions using a similar procedure are given in Table I. These results represent the optimum conditions for ether production; unless otherwise indicated, side products were formed in less than 10% yield based on the carbonyl compound. No attempt was made to maximize product recovery from each reaction. Competing reactions included direct reduction to the corresponding alcohol or formation of the symmetrical ether derived from the carbonyl compound. Except for the preparation of benzyl *tert*-butyl ether and benzhydryl methyl ether, required reaction times were 1 hr or less; reductions of benzaldehyde in *tert*-butyl alcohol were complete within 24 hr, and the benzophenone reduction required more than 1 week. The molar ratio of alcohol to carbonyl compound was varied between 5:1 and 10:1 with little difference in relative product yields. Sulfuric, trifluoroacetic, and trichloroacetic acids were all found to be effective catalysts. With formic acid the reduction products consisted mainly of alkyl formate. The molar ratio of acid to alcohol most effective in yielding ethers from aldehyde reductions (greater than 70% isolated yield) ranged from 0.15 to 1.0 for sulfuric acid and from 0.65 to 2.2 for trifluoroacetic acid. The optimum yield of benzyl *tert*-butyl ether was obtained using a low concentration of sulfuric acid (0.25 ml in 2.8 ml of *tert*-butyl alcohol).

Cyclohexanone reductions by triethylsilane required a greater concentration of acid than that used for aldehyde reductions. Trifluoroacetic acid was more effective than sulfuric acid and gave the best results when the mole ratio of trifluoroacetic acid to alcohol was 3.0. At lower concentrations of acid the yield of cyclohexyl trifluoroacetate, the only side product formed, was substantially increased.[5] With sulfuric acid the optimum yield of cyclohexyl ethyl ether (44%) was obtained with an acid to alcohol ratio of 0.45; with either more or less sulfuric acid additional cyclohexanol was formed at the expense of the ether.

Products were identified by pmr and glpc comparison to authentic samples. Additionally, benzyl *tert*-butyl ether, benzyl heptyl ether, heptyl methyl ether, and cyclohexyl ethyl ether were independently isolated by gas chromatography from the product mixtures after work-up and identified by pmr spectroscopy. Triethylsilanol was the only observed silane product. Isolated yields of products were based on glpc and/or pmr analyses using an internal standard. Duplicate runs showed a variation in the relative yields of ether to side products of ±2%.

The production of ethers from carbonyl compounds by silane reduction in alcoholic acidic media can be explained by the mechanism given in Scheme I. We

Scheme I



$$R_2C{=}O + H^+ \rightleftharpoons R_2C{=}OH^+$$

$$R_2C{=}OH^+ + R''OH \rightleftharpoons R_2C(OH)(\overset{+}{O}HR'') \rightleftharpoons \underset{\mathrm{I}}{R_2C(\overset{+}{O}H_2)(OR'')}$$

$$\mathrm{I} \rightleftharpoons \underset{\mathrm{II}}{R_2C{=}\overset{+}{O}R''} + H_2O$$

$$\mathrm{II} + R'_3SiH + H_2O \longrightarrow R_2CH{-}OR'' + R'_3SiOH$$

have shown that when II is produced independently, reduction by triethylsilane yields the corresponding ether.[6] The major competing reaction is the formation of alcohol and is due to the production of water in the

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(5) With the trifluoroacetic acid to ethanol ratio of 2.0, cyclohexyl trifluoroacetate was formed in 33% yield; at at corresponding ratio of 1.2 the yield of cyclohexyl trifluoroacetate was 61%.

(6) M. P. Doyle, W. Wierenga, and J. E. DeBoer, 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March 1971, No. ORGN-15.

reaction medium, mainly from the esterification of the acid catalyst by alcohol. When a known amount of water was added to the reaction mixture containing benzaldehyde, so that the mole ratio of methanol to water was 1.5, the mole ratio of products, benzyl methyl ether to benzyl alcohol, was 0.65. This result indicates that water is better able to direct the course of reduction than methanol by more than a factor of two. In fact, when water is used in place of alcohol, aldehydes and ketones are nearly quantitatively reduced to the corresponding alcohol.[7] Ether formation from the alcohol does not occur under our reaction conditions.

Although benzophenone can be reduced to benzhydryl methyl ether in moderate yields, this product is labile under the reaction conditions and is reduced to diphenylmethane. Corresponding silane reductions of compounds that form relatively stable carbenium ions have been previously observed.[8]

Our results indicate that silane reductions of aldehydes and ketones in alcoholic acidic media represent a new and general method for the preparation of ethers. We are continuing investigations directed toward the synthesis of ethers, alcohols, and alcohol derivatives by silane reduction of carbonyl compounds. Preliminary evidence suggests that carboxylate esters, as well as compounds containing other functional groups, may be prepared by the silane reduction of carbonyl compounds using a similar procedure.

Acknowledgment. Support for this work from the Research Corporation and National Science Foundation is gratefully acknowledged. We wish to thank Miss Mary Zaleta for participation in part of this study.

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(7) Presented at the 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971.

(8) F. A. Carey and H. S. Tremper, *J. Org. Chem.*, **36**, 758 (1971), and previous articles in this series.

(9) National Science Foundation Undergraduate Research Participant, Summer 1971.

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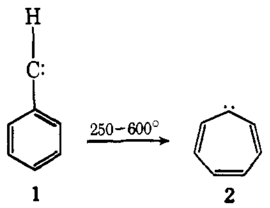
Received November 8, 1971

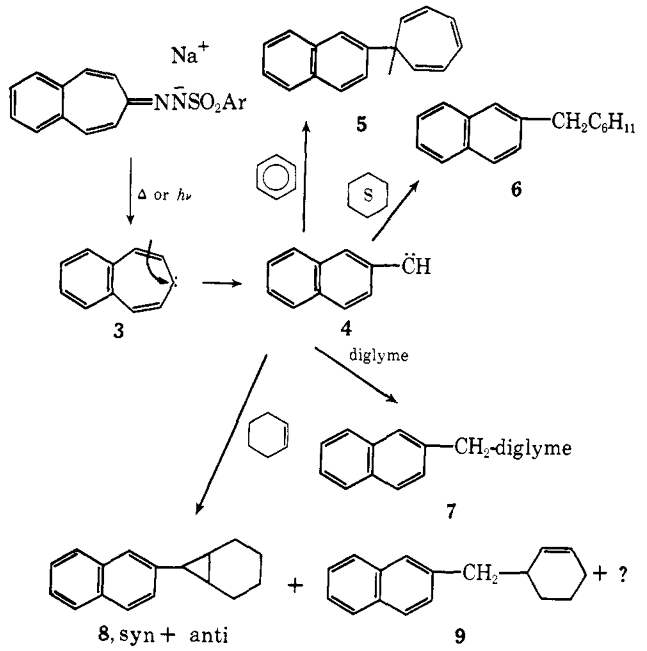
An Example of a Low-Temperature Carbene–Carbene Rearrangement in Solution

Sir:

To date, the interconversion of aryl and aromatic carbenes[1-6] (and nitrenes[4,5]), such as the conversion of phenylcarbene (1) to cycloheptatrienylidene (2), has been limited to the gas phase[7] and rather high temperatures (250–600°).[1-4] At this time, we would like to report the rearrangement of benzocycloheptatrienylidene (3) to β-naphthylcarbene (4) in solution at temperatures as low as room temperature (and, possibly, as low as −55°). This constitutes an example of a carbene–carbene rearrangement which apparently is not subject to either of the previous restrictions (Scheme I).



Scheme I



Benzocycloheptatrienylidene was generated from the corresponding tosylhydrazone sodium salt both thermally and photolytically. Temperatures in the range of 100° were required to effect thermal decomposition. There were no temperature restrictions on the photolyses although we have not yet satisfied ourselves that low-temperature (below room temperature) runs cannot involve an intermediate which gives products during work-up. Rearranged naphthylcarbene was detected by its reaction products with solvent. For example, decomposition of the salt in benzene (80° thermal, 30° photolytic) gave naphthylcycloheptatriene (5)[9-11] as the major product (97 and 59%, respectively) and its decomposition in cyclohexane gave a good yield (51%

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(1) R. C. Joines, A. B. Turner, and W. M. Jones, *J. Amer. Chem. Soc.*, **91**, 7754 (1969); J. A. Myers, R. C. Joines, and W. M. Jones, *ibid.*, **92**, 4740 (1970), and references cited therein.

(2) T. Mitsuhashi and W. M. Jones, *ibid.*, **94**, 677 (1972).

(3) G. G. Vander Stouw, A. R. Kraska, and H. Shechter, *ibid.*, **94**, 1655 (1972); G. G. Vander Stouw, *Diss. Abstr.*, **25** (12), 6974 (1965); *Chem. Abstr.*, **63**, 13126*b* (1965), under the direction of H. Shechter; W. J. Baron, M. Jones, Jr., and P. P. Gaspar, *J. Amer. Chem. Soc.*, **92**, 4739 (1970); E. Hedaya and M. E. Kent, *ibid.*, **93**, 3283 (1971), and references cited.

(4) C. Wentrup and W. D. Crow, *Tetrahedron*, **27**, 361 (1971); C. Wentrup, *ibid.*, **26**, 367 (1970); C. Wentrup and K. Wilczek, *Helv. Chim. Acta*, **53**, 1459 (1970), and previous references.

(5) R. J. Sundberg and S. R. Suter, *J. Org. Chem.*, **35**, 827 (1970), and previous references.

(6) P. Ashkenasi, S. Lupan, A. Scharz, and M. Cais, *Tetrahedron Lett.*, 817 (1969).

(7) For example, we have found that phenylcarbene, when generated in diglyme (up to 165°), shows only solvent insertion products and azine with no detectable trace of heptafulvalene, the dimer of cycloheptatrienylidene. Likewise, under all conditions studied to date (up to 210° in diglyme), cycloheptatrienylidene in solution gives no phenylcarbene products. Possible exceptions to this generality include the base-induced ring contraction of ferrocenyltropyl cations,[6] the formation of azepines from the decomposition of aryl azides in the presence of aliphatic amines,[8] and the formation of pyridine products from reaction of aromatic nitro compounds with triethyl phosphite. In none of these cases, however, has a carbene–carbene rearrangement been confirmed.

(8) R. Huisgen, D. Vossins, and M. Appl, *Chem. Ber.*, **91**, 1 (1958).

(9) C. Jutz and F. Voithenleitner, *ibid.*, **97**, 29 (1964).

(10) Except where noted all new compounds showed spectral properties and analyses consistent with the assigned structures.

(11) Authentic sample prepared for comparison from the reaction of β-naphthyldiazomethane (or the tosylhydrazone salt) with substrate.