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(9) Spectra: NMR ($CDCl_3$, 60 MHz) δ 7.3–6.8 (4 H), 3.4–2.2 (10 H), 2.2–2.1 (4 H), 2.1–1.5 (4 H), 1.2–0.6 (5 H); ir (KBr, HCl salt) 2930, 2670, 1708, 756, 726 cm^{-1}.
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William F. Michne
Sterling-Winthrop Research Institute
Rensselaer, New York 12144

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Improved Procedures for the Reductive Coupling of Carbonyls to Olefins and for the Reduction of Diols to Olefins

Summary: Active Ti^0 powder is a superior reagent for coupling carbonyls to olefins and for reducing diols to olefins.

Sir: We recently reported that ketones, on treatment with a low-valent titanium reagent prepared from $LiAlH_4$–$TiCl_3$, undergo reductive dimerization to produce coupled olefinic products in high yield.[1] Simultaneously, other workers found that low-valent titanium reagents prepared from $Zn–TiCl_4$[2] or $Mg–TiCl_3$[3] effect similar reductive couplings. Interestingly enough, however, whereas we found that both saturated aliphatic ketones and aromatic ketones couple to olefins, these other workers reported success only with aromatic ketones. Saturated aliphatic ketones were observed to undergo only pinacol dimerization to diols without subsequent deoxygenation. Although others have repeated our reactions,[4] and indeed tetraisopropylethylene, one of the more hindered olefins yet synthesized, has been made by two groups[5,6] using our method, we have nevertheless observed since our publication that the coupling of saturated aliphatic ketones to produce olefins can be erratic. Successful results seem to be dependent on the specific batches of reagents used.

We have expended considerable effort in attempts to overcome this problem, and we now report an improved procedure. We have found that an active Ti^0 metal powder, prepared by Rieke's general method,[7] smoothly couples saturated ketones and aldehydes to olefins. In a representative reaction, $TiCl_3$ (1.54 g, 10.0 mmol) was slurried under nitrogen in 50 ml of dry tetrahydrofuran. Potassium pieces (1.25 g, 32 mmol) were added and the mixture was refluxed for 45 min. Cyclohexanone (0.25 g, 2.5 mmol) was added in 5 ml of THF and the reaction was refluxed 12 hr. After cautious quenching of the reaction with ethanol, filtration through sintered glass and evaporation of solvent provided the coupled olefin in 85% yield. We have repeated this reaction with different batches of $TiCl_3$ from three suppliers and have found it to be reproducible. Some of our results are given in Table I.

Table I. Reductive Coupling of Some Carbonyl Compounds to Olefins with Active Ti^0

$$R_2C{=}O + Ti^0 \rightarrow R_2C{=}CR_2$$

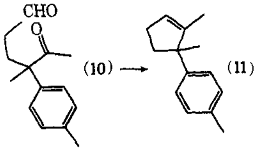
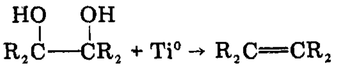
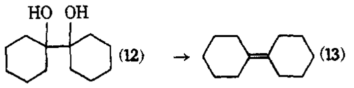
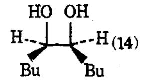
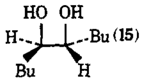
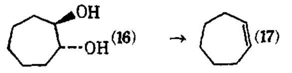
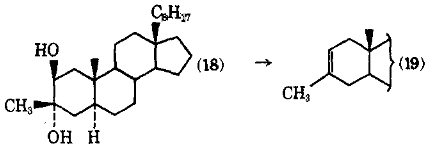
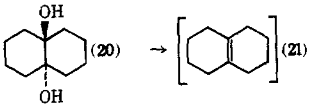
	Isolated olefin yield, %
Cyclopentanone (1)	40
Cyclohexanone (2)	85
Cycloheptanone (3)	86
Cyclooctanone (4)	70
Cyclododecanone (5)	90
Adamantanone (6)	91
Cholestanone (7)	85
Diisopropyl ketone (8)	40
Valeraldehyde (9)	77 (7:3 trans:cis)
	55

Table II. Reduction of Some 1,2 Diols to Olefins with Active Ti^0



$$R_2C(OH){-}C(OH)R_2 + Ti^0 \rightarrow R_2C{=}CR_2$$

		Isolated olefin yield, %
		85
	→ 5-decene (60:40 trans/cis)	75[a]
	→ 5-decene (90:10 trans/cis)	80[a]
		55
		80
		0

[a] VPC yields.

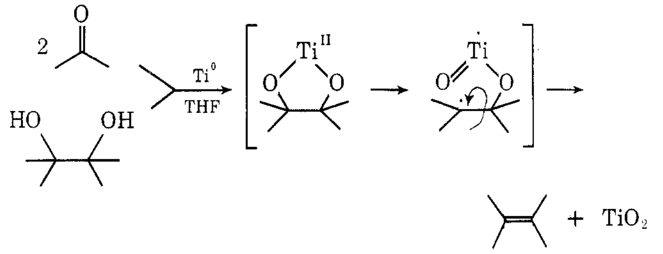
Perhaps the most interesting entries in Table I are the last three. Diisopropyl ketone gives tetraiisopropylethylene (40%) in a yield much higher than that reported[5,6] using $LiAlH_4$–$TiCl_3$ as the coupling agent; so it is clear that quite hindered ketones can be made in acceptable yield. Aldehydes also couple in good yield, but a mixture of double-bond isomers is formed. A control experiment, in which pure *cis*-5-decene was submitted to coupling conditions, indicated that no isomerization of product occurs after the reaction. Intramolecular dicarbonyl coupling to form rings is also possible, although, in the case indicated, the yield is only moderate.

Since pinacol dianions are formed as intermediates in the coupling reaction,[1-3] one would expect Ti^0 to reduce other 1,2 diols to olefins, and we have found this to be the case. It is not necessary to preform the dianions since free diols reduce directly (presumably the dianions are formed in situ by reaction with Ti^0). Some of our results are given in Table II.

Several of the examples require special comment, and provide information which bears on the reaction mechanism. Both the meso and *dl* diols from 5-decene reduce in good yield, but neither reaction is stereospecific. Both the trans diequatorial diol **16** and the trans diaxial diol **18** reduce in good yield, although diol **20** is not reduced.

We wish to reserve a detailed discussion of our mechanistic studies for a full paper to be published later. We simply point out now, however, that all of our data are consistent with the suggestion that a five-membered ring intermediate is formed and then collapses in a nonconcerted manner.

Diaxial glycol **18** can form the required intermediate via a boat conformer, but glycol **20** cannot and is therefore unreactive.



In summary, we have developed new procedures for the reductive coupling of saturated ketones[8] and aldehydes to olefins and for the reduction of 1,2 diols to olefins. These reactions may well be of considerable use in synthesis.

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John E. Mc Murry,* Michael P. Fleming
Thimann Laboratories, University of California
Santa Cruz, California 95064

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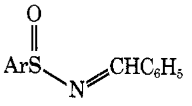
Trimethylsilyl 2-Nitrobenzenesulfenate (2-Nitrobenzenesulfenic Acid)

Summary: Trimethylsilyl 2-nitrobenzenesulfenate, prepared by heating *N*-benzylidene-2-nitrobenzenesulfinamide with trimethylsilyl chloride, is a convenient, high yield source of 2-nitrobenzenesulfenic acid and 2-nitrobenzenesulfenate ion when treated with alcohol and alkoxides, respectively.

Sir: Sulfenic acids are believed to be important intermediates in a variety of organic sulfur reactions including biological transformations.[1] However, their high reactivity and the lack of mild methods to prepare them has hindered a systematic study of their reactions and properties. Of the aromatic sulfenic acids, 2-nitrobenzenesulfenic acid (1) has been the most studied.[2] It is generally believed to be formed in the neutral or alkaline hydrolysis of sulfenyl halides,[2a,c] disulfides,[2h] and sulfenate esters.[2e–g] The major products isolated in these reactions are disulfide (ArSSAr), thiolsulfonate ($ArSO_2SAr$), and sulfinic acid ($ArSO_2H$).[2] Under certain conditions, orthanilic acid is also obtained.[2a,c,g] These products are all believed to involve initial formation of the sulfenic acid, **1**, with the disulfide and thiolsulfonate being formed by reaction of the solvent with the intermediate thiolsulfinate [ArS(O)SAr].[2–4] As a consequence of the methods used to generate **1**, neither the sulfenic acid nor the thiolsulfinate has ever been isolated.

ArSOX
1, X = H
2, X = $SiMe_3$



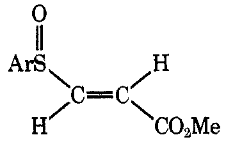
3

Ar = 2-nitrophenyl

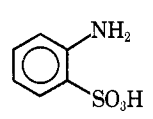
Recently, we reported that the thermolysis of *N*-alkylidenearenesulfinamides is a useful method for generating arylsulfenic acids under mild nonaqueous conditions.[3] We wish to report the use of this method to prepare trimethylsilyl 2-nitrobenzenesulfenate (**2**) which when treated with alcohol provides a convenient high-yield source of **1**. The reactions of **1** prepared in this way are reported.

Compound **2** is a bright-orange liquid obtained in 75–80% yield by heating **3**[3,5] (mp 103–104°)[6] with trimethylsilyl chloride–hexamethyldisilazane (2:1)[1d] and is the first example of the trapping of an unstable sulfenic acid by these reagents. The similarity of the ir and NMR spectra of **2** with that of methyl 2-nitrobenzenesulfenate[7] is evidence for the proposed structure.[8]

When **2** was treated with 4 equiv of ethanol in the presence of methyl propynoate, **4** (mp 153–154°)[6] was obtained in 82% yield confirming that **2** is an unequivocal, high-yield source of **1**. The formation of **1** from **2** in ethanol–water–HCl and ethanol–water mixtures gave orthanilic acid (**5**, 54–66%) and **6** (mp 53–54°,[6] 15–20%) as major products. Disulfide and thiolsulfonate were minor products. These conditions are similar to those in which **1** is believed to be formed from sulfenyl halides.[2a,b]



4



5

$$ArS(=O)OCH_2CH_3$$

6

The sequence of steps leading from **1** to **5** is unknown, although the ability of an *o*-nitro group to exchange its oxygens with an adjacent sulfur is well known.[9] Hogg and Stewart have recently suggested that thiolate and sulfenate ions may be reducing agents in the rearrangement of **1** to **5**.[2g] Under our conditions, however, this seems unlikely since disulfide was a minor product and sulfinic–sulfonic acids were not detected.

Ethyl 2-nitrobenzenesulfinate (**6**), previously undetected in the reactions of **1** in alcohols, is probably formed by nucleophilic attack of the solvent on the sulfinyl sulfur of the