(38) Capillary melting points were determined on a Mel-Temp apparatus and are uncorrected. Infrared spectra were taken as neat films or $CHCl_3$ solutions on a Perkin-Elmer Infracord or Beckman IR-18 A-X. Proton magentic resonance (NMR) spectra were recorded in $CDCl_3$ or CCl_4 solution on a Varian T-60, EM-390, or HR-220 instrument. Chemical shifts are reported as parts per million (δ) downfield from tetramethylsilane. GLC–mass spectra were obtained on an LKB-9000 instrument using a 1/8 in. × 6 ft Dexsil 300 column.
Reagent grade hexane was distilled from lithium aluminum hydride prior to use. Tetramethylethylenediamine (TMEDA) was distilled from lithium aluminum hydride and could be stored, protected from moisture for several weeks. 2,4,6-Triisopropylbenzenesulfonylhydrazide was prepared as reported.[11] Alkyllithium reagents were obtained from Alfa-Ventron Corp. and standardized prior to use.
"Standard workup" consisted of pouring the mixture into water, separating the organic layer, and reextracting the aqueous layer with ether. The combined organic layers were washed to neutrality (removing TMEDA) with water and dried over magnesium sulfate. After concentration of the filtered solution in vacuo, it was diluted to known volume and an aliquot taken for GLC analysis. The aliquot was analyzed on a 1/8 in. × 15 ft 6% SE-30 on Chromosorb W column (column A) using solutions of purified product as standard. Preparative GLC was done on a 1/4 in. × 5 ft 20% SE-30 on Chromosorb W (column B). Microanalyses were performed by Galbraith Laboratories, Inc.
(39) Large particles tended to remain undissolved and were occluded in the product as it crystallized.
(40) Excess acid slows decomposition of the trisylhydrazide to diimide.
(41) This solution was treated with D_2O prior to recording the spectrum to ensure total N–H exchange.
(42) C. E. Griffen, *J. Org. Chem.*, **25**, 665 (1960).
(43) The forerun was 0.44 g of **25** contaminated with about 10% 1,3,5-triisopropylbenzene.
(44) S. Satsumabayashi, K. Nakajo, R. Soneda, and S. Motoko, *Bull. Chem. Soc. Jpn.*, **43**, 1586 (1970).

Notes

Leaving-Group Variation in Aprotic Bamford–Stevens Carbene Generation

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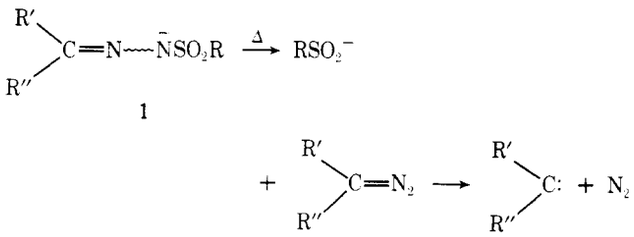
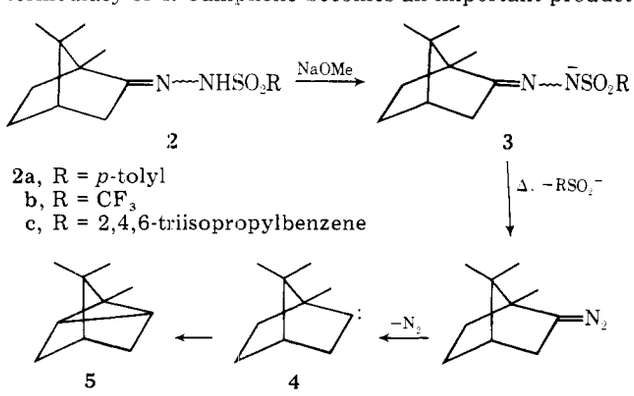
Thermal decomposition of the monoanions of tosylhydrazones **1** (R = *p*-tolyl) in aprotic solvents has become the standard method for generation of dialkyl carbenes.[1] The reaction is typically carried out at temperatures of 130 °C or higher, often in refluxing diglyme (161 °C). Carbenes can also be generated photochemically from **1**,[2] but the reaction is



1

difficult to run on a large scale. In connection with another problem,[3] we had reason to investigate the variation of the R group in **1** and report here the results of that study which show that "trisylhydrazones" (**1**, R = 2,4,6-triisopropylbenzene) decompose at a much lower temperature in this aprotic Bamford–Stevens reaction.

We chose the camphor system **2** for our study, since exclusive formation of tricyclene **5** is a standard test[1] for the intermediacy of **4**. Camphene becomes an important product



2

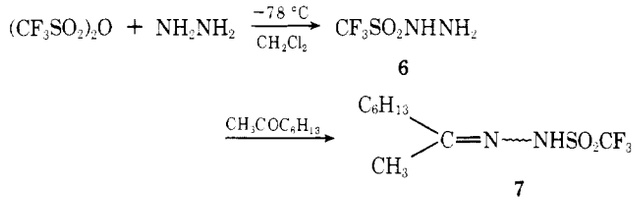
2a, R = *p*-tolyl
b, R = CF_3
c, R = 2,4,6-triisopropylbenzene

3

5 **4**

under protic conditions, and bornylene is the product of Shapiro reaction[1b,4] conditions. Indeed, decomposition of **3a** at 161 °C produces **5** in essentially quantitative yield after 40 min.

In seeking a leaving group which would allow the reaction to proceed at a lower temperature, our attention was first directed toward trifylhydrazone **2b.** The enhanced leaving-group ability of the trifluoromethanesulfonate group[5] has been amply documented, particularly in the solvolytic generation of vinyl cations.[6] β eliminations of the trifluoromethylsulfinate group from nitrogen and carbon are also accelerated,[7] but the only reported α elimination, that of benzil monotrifylhydrazone, was merely reported to give the diazo ketone "quickly" at about 0 °C. Direct comparison with the tosylhydrazone was not made.[8] We initially attempted to prepare trifylhydrazide **6** as shown and were able to trap it in low yield at −78 °C with reactive ketones such as 2-octanone. All attempts at isolation of **6,** however, led to decomposition as first noted by Powell



6

7

and Whiting.[9] Less reactive ketones, including camphor, could not be trapped. Trifylhydrazone **2b** was therefore prepared by treatment of camphor hydrazone[10] with trifylanhydride in the presence of base.

Thermal decomposition of the sodium salt of **2b** at 161 °C does indeed produce **5** in a yield comparable with that obtained from **2a.** Unfortunately, the reaction is accelerated only slightly at best as shown in Table I for refluxing glyme (bp 85 °C). At this temperature both **3a** and **3b** decompose too slowly for practical purposes. We conclude that the increased leaving-group ability of the triflinate anion is about equally offset by increased stabilization of **3b,** making trifylhydrazones of little value for the aprotic Bamford–Stevens sequence.

We therefore sought an R group which might selectively destabilize the starting anion **3.** The report[11] that trisylhydrazide decomposes to diimide faster than tosylhydrazide prompted the study of decomposition of trisylhydrazone **2c.** The preparation of a wide variety of trisylhydrazones has been reported.[3,11] Indeed, thermal decomposition of the sodium salt **3c** is far faster than that of **3a** or **3b** as shown in Table I. In all

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Table I. Relative Rate of Decomposition of 3 in Refluxing Glyme (85 °C)

Hydrazone	% hydrazone remaining[a] t = 15 min	1 h	2 h	4 h
3a	94	87	*b*	60
3b	91	84	*b*	54
3c	49	15	0.4	<0.1

[a] Determined by HPLC as described in the Experimental Section. [b] Not determined.

three cases, **5** is formed with <2% camphene as an impurity. The reaction can be conveniently run in glyme or even THF, solvents much easier to purify and separate from product than diglyme. This dramatic decrease in reaction temperature should be of special value in the production of unstable carbene-derived products.[12] The enhanced rate of this elimination and those reported earlier[3,11] reflect steric destabilization of **3c** by the bulky ortho substituents.

Experimental Section[13]

Camphor Trifluoromethanesulfonylhydrazone (2b). Camphor hydrazone was prepared as described elsewhere[10] using 12.8 g (0.40 mol) of anhydrous hydrazine, 20 mL of ethanol, and 15.2 g (0.10 mol) of camphor. The concentrated crude product was not purified but simply dissolved in 100 mL of dichloromethane and 10.0 g (0.10 mol) of triethylamine. The temperature was lowered to −78 °C and 28.2 g (0.10 mol) of trifluoromethanesulfonic anhydride was added to the stirred solution. After addition was complete, the reaction mixture was allowed to warm to room temperature and then washed with 1 N HCl, water, and brine, dried over magnesium sulfate, and concentrated in vacuo. The resulting crude oil was taken up in 50 mL of heptane, heated on a steam bath, filtered hot, and allowed to crystallize in the refrigerator for 2 days. The prismatic crystals were washed with cold hexane and dried overnight to give 10.0 g (34%) of **2b**, mp 85–89 °C. One recrystallization from hexane raised the melting point to 88–90 °C: NMR δ 0.75, 0.95, 1.03 (3 s, 3 H each), 1.2–2.8 (m, 7 H), 7.95 (br s, 1 H); IR (cm^{-1}) 3320 (N–H), 1670 (C=N), 1410, 1135 ($-SO_2$), 1225, 1205, 1000.

Anal. Calcd for $C_{11}H_{17}F_3N_2O_2S$: C, 44.29; H, 5.74; N, 9.39. Found: C, 44.32; H, 5.82; N, 9.31.

Thermal Decomposition. General Procedure. The camphor sulfonylhydrazones **2** (1.0 mmol) were dissolved in 10 mL of freshly distilled solvent (diglyme, glyme, or THF). To the stirred solution was then added 4.0 mmol of sodium methoxide. The resulting milky mixture was heated under reflux for the appropriate time, as shown for the glyme experiments in Table I. The disappearance of **2** was conveniently followed by HPLC analysis on a Waters Associates 3.9 mm × 30 cm μ-Porsil column (hexane/chloroform/methanol solvent) using aliquots which were acidified with 1 N HCl and taken to known volume with ether. The results for glyme as solvent are shown in Table I. Product mixtures were worked up by extracting with 1 N NaOH and were analyzed by GLC on a ¼ in. × 10 ft 15% FFAP on Chromosorb W column at 120 °C, using *o*-xylene as internal standard. Tricyclene was the major product observed in all cases (75–95% yield), with camphene detected in trace quantity (≤2%).

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Registry No.—**2a** Na, 63866-11-5; **2b**, 63866-12-6; **2b** Na, 63866-13-7; **2c** Na, 63866-14-8; **5**, 508-32-7; camphor hydrazone, 770-53-6; trifluoromethanesulfonic anhydride, 358-23-6.

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(13) For general conditions see ref 3.

The Acetyl Function As a Protecting Group for Phenols

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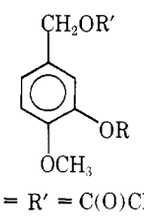
In the course of our current investigation of intramolecular phenolic coupling reactions[1] a number of diphenolic esters were required (e.g., **8** and **10**). While we were considering methods by which the phenolic groups could be protected during preparation of the ester linkages, our attention was drawn to a report concerning the reduction of phenyl esters.[2] In this study it was found that substituted phenyl esters of 3-phenylpropionic acid were reduced at least an order of magnitude more rapidly than the methyl ester. This observation suggested that the acetyl function might be useful as a protecting group for phenols. Although acetyls have been utilized for this purpose previously, they normally have been removed by treatment with aqueous acid or base.[3] The acid or base cleavage of phenols suffers from the disadvantage of not always being selective in the presence of other ester functional groups. A procedure for the selective removal of the acetyl group from phenols by reductive methods would greatly extend its utility as a protecting group.

The procedure was initially tested on the readily available diacetate **1**. Treatment of **1** with $NaBH_4$ in dimethoxyethane



1, R = R′ = C(O)CH_3
2, R = H; R′ = C(O)CH_3
3, R = C(O)CH_3; R′ = H

(DME) for 18 h at 40 °C afforded an 87% yield of the monoacetate **2**. The structure of **2** was assigned by comparison of its NMR spectrum with spectra of related compounds. The resonances due to the benzyl protons appear at δ 4.90 in the diacetate **1** and at δ 4.36 and 4.56 in alcohol **3** and isovanillin alcohol, respectively. Since the corresponding resonance occurs at δ 4.93 in **2**, **2** must be a benzyl acetate.

When *p*-acetoxybenzyl acetate (**4**)[4] was treated in the same manner, *p*-cresol was obtained in quantitative yield. No *p*-hydroxybenzyl acetate (**5**) could be isolated. Hayaski and Oka

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