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NEW METHODS AND REAGENTS IN ORGANIC SYNTHESIS. 87.[1]
REACTION OF TRIMETHYLSILYLDIAZOMETHANE WITH QUINONES*

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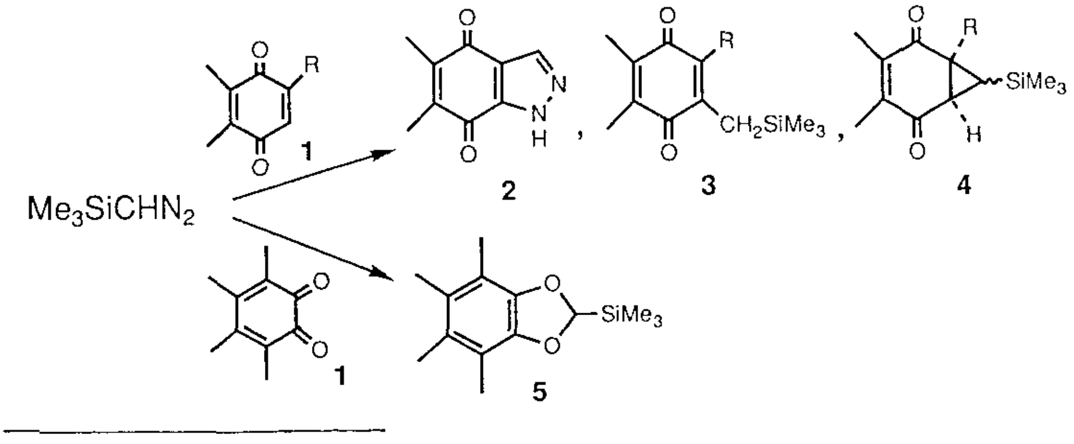
Abstract - Reaction of trimethylsilyldiazomethane with various quinones affords indazoles **2**, 2-substituted 3-trimethylsilylmethyl-1,4-quinones **3**, silylcyclopropanes **4**, and trimethylsilylmethylenedioxy derivatives **5**, depending upon substrates.

We have already reported[2] that most of reactions of trimethylsilyldiazomethane ($TMSCHN_2$) with various olefins in the presence or absence of metal salt catalysts give silylcyclopropanes. As an extension of this work, we now wish to report the reaction of $TMSCHN_2$ with quinones, which gives various products **2**-**5**, depending upon substrates.



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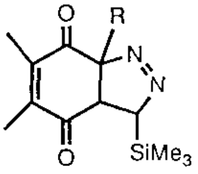
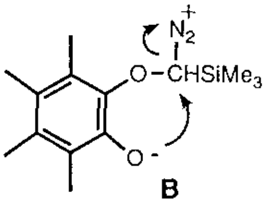
* Dedicated to the memory of the late Professor Tetsuji Kametani.

Diversity of the reaction will be apparent from the Table. Treatment of 1,4-naphthoquinone (**1a**) (1 mmol) with $TMSCHN_2$ (1.2 mmol) at 0°C for 4 h in dry diethyl ether (15 ml) under argon gave the benzindazole **2a** in high yield, after separation on a silica gel column (hexane : ethyl acetate = 3 : 1). The indazole **2a** may be formed by 1,3-dipolar cycloaddition of $TMSCHN_2$ to **1a**, followed by desilylation with water during column chromatography, then by oxidation with air. Similarly, 5,8-diacetoxy-1,4-naphthoquinone (**1b**) afforded the benzindazole **2b**. Unsymmetrical quinones, such as 5-acetoxy-1,4-naphthoquinone (**1c**) or 2-methyl-1,4-benzoquinone (**1d**), also reacted with $TMSCHN_2$ to give the corresponding indazoles, but the indazoles obtained were an inseparable mixture of **2c** (or **2d**) and its regioisomer **2c'** (or **2d'**) with high to moderate regioselectivity. Unfortunately, each regiochemistry for the major products and minor ones could not be determined by their spectral data. Interestingly, the reaction of **1d** with diazomethane has been reported to give either **2d** or **2d'** as a sole product.[3]

In contrast to the above results, the reaction of 2-methyl-1,4-naphthoquinone (**1e**) with $TMSCHN_2$ at reflux in dry benzene gave the 3-trimethylsilylmethyl-1,4-naphthoquinone **3e** and a mixture of exo- and endo-isomers of silylcyclopropanes **4e**, and no heterocyclic compounds could be detected. Possibly, **3e** and **4e** are produced by expulsion of nitrogen from the initially formed pyrazoline intermediate **A**.[4] 2-Methoxy-1,4-naphthoquinone (**1f**), another 2-substituted 1,4-naphthoquinone, also gave **3f** and **4f** in preference of the latter. In the case of 2-acetoxy-1,4-naphthoquinone (**1g**) the reaction proceeded at room temperature, but the product was the benzindazole **2a** which would involve the elimination of acetic acid from the intermediate **A**. The result is similar to those of the reaction of diazomethane with 1,4-naphthoquinones bearing substituents such as halogen, methanesulfinyl, and mesyl groups at 2-position of the quinone ring.[5]

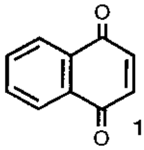
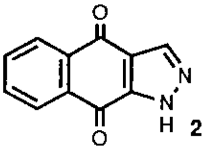
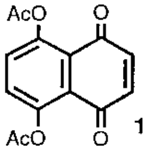
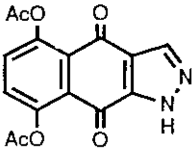
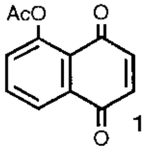
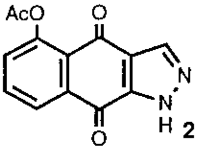
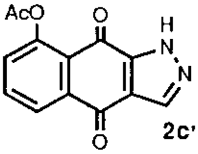
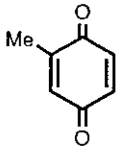
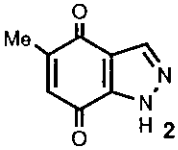
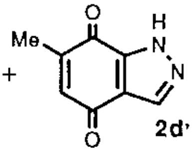
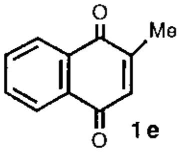
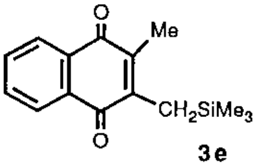
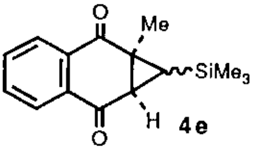
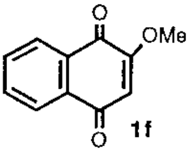
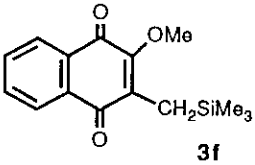
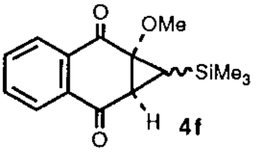


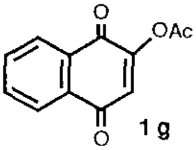
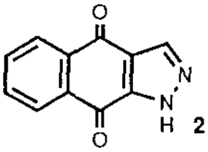
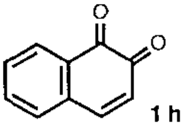
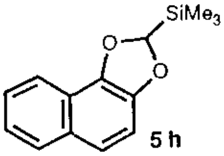
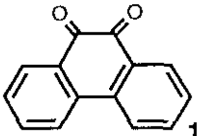
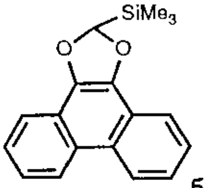
A



B

Table[a] Reaction of Trimethylsilyldiazomethane with Quinones

Quinones	Conditions		Products	Yield	mp°C or
	Solvent	Temp. & Time		(%)	bp°C/mmHg[b]
 **1a**	Et_2O	0°C, 4 h	 **2a**	89	>310 (349)[c]
 **1b**	Et_2O	0°C, 2 h	 **2b**	64	165-166
 **1c**	Et_2O	0°C, 2 h	 **2c** +  **2c'**	77[d]	>285
 **1d**	Et_2O	0°C, 4 h	 **2d** +  **2d'**	59[e]	208-210 (205)[f]
 **1e**	C_6H_6	reflux[g] 8 h	 **3e**	18	76/0.05
			 **4e** (exo/endo = 73/27)[h]	14	85/0.03
 **1f**	toluene	reflux[g] 30 h	 **3f**	11	87/0.05
			 **4f** (exo/endo = 86/14)[h]	64	88/0.05

 **1g**	Et$_2$O	0°C, 2 h r.t., 12 h	 **2a**	53	>310 (349)^c
 **1h**	C_6H_6	reflux 4 h	 **5h**	27	70-80/0.01
 **1i**	1,2-dichloro-ethane	r.t., 2 h reflux, 6 h	 **5i**	42	106-107

a) All the products gave satisfactory spectral data and elemental analysis (or mass spectra). b) Distillation was carried out by a Kugelrohr apparatus. c) L.F. Fieser and M.A. Peters, *J. Am. Chem. Soc.*, 1931, **53**, 4080. d) The ^{1}H-nmr (400 MHz) spectrum of the mixture showed two acetyl proton signals at 2.38 and 2.41 ppm (the ratio was 9 : 1). e) The ^{1}H-nmr (400 MHz) spectrum of the mixture showed two methyl proton signals at 2.06 and 2.07 ppm (the ratio was 3 : 7) and two olefinic proton signals at 6.66 and 6.69 ppm. f) Reference 3. g) The reaction did not occur at room temperature. h) The stereochemistry and the ratio of exo/endo isomers were determined by ^{1}H-nmr : **4e**, δ : 0.16, -0.27 (SiMe$_3$); **4f**, δ : 0.10, -0.24 (SiMe$_3$).

Finally, we investigated the reaction with 1,2-quinones. 1,2-Naphthoquinone (**1h**) has been reported to give resinous products by the reaction with diazomethane.[6] But the reaction with TMSCHN$_2$ at reflux in dry benzene afforded the trimethylsilylmethylenedioxy derivative **5h** though in 27 % yield. Phenanthrenequinone (**1i**) also gave the corresponding trimethylsilylmethylenedioxy derivative **5i**, while the reaction with diazomethane furnished the spirophenanthroylethylene oxide.[7] A possible intermediate in this reaction would be the betaine **B**,[6,8] from which nitrogen would be expelled to give **5**. Desilylation of **5** was easily achieved with tetra-n-butylammonium fluoride in acetonitrile in good yield.[9]

In conclusion, $TMSCHN_2$ smoothly reacts with various quinones to give **2**-**5**, depending upon substrates.

ACKNOWLEDGEMENT

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REFERENCES AND NOTES

1. For Part 86, see T. Aoyama and T. Shioiri, *Chem. Pharm. Bull.*, 1989, **37**, 2216.
2. T. Aoyama, Y. Iwamoto, S. Nishigaki, and T. Shioiri, *Chem. Pharm. Bull.*, 1989, **37**, 253.
3. W.I. Awad, A.R.A. Raouf, and A. Boulos, *J. Chem. U.A.R.*, 1966, **9**, 267.
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5. B. Eistert, H. Fink, and A. Müller, *Chem. Ber.*, 1962, **95**, 2403.
6. L.F. Fieser and J.L. Hartwell, *J. Am. Chem. Soc.*, 1935, **57**, 1479.
7. B. Eistert, G. Fink, and R. Wollheim, *Chem. Ber.*, 1958, **91**, 2710.
8. Analogous intermediates have been proposed in the reaction of 1,2-quinones with diazoalkanes such as diazoethane and diphenyldiazomethane, see A. Schönberg, A. Mustafa, W.I. Awad, and G.E.-D.M. Moussa, *J. Am. Chem. Soc.*, 1954, **76**, 2273.
9. Trimethylsilylmethylenedioxy derivative **5h** (0.5 mmol) was stirred with tetra-n-butylammonium fluoride (0.75 mmol) at room temperature in acetonitrile (5 ml) for 2 h to give naphtho[1,2-d]-1,3-dioxole as an oil in 94 % yield. Analogously phenanthro-[9,10-d]-1,3-dioxole was obtained from **5i** in 57 % yield, mp 128°C (Lit., 124 ~125.5°C, W.M. Padgett and J. Hyman, Fr. 1,454,116 (*Chem. Abstr.*, 1967, **67**, 73600p)).

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