Tetrahedron Letters,Vol.25,No.45,pp 5139-5142,1984 0040-4039/84 $3.00 + .00
Printed in Great Britain

NEW GENERATION AND CYCLOADDITION OF α-(N-TERT-BUTYLIMINO)-o-QUINODIMETHANE

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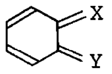
Abstract: CsF induced 1,4-elimination of ammonium bromide 7, prepared by quaternization of N-*tert*-butyl o-(dimethylaminomethyl)benzimidoylsilane 6, provides a new generation of α-(N-*tert*-butylimino)-o-quinodimethane (3a), which gives benzocyclobutenone N-*tert*-butylimine (8) in the absence of dienophile. Trapping of 3a with electron deficient olefins affords Diels-Alder adducts regioselectively.

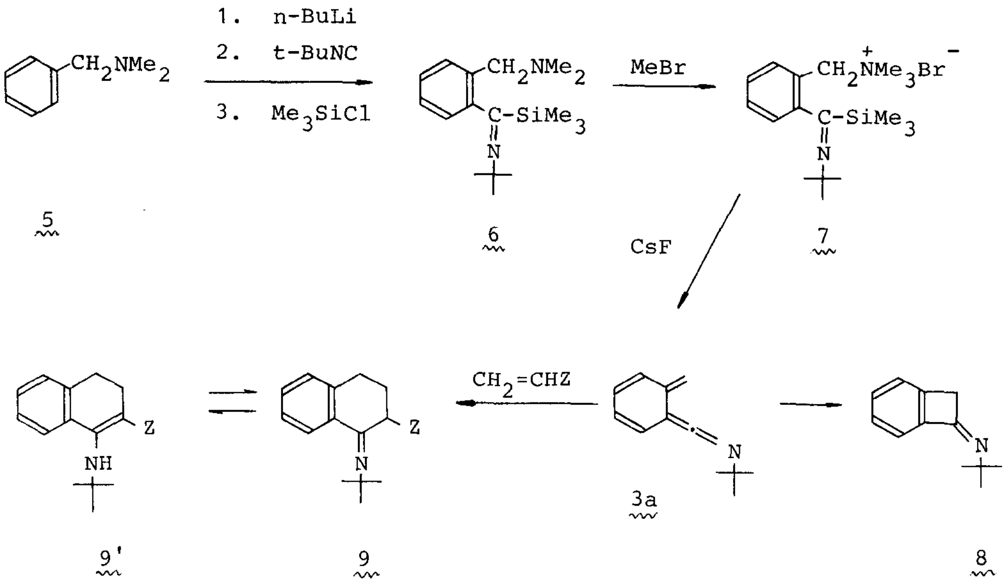
Fluoride induced 1,4-elimination involving silyl group provides a new methodology for the generation of o-quinodimethanes (1)[1] and o-quinone methide imine (2)[2], whose Diels-Alder reactions are useful for convenient synthesis of polycycles.



1 X: CH_2, Y: CH_2
2 X: CH_2, Y: NR
3 X: CH_2, Y: C=NR
4 X: CH_2, Y: C=O

α-(N-Alkylimino)-o-quinodimethane (3) and α-oxo-o-quinodimethane (4)[3], which are structurally related with 1 and 2, seem to be of potential use in organic synthesis, because their Diels-Alder cycloadditions produce functionalized polycycles.

Herein, we wish to describe the first generation of a novel α-(N-*tert*-butylimino)-o-quinodimethane (3a) by means of the silicon leading 1,4-elimination technique.

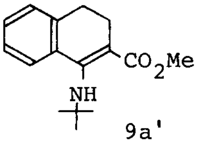
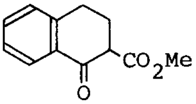
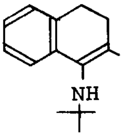
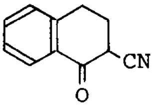
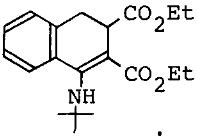
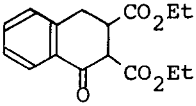
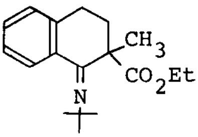
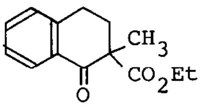


A requisite precursor 6 was prepared from benzyldimethylamine (5) in a ca. 60% yield via α,α-addition[4] of o-lithiobenzyldimethylamine[5] to *tert*-butyl isocyanide followed by silylation[4] of the resultant lithioaldimine intermediate [6 (bp 100 °C/3 mmHg) : IR(neat) 1636 cm^{-1}; NMR($CDCl_3$) δ 1.02 (s, 9H), 2.20 (s, 6H), 3.23 (s, 2H), 6.62-7.60 (m, 4H)]. Ammonium bromide 7 was prepared by a reaction of 6 with methyl bromide.[6]

The ammonium bromide 7 was treated with CsF in acetonitrile at room temperature to afford benzocyclobutenone N-*tert*-butylimine (8) in 55% yield after Kugel rohr distillation (bp 96-99 °C/7 mmHg) [8 : IR(neat) 1690 cm^{-1}; NMR ($CDCl_3$) (a syn and anti mixture) δ 1.38 and 1.50 (two s, 9H), 3.88 and 4.05 (two s, 2H), 7.15-7.78 (m, 4H)]. Hydrolysis of 8 with aqueous oxalic acid at room temperature furnished benzocyclobutenone (10)[7] in a quantitative yield. The formation of 8 may be reasonably explained by assuming an intramolecular ring closure of α-(N-*tert*-butylimino)-o-quinodimethane (3a). The present reaction is closely related with a vacuum pyrolysis[3] (590-610 °C/0.1-0.01 mmHg) of o-bis-(trimethylsilyl)methylbenzoyl chloride giving 2-(trimethylsilyl)benzocyclobutenone, in which α-oxo-o-quinodimethane intermediate (**4**) might be assumed.

The intermediary of **3a** in the present reaction was manifested in the Diels-Alder trapping with dienophiles, which is summarized in Table 1.

Table 1

Dienophile	Cycloadduct (%)$^{a)b)}$		Hydrolyzed Adduct$^{c)}$	
$CH_2=CHCO_2Me$	 **9a'**	(55)	 **11a**	d)
$CH_2=CHCN$	 **9b'**	(58)	 **11b**	d)
$EtO_2CCH=CHCO_2Et$	 **9c'**	(55)	 **11c**	d)
$CH_2=C(CH_3)CO_2Et$	 **9d**	(49)	 **11d**	

a) Yields are based on the precursor **6**. b) Reference 8. c) Reference 9.
d) A mixture of keto-enol isomers.

The Diels-Alder trapping of **3a** was conducted according to the following procedure. To a stirred mixture of CsF (7.5 mmol) and acrylonitrile (7.5 mmol) in acetonitrile (4 mL) was dropwise added a solution of the ammonium bromide **7**

(2.5 mmol) in acetonitrile (3 mL) over 3 hr at room temperature, and stirred for an additional 1 hr. The reaction mixture was diluted with ether and washed with aqueous $NaHCO_3$ to give regioselectively 1-*tert*-butylamino-2-cyano-3,4-dihydronaphthalene (**9b'**), a tautomer of **9b**, in 58% yield after Kugel rohr distillation (bp 95-100 °C/1 mmHg) [**9b'** : IR(neat) 2195, 1605, 1590, 1560 cm^{-1}; NMR($CDCl_3$) δ 1.28 (s, 9H), 2.18-2.57 (m, 2H), 2.59-2.95 (m, 2H), 3.58-3.83 (broad 1H), 7.07-7.86 (m, 4H)]. Hydrolysis of **9b'** with aqueous oxalic acid at room temperature for 10 hr afforded 2-cyanotetralone (**11b**) (>95%) [**11b** : IR(neat) 2260, 1708 cm^{-1}; NMR($CDCl_3$) δ 2.59-3.58 (m, 5H), 7.05-7.90 (m, 3H), 7.92-8.40 (m, 1H)].

References and Notes

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6) Ammonium bromide **7**, prepared from **5** without isolation of **6**, can be used for the generation of **3a** without trouble.

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8) **9c'** (bp 133-138 °C/1 mmHg): IR(neat) 1728, 1665, 1615, 1598, 1565 cm^{-1}; NMR($CDCl_3$) δ 1.20 (s, 9H), 1.33 (t, 3H), 1.35 (t, 3H), 2.73-3.27 (m, 3H), 3.96 (q, 2H), 4.29 (q, 2H), 7.11-8.00 (m, 4H). **9d** (bp 97 °C/1 mmHg): IR (neat) 1725, 1650 cm^{-1}; NMR($CDCl_3$) δ 1.10 (t, 3H), 1.18 (s, 9H), 1.30 (s, 3H), 2.30-3.05 (m, 4H), 4.05 (q, 2H), 7.05-7.62 (m, 4H).

9) **11d** (bp 90 °C/1 mmHg): IR(neat) 1732, 1690 cm^{-1}; NMR($CDCl_3$) δ 1.15 (t, 3H), 1.50 (s, 3H), 1.6-2.4 (m, 1H), 2.43-2.72 (m, 1H), 2.73-3.25 (m, 2H), 4.18 (q, 2H), 7.3-8.3 (m, 4H).

(Received in Japan 16 July 1984)