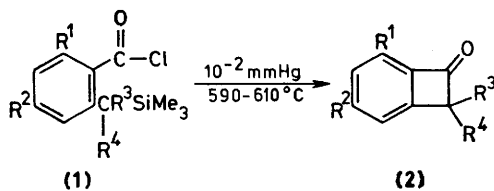


Synthesis and Chemistry of 2-Trimethylsilylbenzocyclobutenones

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Summary Pyrolysis of *o*-trimethylsilylmethyl- and *o*-bis(trimethylsilyl)methyl-benzoyl chlorides affords 2-silylated benzocyclobutenones.

BENZOCYCLOBUTENONE and its derivatives have recently been of much interest in synthesis.¹ Benzocyclobutenes functionalized in the four-membered ring are available;¹ however, similarly functionalized benzocyclobutenones are uncommon.² The ability of silicon to stabilize adjacent radical³ and carbanion⁴ centres makes 2-trimethylsilylbenzocyclobutenones attractive intermediates for the synthesis of functionalized benzocyclobutenones. We report here that pyrolysis of readily available *o*-bis(trimethylsilyl)methylbenzoyl chlorides affords 2-trimethylsilylbenzocyclobutenones in good yields. Furthermore, the 2-lithio-2-trimethylsilylbenzocyclobutenone acetal is stable at low temperatures and has potential for the synthesis of functionalized benzocyclobutenones.



- a, R¹-R⁴ = H
 b, R¹-R³ = H; R⁴ = SiMe₃
 c, R¹, R² = H; R³, R⁴ = SiMe₃
 d, R¹ = OMe; R², R³ = H; R⁴ = SiMe₃
 e, R¹ = OMe; R² = H; R³, R⁴ = SiMe₃
 f, R¹, R³, R⁴ = H; R² = CH₂SiMe₃
 g, R¹, R³ = H; R² = CH₂SiMe₃; R⁴ = SiMe₃

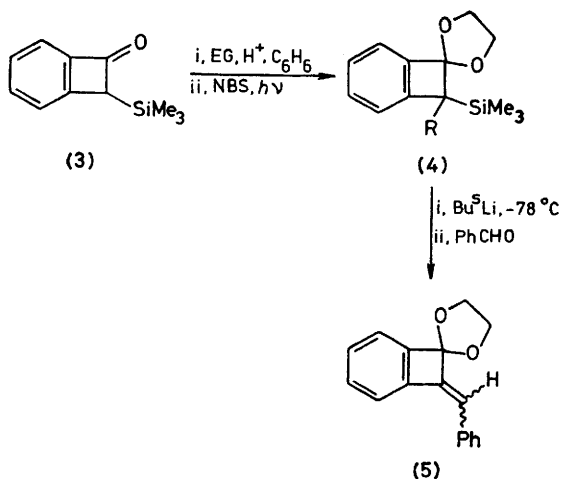
† The compound (1a) was distilled (*ca.* 1 g/h; 70–75 °C bath and 0.1–0.01 mmHg) into a 30 × 2.5 cm horizontal quartz tube loosely packed with quartz chips maintained at 590–610 °C.

Vacuum pyrolysis of (1a)⁵ afforded a *ca.* 1:1 mixture of (2a) and (2b) in 60% isolated yield.† The low selectivity for the pyrolysis of (1a) prompted examination of the chemistry of the bis(trimethylsilyl) compound (1b). The acid corresponding to (1b) was obtained in 80% overall yield in a one-pot reaction by treating *o*-methylbenzoic acid in tetrahydrofuran (THF)-hexamethylphosphoric triamide (HMPA) sequentially with BuⁿLi (1.1 equiv.), Bu^sLi (1.1 equiv.), trimethylsilyl chloride (1.1 equiv.), Bu^sLi (1.1 equiv.), and trimethylsilyl chloride (3 equiv.). Pyrolysis of (1b) on a 20 g scale afforded a 73% distilled yield of (2b) with a smaller amount (7%) of (2c) as residue. In contrast to our experience with the pyrolysis of *o*-methylbenzoyl chlorides,⁶ the pyrolyses of the silylated systems are remarkably clean, the crude product being obtained as an easily purified yellow oil. While we have examined only four systems under unoptimized conditions, the reaction appears general (Table). Furthermore, it appears that the thermal loss of trimethylsilyl chloride is only slightly favoured relative to loss of hydrogen chloride.

TABLE. Pyrolysis of acid chlorides.^a

Compound ^b	Benzocyclobutenones ^c (Yield, %)
(1a)	(2a) (29); (2b) (31)
(1b)	(2b) (73); (2c) (7)
(1d)	(2d) (44); (2e) (19)
(1f)	(2g) (56); (2f) (31) ^d

^a The acid chlorides were obtained by treating the acid with thionyl chloride in methylene dichloride, and were used crude.
^b The acids corresponding to the acid chlorides had: (1a),⁵ (1b), m.p. 146.5–147.5 °C; (1d), 144–146 °C; (1f), 131–134 °C.
^c All products showed the expected spectroscopic properties (i.r., ¹H n.m.r.) and gave acceptable combustion or exact mass spectroscopic measurements. The products were liquids except for (2e), m.p. 46–47 °C. ^d Yields are by g.l.c.



EG = Ethylene glycol.

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While the monobromoacetal of benzocyclobutenone could not be prepared by free-radical bromination of the unsubstituted benzocyclobutenone acetal, the trimethylsilyl acetal (**4**; R = H) smoothly reacted with *N*-bromosuccinimide (NBS)- $h\nu$ to afford (**4**; R = Br, 66% after Fluorosil chromatography), m.p. 85.5–87.5 °C. Metal-halogen exchange with $\text{Bu}^{\text{t}}\text{Li}$ afforded the lithium compound which was treated with methanol to afford 2-trimethylsilylbenzocyclobutenone acetal, and with benzaldehyde to yield the functionalized system (**5**) (60%). Thus, the lithio-compound (**4**; R = Li) is the synthon for the enolate of benzocyclobutenone \ddagger and has potential utility in the synthesis of functionalized benzocyclobutene systems. \S

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\ddagger The enol and enolate anion of benzocyclobutenone are destabilized by their benzocyclobutadiene character.

\S Compound (**2b**) can be converted into (**2a**) by $\text{KF}\cdot 2\text{H}_2\text{O}$ in dimethyl sulphoxide.

¹ For leading references, see T. Kametani, *Acc. Chem. Res.*, 1976, **9**, 319; W. Oppolzer, *Synthesis*, 1978, 793.

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³ J. W. Wilt and P. M. Aznavoorian, *J. Org. Chem.*, 1978, **43**, 1285 and references therein.

⁴ For leading references, see E. Ehlinger and P. D. Magnus, *J. Am. Chem. Soc.*, 1980, **102**, 5004.

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⁶ P. Schiess and M. Heitzmann, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 469.