

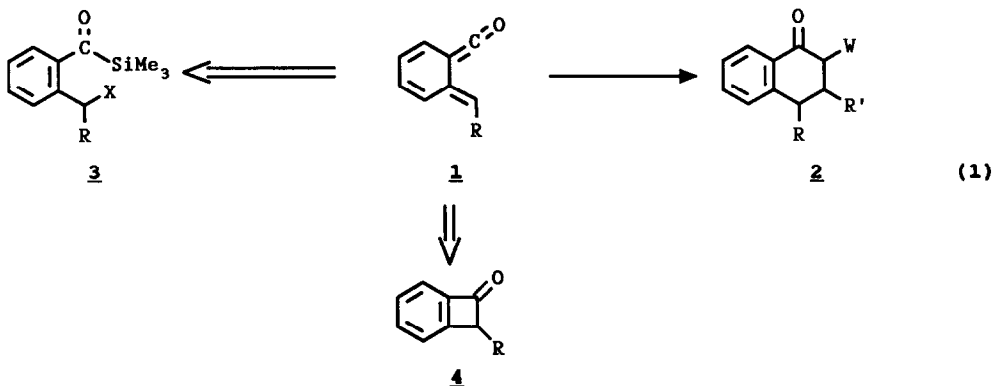
BENZOCYCLOBUTENONES FROM ACYLSILANES

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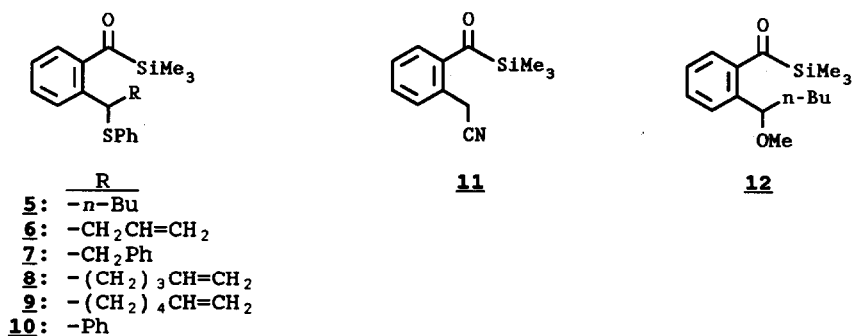
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Summary: Reactions of *o*-(α -phenylthio)alkylbenzoyltrimethylsilanes with a suitable catalyst such as Group 6 metal carbonyls in refluxing toluene or dioxane afforded benzocyclobutenones.

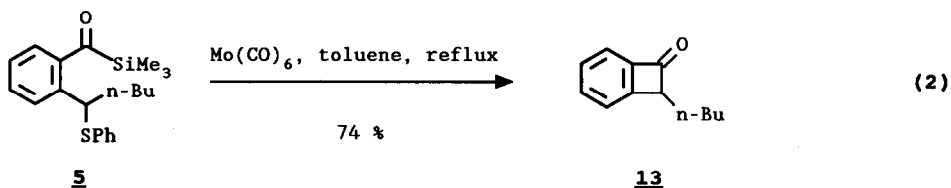
The generation of *o*-quinodimethanes from the stable precursors and subsequent Diels Alder reaction constitute a powerful synthetic strategy for construction of 6-membered rings¹. Notably absent in the list of the transient species is the methylene ketene species **1**, which if readily accessible should be very useful for preparation of tetralones **2** under the typical Diels Alder condition. And this was considered to be essential in one of our projected synthesis. One of the potential candidates for the stable precursor for the *o*-quinodimethane **1** may be acylsilanes **3**², readily available from the corresponding carboxylic acids³ (Eq. 1). But numerous attempts to generate *o*-quinodimethanes directly from acylsilanes were not fruitful⁴.



Another possible precursor is benzocyclobutenones **4**⁵, for which, among a number of syntheses, the thermal cycloaddition of benzynes to alkenes such as ketene acetals is certainly the most direct route⁶. But, in our hand, this reaction gave poor yields of products especially with higher alkenes. Still remaining possibility would be to find a suitable method for ring closure of the acylsilanes **5** - **12**⁷ to benzocyclobutenones.

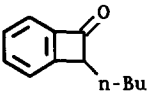
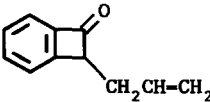
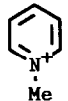
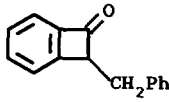
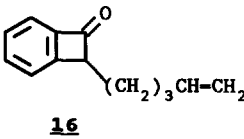
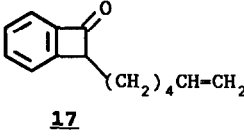
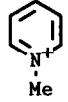
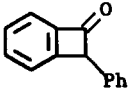


For these conversions, there was a need to employ a transition metal catalyst capable of undergoing oxidative addition and reductive elimination⁸. In this regard, the Group 6 carbonyls⁹ seemed to be appropriate. And an added bonus of using those catalysts is that the central metals are thiophilic^{9c, 10}. Consequently, a toluene (3 mL) solution of the acylsilane 5 (200.1 mg, 0.56 mmol) and Mo(CO)_6 (295.7 mg, 1.12 mmol)¹¹ was refluxed for 4 h under N_2 until complete consumption of the starting material. After aqueous work-up and flash(SiO_2) chromatography, the corresponding benzocyclobutenone 13 (72.3 mg) was obtained in 74% yield.



Accordingly, the acylsilanes were subject to the present reaction with various Group 6 compounds, the results of which are summarized in Table 1. Acylsilanes with various structures could be accommodated. Also, the reagent could be any one of Group 6 metal carbonyls except for the case of W(CO)_6 , although it is difficult to pinpoint which would be the reagent of choice. It should be mentioned, however, that Cr(CO)_6 reactions usually gave a mixture of Cr(CO)_3 complex and free forms of benzocyclobutenones, out of which the metal-free products was isolated after treatment with excess I_2 . Also, it is interesting to note that $\text{Pd(PPh}_3)_4$ could catalyze the reaction efficiently despite of the inferior reactivity (Entry 13). However, the acylsilanes 11 and 12 without the thioether functionality gave complex mixtures with any of the reagents listed above. And low-boiling solvents such as THF, benzene, acetonitrile, etc. regardless of ligand power gave poorer yields of products.

Table 1. Preparation of Benzocyclobutenones^a.

Entry	Starting Material	Reagent	Rxn Time (h)	Product	Yield (%)
1	<u>5</u>	Cr(CO) ₆	4		61 ^b
2		Mo(CO) ₆	4	<u>13</u>	74
3	<u>6</u>	Cr(CO) ₆	2		43 ^b
4		Mo(CO) ₆	2	<u>14</u>	54
5		Mo(CO) ₅ I ⁻	4		76
6	<u>7</u>	Cr(CO) ₆	4		75 ^b
7		Mo(CO) ₆	4	<u>15</u>	66
8		W(CO) ₆	4		56
9	<u>8</u>	Mo(CO) ₆	2		60
10	<u>9</u>	Cr(CO) ₆	6 ^c		55 ^b
11		Mo(CO) ₆	6	<u>17</u>	46
12		Cr(CO) ₅ I ⁻	4		60
13		Pd(PPh ₃) ₄ ^d	77 ^e		60
14	<u>10</u>	Cr(CO) ₆	20 ^c		43 ^b
15		Mo(CO) ₆	2	<u>18</u>	51

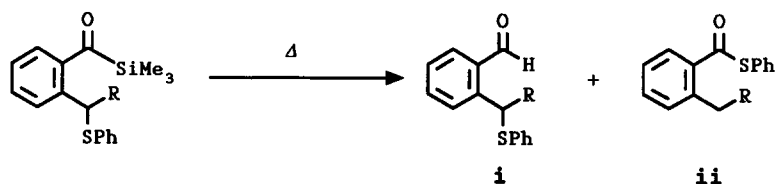
^aAll reactions were carried out with 1.5 - 2.0 equiv of the reagent under N₂ in refluxing toluene unless otherwise noted. ^bAfter treatment with I₂. ^cIn refluxing dioxane. ^dWith 0.1 equiv of Pd(PPh₃)₄. ^eIn refluxing THF.

In conclusion, a new and versatile method for benzocyclobutenones is developed starting from acylsilanes. Their utilization in synthesis will be reported in the future.

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References and Notes:

- (a) J. L. Charlton, and M. Alauddin, *Tetrahedron*, **43**, 2873 (1987). (b) H. N. C. Wong, K.-L. Lau, and K.-F. Tam, *Top. Curr. Chem.*, **133**, 85 (1986). (c) W. Oppolzer, *Synthesis*, 793 (1978).
- For a review, see: A. Ricci, and A. Degl'Innocenti, *Synthesis*, 647 (1989).
- J. Kang, J. H. Lee, K. S. Kim, J. U. Jeong, and C. Pyun, *Tetrahedron Lett.*, **28**, 3261 (1987).
- Details will be reported in a forthcoming publication.
- For examples of electrocyclic opening and cycloaddition of benzocyclobutenes, see: (a) B. J. Arnold, P. G. Sammes, and T. W. Wallace, *J. Chem. Soc., Perkin Trans. I*, 409 (1974). (b) T. Kametani, M. Takeshita, H. Nemeto, and K. Fukumoto, *Chem. Pharm. Bull.*, **26**, 556 (1978). (c) D. I. Macdonald, and T. Durst, *J. Org. Chem.*, **53**, 3663 (1988). (d) N. Harada, T. Sugioka, Y. Ando, H. Uda, and T. Kuriki, *J. Am. Chem. Soc.*, **110**, 8483 (1988). (e) W. Choy, and H. Yang, *J. Org. Chem.*, **53**, 5796 (1988). (f) M. Azadi-Ardakani, and T. W. Wallace, *Tetrahedron*, **44**, 5939 (1988).
- (a) I. L. Klundt, *Chem. Rev.*, **70**, 471 (1970). (b) R. P. Thummel, *Acc. Chem. Res.*, **13**, 70 (1980). (c) R. V. Stevens, and G. S. Bisacchi, *J. Org. Chem.*, **47**, 2393 (1982).
- The acylsilanes were made from the corresponding carboxylic acids³, which were in turn prepared by dianion alkylation of α -phenylthio- or α -methoxy-*o*-toluic acids (5 - 9 and 12) or by lactone cleavage with PhS⁻ or CN⁻ (10 and 11).
- Direct heating of the acylsilanes, 5 - 10, without any catalyst gave an array of products, among which the corresponding aldehyde i, a simple protodesilylated product, and thioester ii were major ones.



- (a) B. M. Trost, and M. Lautens, *J. Am. Chem. Soc.*, **109**, 1469 (1987); *Tetrahedron*, **43**, 4817 (1987). (b) B. M. Trost, G. B. Tometzki, and M.-H. Hung, *J. Am. Chem. Soc.*, **109**, 2176 (1987). (c) Y. Mosuyama, K. Yamada, and Y. Kuruso, *Tetrahedron Lett.*, **28**, 443 (1987).
- (a) L. L. Yeung, Y. C. Yip, and T.-Y. Luh, *Chem. Commun.*, 981 (1987). (b) F. G. Fang, and S. J. Danishefsky, *Tetrahedron Lett.*, **30**, 2747 (1989).
- The use of excess M(CO)₆ was necessary in order to compensate the loss of the reagent due to sublimation during the reaction.