
General and Convenient Route to Alkenylidenecyclopropanes: Generation of Alkenylidenecarbenes from 1,1-Dibromocyclopropanes under Phase-transfer Conditions

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Alkenylidenecyclopropanes have been prepared in a stereospecific manner by the reaction of 1,1-disubstituted 2,2-dibromocyclopropanes with sodium hydroxide under phase-transfer conditions in the presence of alkenes.

Alkenylidenecyclopropanes, versatile intermediates in organic synthesis,^{1,2} are obtained when alkenes react with alkenylidenecarbenes. The drawback to this reaction, however, is the lack of a general, efficient method for the generation of

alkenylidenecarbenes under mild conditions. These carbenes have been generated by treating halogenoalkynes,³⁻⁵ halogenoallenes,⁶⁻⁸ and polyhalogenocyclopropanes^{9,10} with strong bases such as potassium *t*-butoxide and methyllithium. With

these methods, not only are the starting materials inaccessible, except for polyhalogenocyclopropanes, but the yields of the alkenylidenecyclopropanes are generally low. Moreover, the reported methods have not hitherto been applied to the synthesis of (2,2-diarylethenylidene)cyclopropanes.

Previously, we have reported that aryl vinyl ethers can be synthesized under mild conditions by dehydrohalogenation of 1-aryloxy-2-halogenoethanes with aqueous sodium hydroxide in benzene using tetrabutylammonium hydrogen sulphate as a phase-transfer agent.¹¹ This result indicated that the NaOH-Bu₄NHSO₄ system in benzene serves as a strong base.

We now report a general and convenient method for the preparation of alkenylidenecyclopropanes from 1,1-disubstituted 2,2-dibromocyclopropanes **1** and alkenes **2**. Although we do not have unambiguous evidence for the formation of alkenylidenecarbenes, it is highly probable that the carbenes are involved as key intermediates in this reaction.

In practice, alkenylidenecarbenes were generated by double dehydrobromination from **1** with aqueous sodium hydroxide (Method A) or powdered sodium hydroxide (Method B) in benzene in the presence of Bu₄NHSO₄ which serves as a phase-transfer agent.*

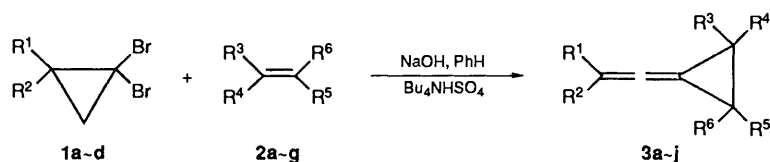
The alkenylidenecarbenes thus generated reacted with alkenes to afford alkenylidenecyclopropanes **3**, their yields depending on the structures of **1** and **2**. The results are

summarized in Table 1. The products were isolated by flash column chromatography on silica gel and the structures of the products were confirmed from their spectral properties.

In these reactions, toluene and THF can be used as solvents in the place of benzene without appreciable change in the product yields. The other quaternary ammonium salts such as benzyltriethylammonium chloride and tetrabutylammonium bromide can also be used as phase-transfer agents, but the yields of alkenylidenecyclopropanes were low.

The noteworthy features of alkenylidenecyclopropane-forming reactions are as follows. (1) The alkenylidenecarbenes add to **2** in a stereospecific fashion as can be seen from the results of runs 1 and 2 in Table 1. Such a stereospecificity was also observed for a variety of carbenes including vinylidenecarbene.¹² (2) (2,2-Diarylalkenylidene)carbenes are generated

* A plausible pathway for the generation of alkenylidenecarbenes is as follows. The first step is a base-promoted dehydrobromination from 1,1-disubstituted 2,2-dibromocyclopropanes to produce 3,3-disubstituted 1-bromocyclopropanes, although the cyclopropanes could not be isolated under the reaction conditions. The subsequent dehydrobromination from the bromocyclopropanes with base affords alkenylidenecarbenes, accompanying the ring opening of the cyclopropanes. This dehydrobromination to generate alkenylidenecarbenes has already been proposed by Baird *et al.*¹⁰

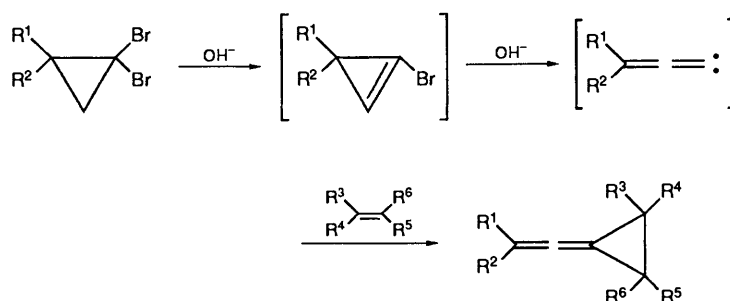


- a; R¹ = R² = Ph
 b; R¹ = 2-Naphthyl, R² = Ph
 c; R¹ = Ph, R² = Me
 d; R¹ = R² = Me
- a; R¹ = R² = Ph, R³ = R⁵ = Me, R⁴ = R⁶ = H
 b; R¹ = R² = Ph, R³ = R⁶ = Me, R⁴ = R⁵ = H
 c; R¹ = R² = Ph, R³ = R⁶ = (CH₂)₄, R⁴ = R⁵ = H
 d; R¹ = R² = Ph, R³ = R⁴ = R⁵ = Me, R⁶ = H
 e; R¹ = R² = Ph, R³ = R⁴ = R⁵ = R⁶ = Me
 f; R¹ = R² = Ph, R³ = R⁴ = R⁵ = H, R⁶ = OEt
 g; R¹ = R² = R³ = Ph, R⁴ = Me, R⁵ = R⁶ = H
 h; R¹ = Ph, R² = 2-Naphthyl, R³ = R⁴ = R⁵ = R⁶ = Me
 i; R¹ = Ph, R² = Me, R³ = R⁴ = R⁵ = R⁶ = Me
 j; R¹ = R² = R⁴ = Me, R³ = Ph, R⁵ = R⁶ = H

Table 1 Preparation of alkenylidenecyclopropanes

Run	Cyclopropane	Alkene	Product	Method	Yield (%) ^a
1	1a		2a 3a	B	65
2	1a		2b 3b	A	42
3	1a		2c 3c	A	44
4	1a		2d 3d	A	74
5	1a		2e 3e	A	70
6	1a		2f 3f	B	96
7	1a		2g 3g	A	59
8	1b	2e	3h	B	75
9	1c	2e	3i	B	55
10	1d	2g	3j	A	22
11	1d	2g	3j	B	62

^a Isolated yields based on the amounts of the starting dibromocyclopropanes **1a-d**.



Scheme 1

efficiently from 1,1-diaryl-2,2-dibromocyclopropanes under both aqueous and non-aqueous phase-transfer conditions. (3) (2-Methylpropenylidene)carbene is, however, generated efficiently from 1,1-dibromo-2,2-dimethylcyclopropane under non-aqueous phase-transfer conditions. (4) Diphenylvinylidenecarbene can also be generated from 1,1-dichloro-2,2-diphenylcyclopropane under the similar conditions, but with lower efficiency; in this case, the yields of the alkenylidene-cyclopropanes were $\leq 30\%$. (5) The alkenylidenecarbenes have an electrophilic character; thus the carbenes generated in the above method did not react with electron-deficient alkenes such as acrylonitrile.

Experimental

Typical Procedure (Method A) for the Preparation of 1-(Diphenylethenylidene)-2,2,3,3-tetramethylcyclopropane 3e.—A mixture of Bu_4NHSO_4 (6 mmol) and aqueous 50% NaOH (150 cm^3) was added to a benzene solution containing 1,1-dibromo-2,2-diphenylcyclopropane **1a** (3 mmol) and an excess of 2,3-dimethylbut-2-ene **2e** and the mixture was vigorously stirred at room temperature for 24 h. Flash column chromatography of the resulting mixture on silica gel with hexane gave **3e** (70%); $\delta_{\text{H}}(\text{CDCl}_3)$ 1.38 (12 H, s, CH_3) and 7.21–7.39 (10 H, m, Ph); $\delta_{\text{C}}(\text{CDCl}_3)$ 31.7, 21.6, 126.3, 128.1, 128.2, 128.3 and 186.7; $\nu_{\text{max}}/\text{cm}^{-1}$ 1984 ($\text{C}=\text{C}$); m/z 274 M^+ .

Typical Procedure (Method B) for the Preparation of 1-(Dimethylethenylidene)-1-methyl-1-phenylcyclopropane 3j.—A mixture of Bu_4NHSO_4 (2 mmol) and powdered NaOH (8 g) was added to a benzene solution containing 1,1-dibromo-2,2-

dimethylcyclopropane **1d** (1 mmol) and an excess of 2-phenylpropene **2g**. The mixture was vigorously stirred at room temperature for 24 h. Work-up of the reaction mixture in a manner similar to that described above afforded **3j**³ (62%); $\delta_{\text{H}}(\text{CDCl}_3)$ 1.61 (3 H, s, CH_3), 1.68 (1 H, d, J 7.71), 1.72 (1 H, d, J 7.71), 1.79 (3 H, s, CH_3), 1.80 (3 H, s, CH_3) and 7.14–7.48 (5 H, m, Ph); $\delta_{\text{C}}(\text{CDCl}_3)$ 21.3, 21.4, 23.7, 24.3, 27.5, 99.2, 112.4, 125.5, 125.9, 126.5, 128.2 and 186.4; $\nu_{\text{max}}/\text{cm}^{-1}$ 2020 ($\text{C}=\text{C}$).

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