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Synthesis of exocyclic *cisoid* dienes by Ramberg–Bäcklund rearrangement

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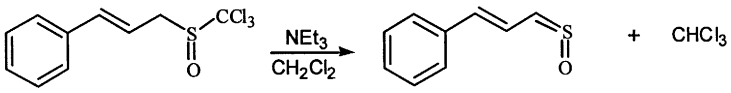
Abstract

Bicyclic and monocyclic *cisoid* dienes were synthesized by an amine-catalyzed Ramberg–Bäcklund rearrangement of allylic trichloromethyl sulfones, in good yields. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Ramberg–Bäcklund rearrangement; trichloromethyl sulfones; synthesis of *cisoid* dienes.

A novel and highly efficient method for the synthesis of sulfines (thiocarbonyl *S*-oxide) via base-induced β-elimination of chloroform from trichloromethyl sulfoxides has been reported from our laboratory (Eq. (1)).[1] It opened up a new method for the synthesis and helped the study of different sulfines. Sulfines received considerable attention because of their synthetic applications and mechanistic interest. In this regard, we have reported the dual reactivity of sulfines towards Diels–Alder reaction as diene or dienophile.[2]



(1)

In the continuation of our studies we have attempted to synthesize sulfenes by the base-induced β-elimination of chloroform from trichloromethyl sulfones. Surprisingly, elimination of sulfur dioxide and HCl was observed.[3] A similar elimination has been reported in earlier literature in a reaction known as Ramberg–Bäcklund rearrangement.[4] The base used to drive Ramberg–Bäcklund rearrangement was aqueous alkali. Exposure of trichloromethyl sulfones to such a drastic condition invariably leads to a mixture of products and the yield of the expected 1,1-dichloroalkene is often low. Indeed, at least three different products are formed in an alkali-induced Ramberg–Bäcklund rearrangement.[5] However, the discovery of facile elimination of sulfur dioxide and HCl by an organic base like DBU prompted us to investigate the synthetic utility of Ramberg–Bäcklund rearrangement.

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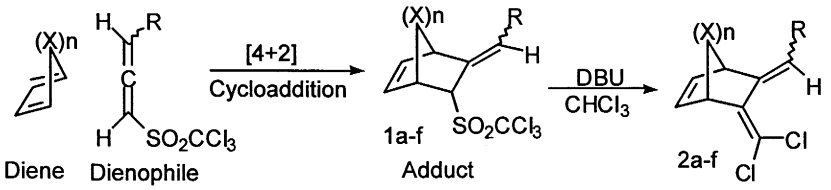
The general route for the synthesis of 1,1-dichloroalkenes is based on organophosphorous or organosilicon chemistry, in which aldehyde or ketone is used as the starting material. The reagents used include triphenylphosphine/CCl_4,[6] triphenylphosphine/$HCCl_3$/KO-*t*-Bu,[7] tri(dimethylamino)phosphine/CCl_4,[8] diethyl (trichloromethanephosphonate)dichloromethyllithium[9] and (trichloromethylsilyl)dichloromethyllithium.[10] Yet another method employed in the synthesis of 1,1-dichloroalkene is the decomposition of β,β,β-trichloroalkyl ethers with 1 equivalent of butyllithium.[11] The present method involves the conversion of the trichloromethyl sulfonyl group to 1,1-dichloroalkene. The reaction of trichloromethane sulfonyl allene with diene gives Diels–Alder adduct which is used in the elimination reaction. In this communication we describe the utility of an amine-catalyzed Ramberg–Bäcklund rearrangement in trichloromethyl sulfones for the synthesis of *cisoid* dienes in good yield.

In view of the general distribution of a bicylic skeleton among natural products, we have mainly focused our attention on the use of this method for the synthesis of bicyclic *cisoid* dienes, which can serve as a synthon in natural products synthesis.[12] Further, such systems are extensively used in organic synthesis in general and also in new molecule synthesis.[13] However, the reaction also works well for monocyclic trichloromethyl sulfone. The *cisoid* disposition of the diene moiety allows further modification by Diels–Alder reaction. In addition, these molecules have two reactive chlorine groups that can be used for further functional group modifications.

Starting materials required for the Ramberg–Bäcklund rearrangement were prepared by the [4+2] cycloaddition of allenyl trichloromethyl sulfone with conjugated diene as reported earlier.[14]



(2)

a, X = CH_2, n = 0, R = H; b, X = O, n = 0, R = H
c, X = CH_2, n = 0, R= Ph; d, X = C_2H_4, n = 1, R = H
e, Diene: Anthracene, R = H f, Diene: CH_2=C(CH_3)-C(CH_3)=CH_2, R = H

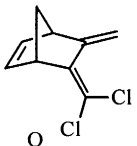
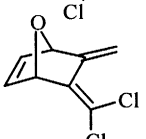
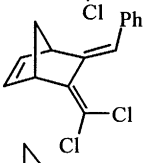
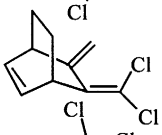
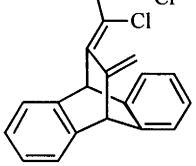
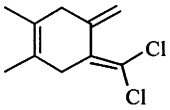
The prepared trichloromethyl sulfones (**1a**–**f**) were subjected to Ramberg–Bäcklund rearrangement. The reaction was carried out in dry chloroform in the presence of DBU as the base. The general reaction is shown in Eq. (2).

The yield and spectral data of the Ramberg–Bäcklund rearrangement products are shown in Table 1.

Preparation of anthracene-allenyl trichloromethane sulfonyl adduct **1e**: Anthracene, 90 mg (0.5 mmol) and allene trichloromethyl sulfone, 125 mg (1.2 equivalent) in 5 mL dry chloroform were placed in a sealed tube. The contents were maintained at 80°C for 10 days. At the end of the reaction chloroform was evaporated and the product was recrystallized from hexane yielding 139 mg (71%) of cycloadduct **1e**.[15]

General procedure for Ramberg–Bäcklund rearrangement: A solution of the Diels–Alder adduct (**1a**–**f**, 0.5 mmol) in 5 mL of dry chloroform was cooled to 0°C. To this DBU solution (1 equivalent) 1 mL of dry chloroform was added through a syringe over a period of 2 min with stirring. The reaction mixture was warmed to room temperature over a period of 30 min and the stirring was continued for a further 2 h. At the end of the reaction the contents were diluted with 20 mL of chloroform and placed in a separating funnel. The solution was washed successively with 1% HCl (3×20 ml), 5% $NaHCO_3$ (3×25 ml) and

Table 1
Yield and spectral data of products **2a–f**

No	Product	Yield (%)	^{1}H NMR (δ,300 Mz, $CDCl_3$)	Molecular Formula	HRMS found, calc.
2a		92	6.40, m (1H), 6.32, bs (1H), 5.31, m (1H), 5.76, bs (1H), 3.83, bs, (1H), 3.41, bs (1H), 1.74, m (2H)	$C_9H_9Cl_2$	187.0070 (MH^+) 187.0081
2b		88	6.66, dd (3,1, 1H), 6.57, dd (3,1, 1H), 5.76, bs (1H), 5.52, bs (1H), 5.38, bs (1H), 5.20, bs (1H)	$C_8H_6OCl_2$	188.9871 (MH^+) 188.9873
2c*		85	7.42-7.14, m (11H), 6.68, bs, (1H), 6.52-6.41, m (4H), 3.97, bs (1H), 3.91, bs (2H), 3.50, bs (1H), 1.86, m (2H), 1.77, dt (8,2, 1H), 1.74 dt, (8,2, 1H)	$C_{15}H_{12}Cl_2$	262.0321 (M^+) 262.0316
2d		83	6.42, m (1H), 6.28, m (1H), 5.80, bs (1H), 5.25, bs (1H), 3.96. bd (6, 1H), 3.27, bdd (6,2, 1H), 1.66, m (2H), 1.42, m (2H)	$C_{10}H_{12}Cl_2$	200.0157 (M^+) 200.0159
2e		86	7.37-7.32, m (4H), 7.15-7.32, m (4H), 5.93, bs (1H), 5.59, bs (1H), 5.55, bs (1H), 4.85, bs (1H)	$C_{18}H_{12}Cl_2$	298.0315 (M^+) 298.0316
2f		77	7.05, dd (8,3, 2H), 2.33, m (4H), 2.27, s (3H), 2.26, s (3H)	$C_{10}H_{12}Cl_2$	203.0402 (MH^+) 203.0394

* 1:1 mixture of double bond isomers.

brine solution (2×25 ml) and dried over anhydrous $MgSO_4$. The solvent chloroform was removed under vacuum evaporation and the product was chromatographed over silica gel using a hexane:ethyl acetate (9:1) solvent system.

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15. Compound **1e**: ^{1}H NMR (δ, 300 MHz) in $CDCl_3$, 7.50 (m, 1H), 5.35 (m, 3H), 7.19 (m, 4H), 5.68 (bd, 2 Hz, 1H), 5.50 (bd, 2 Hz, 1H), 5.10 (bd, 2 Hz, 1H), 4.92 (m, 2H). ^{13}C NMR (δ, 75 MHz, $CDCl_3$) 141.22, 139.39, 138.50, 137.44, 127,51, 127.28, 126.97, 126.62, 126.54, 124.20, 123.60, 123.54, 117.24, 113.75, 63.33, 55.05, 48.17. M.p. 143–145°C. HRMS (CI), $C_{18}H_{14}SO_2Cl_3$ (MH^+) found: 398.9779; calcd: 398.9780.