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Coupling Reaction of Allyl Sulfones Using Sodium Hydroxide in Liquid Ammonia

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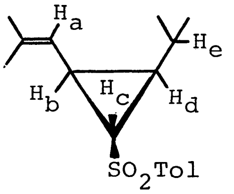
Vinylcyclopropane derivatives containing two isomers were respectively obtained in good yields in the reactions of 3-methyl-2-butenyl, geranyl, and neryl p-tolyl sulfones with NaOH in liquid ammonia. On the other hand, the reaction with crotyl p-tolyl sulfone gave 2-ethyl-1,3-di-p-toluenesulfonylpropane in good yield.

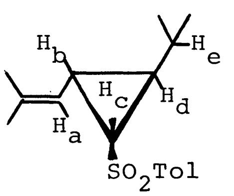
While the synthetic potential of sulfonyl carbanion has been well recognized and reviewed extensively,[1,2] the displacement of the sulfone by a carbon nucleophile is relatively rare.[3,4] Thus, the formation of carbon-carbon bond by utilizing these natures of sulfone is of great value.[4-7]

In this communication, we wish to report the coupling reaction of allyl sulfones using NaOH-liquid ammonia system.[8,9] The first attempt was made in the reaction of 3-methyl-2-butenyl p-tolyl sulfone 1b with NaOH in liquid ammonia. A typical procedure of the reaction is described below. A solution of 1b (2000 mg, 8.92 mmol) and NaOH (750 mg, 17.9 mmol) in liquid ammonia (10 ml) in a titanium autoclave was stirred for 72 h at room temperature. After removal of NH_3, the reaction mixture was extracted with $CHCl_3$ and the extracts were separated by silica gel column chromatography using $CHCl_3$ as an eluent to afford two isomers of 3-(1-methylethyl)-2-(2-methylpropen-1-yl)-1-p-toluenesulfonylcyclopropanes 2b and 3b in 80% yield along with a small amount of methyl p-tolyl sulfone 5 (11%). The ratio of 2b and 3b was roughly 3 : 2.

The structures of 2b[10] and 3b[11] were identified by MS, IR, ^1H NMR, ^{13}C NMR spectra and elemental analysis, and the configurations of cyclopropane rings in 2b and 3b were determined by their ^1H NMR coupling constants on the basis that in cyclopropanes, cis coupling constants are invariably larger than trans coupling constants.[12]



2b

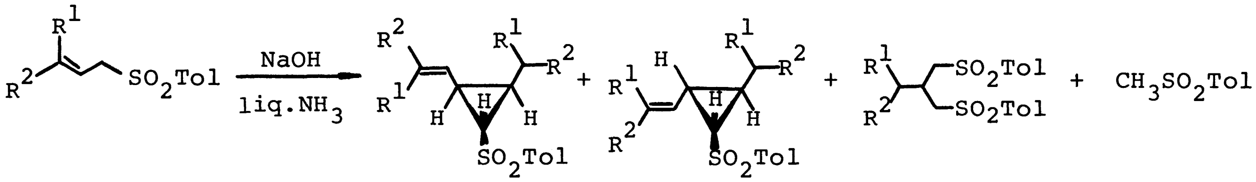


3b

The reaction with geranyl or neryl p-tolyl sulfones 1c and 1d gave two isomers of the vinylcyclopropane derivatives 2c and 3c, respectively.

Different from these allylic sulfones, the reaction with crotyl p-tolyl sulfone 1a for 48 h at room temperature gave 2-ethyl-1,3-di-p-toluenesulfonylpropane 4a[13] in 66% yield as a major product. The results are shown in Table 1.

Table 1. Reaction of Allyl Sulfones with NaOH in Liquid Ammonia[a]



1 2 3 4 5

1a : $R^1 = CH_3$, $R^2 = H$, or $R^1 = H$, $R^2 = CH_3$ (1 : 1 mixture of cis and trans)
1b : $R^1 = R^2 = CH_3$
1c : $R^1 = CH_3$, $R^2 = (CH_3)_2C{=}CHCH_2CH_2$
1d : $R^1 = (CH_3)_2C{=}CHCH_2CH_2$, $R^2 = CH_3$

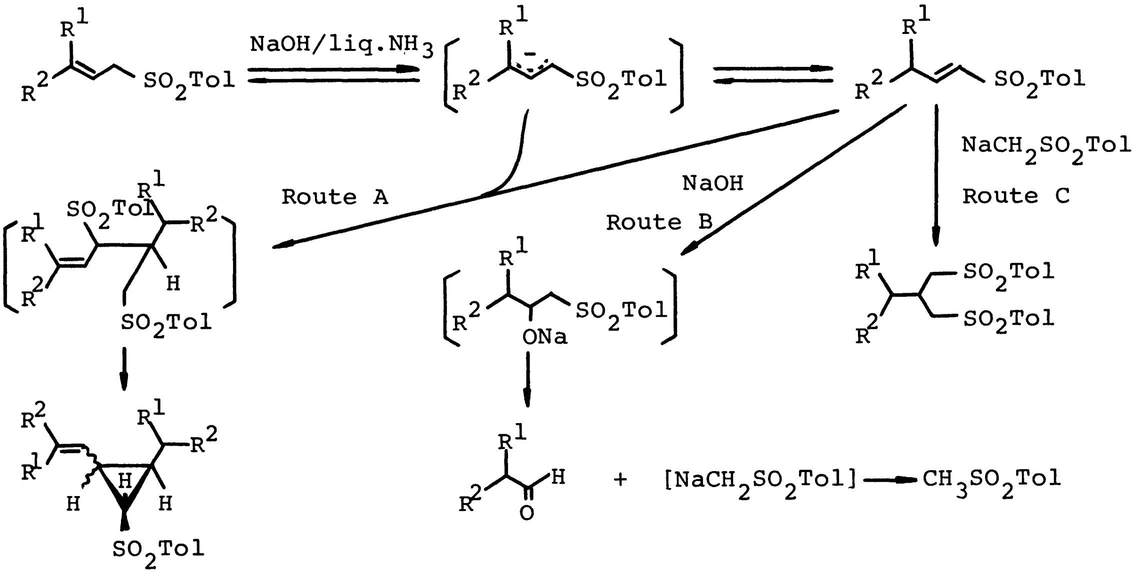
Allyl sulfone		Temp/°C	Time/h	Product/% 2	3	4	5
Crotyl p-tolyl sulfone	(1a)[b]	R.T.	48	0	0	66	5
3-Methyl-2-butenyl p-tolyl sulfone	(1b)[c]	R.T.	72	48	32	0	11
Geranyl p-tolyl sulfone	(1c)[d]	50	48	60(2c + 3c)[e]		0	17
Neryl p-tolyl sulfone	(1d)[d]	50	48	81(2c + 3c)[e],[f]		0	trace

a) NaOH : 2 equiv., liq.NH_3 : 10 ml. b) 4.76 mmol. c) 8.92 mmol. d) 2 mmol.
e) The ratio of 2c and 3c was ca. 3 : 2. f) Vinylcyclopropanes obtained from 1d were identical with those from 1c.

Since it is well known that allyl sulfones isomerize to the corresponding vinyl sulfones via α sulfonyl carbanions under basic conditions we studied the reactions of trans-3-methyl-1-(p-toluenesulfonyl)-1-butene 6 and trans-1-(p-toluenesulfonyl)-1-butene 7 under similar reaction conditions. After 24 h at room temperature, 6 gave vinylcyclopropanes 2b and 3b in 35 and 23% yields, respectively. In this reaction, 1b was also obtained in 21% yield. Similarly, 7 afforded 4a in 26% yield after 60 h at room temperature. Consequently, it appears that the corresponding vinyl sulfones are the intermediates in a series of the reactions with allyl sulfones.

The plausible mechanisms of the reactions with allyl sulfones are shown in the Scheme 1.

The initial step is an isomerization of an allylic sulfone to a vinyl sulfone via α sulfonyl carbanion.[14] Judging from the fact that the treatment of vinyl sulfone 6 with NaOH in liquid ammonia forms allyl sulfone 1b, allyl p-tolyl sulfones are in equilibrium with the corresponding vinyl p-tolyl sulfones.[15]



Scheme 1.

Michael type addition of α sulfonyl carbanion to the resulting vinyl sulfone followed by the displacement on the allylic sulfone site affords vinylcyclopropane derivatives (Route A).16,17) The formation of methyl p-tolyl sulfone 5 18) may be attributable to the addition of NaOH to vinyl sulfones to yield β-hydroxysulfones which may undergo retro aldol reaction to give 5 (Route B). In the reaction with crotyl p-tolyl sulfone 1a, the addition of sodium p-toluenesulfonylmethylide formed by Route B to vinyl sulfone 7 preferentially occurred (Route C).

Work along the expansion of synthetic utilities using allyl sulfones is in progress in our laboratory.

We wish to thank Dr. Yutaka Fujise, Department of Chemistry, Tohoku university, for the measurements of ^{1}H NMR and ^{13}C NMR spectra of the compounds, 2b and 3b.

References

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9) R. Asami and K. Shimo, Sci. Repts. Reserch Insts., Tohoku Univ., 9A, 341 (1957).
10) 2b : colorless needles, mp 65.0-66.5 °C (hexane), MS(m/z) ; 292(M$^+$, 3%), 137 (bp), 55(29%), 43(41%), IR(KBr) ; 1300, 1150 cm^{-1}, ^{1}H NMR(CDCl$_3$) ; δ 0.75(d, 3H, J=6.5 Hz), 0.93(d, 3H, J=6.5 Hz), 1.24(d.sept, 1H, J=10.5, 6.5 Hz, H$_e$),

1.51(ddd, 1H, J=10.5, 9.5, 5.0 Hz, H_d), 1.69(br.s, 3H), 1.72(br.s, 3H), 2.11 (t, 1H, J=5.0 Hz, H_c), 2.43(s, 3H), 2.54(ddd, 1H, J=9.5, 9.0, 5.0 Hz, H_b), 4.81(br.d, 1H, J=9.0 Hz, H_a), 7.35(d, 2H, J=8.5 Hz), 7.79(d, 2H, J=8.5 Hz), ^{13}C NMR($CDCl_3$) ; δ 18.378(q), 21.368(q), 21.585(q), 22.235(q), 23.882(d), 25.703(q), 27.393(d), 33.505(d), 46.422(d), 117.724(d), 127.558(d x 2), 129.687(d x 2), 137.268(s), 138.093(s), 143.988(s), Found ; C, 69.53, H, 8.47 S, 11.13%. Calcd for $C_{17}H_{24}O_2S$; C, 69.87, H, 8.21, S, 10.96%.

11) **3b** : colorless needles, mp 85.5-86.5 °C (hexane), MS(m/z) ; 292(M^+, 2%), 137 (bp), 55(17%), 43(30%), IR(KBr) ; 1310, 1150 cm^{-1}, ^1H NMR($CDCl_3$) ; δ 1.06(d, 3H, J=6.5 Hz), 1.13(d, 3H, J=6.5 Hz), 1.34(d.sept, 1H, J=8.5, 6.5 Hz, H_e), 1.61(br.s, 3H), 1.88(br.s, 3H), 1.90(ddd, 1H, J=8.5, 7.5, 5.5 Hz, H_d), 2.02(td, 1H, J=8.5, 7.5 Hz, H_b), 2.51(dd, 1H, J=8.5, 5.5 Hz, H_c), 2.59(s, 3H), 5.55 (br.d, 1H, J=8.5 Hz, H_a), 7.53(d, 2H, J=8.5 Hz), 7.97(d, 2H, J=8.5 Hz), ^{13}C NMR($CDCl_3$) ; δ 17.901(q), 21.368(q x 2), 21.542(q), 25.616(q), 26.483(d), 31.598(d), 34.458(d), 45.035(d), 119.583(d), 127.517(d x 2), 129.292(d x 2), 135.492(s), 138.612(s), 143.731(s), Found ; C, 69.34, H, 8.34, S, 11.21%. Calcd for $C_{17}H_{24}O_2S$; C, 69.87, H, 8.21, S, 10.96%.

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13) **4a** : oil, MS(m/z) ; 380(M^+), IR(oil) ; 1300, 1140 cm^{-1}, ^1H NMR(C_6D_6) ; δ 0.55 (t, 3H, J=7.5 Hz, CH_3), 1.60(quint, 2H, J=7.5 Hz, $CH_3\underline{CH_2}$), 1.95(s, 6H, CH_3), 2.50(m, 1H, CH), 2.90(d, d, 2H, J=6.0 Hz, CH_2), 3.35(d, d, 2H, J=7.5 Hz, CH_2), 6.86(d, 4H, J=7.5 Hz, Ar), 7.83(d, 4H, J=7.5 Hz, Ar).

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