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DIANION OF *N*-PHENYL-2-(PHENYLSULFONYLMETHYL)PROPENAMIDE: AN EFFICIENT SYNTHETIC REAGENT FOR (*E*)-TRISUBSTITUTED OLEFINS AND 5,6-DIHYDRO-2*H*-PYRANS

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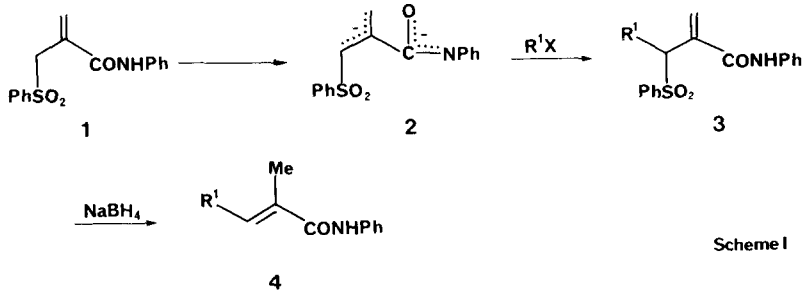
Summary: The dianion of *N*-phenyl-2-(phenylsulfonylmethyl)propenamide was found to be an efficient reagent for the synthesis of (*E*)-α,β-unsaturated amides and 5,6-dihydro-2*H*-pyrans.

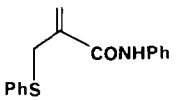
In recent years the chemistry of polyanions has attracted increased attention since these species can serve as reactive intermediates in organic synthesis[1] and studies of their structures can lead to further understanding the nature of the bonding in bridged metal-carbon systems.[2] The purpose of this communication is to report our observations on the utility of the dianion of *N*-phenyl-2-(phenylsulfonylmethyl)propenamide[3] as a new reagent for the preparation of (*E*)-trisubstituted olefins and 5,6-dihydro-2*H*-pyrans.

Treatment of the amide 1 with 2.1 equiv of butyllithium in THF containing 2.1 equiv of HMPA, cooled to -78°C, gave a reddish orange solution of the dianion 2 within 30 min. The dianion reacted regioselectively with iodooctane at the α-position of the phenylsulfonyl group to give 2-methylene-*N*-phenyl-3-(phenylsulfonyl)undecanamide (3c)[4] in 78% yield (Table 1).



Scheme I

In contrast, reaction of the dianion derived from *N*-phenyl-2-(phenylthiomethyl)propenamide (5) with iododecane led to the formation of a mixture of α-product (15%) and γ-product (13%); furthermore the monoanion of methyl 2-(phenylsulfonylmethyl)propenoate (6) was extremely labile compared to the amide dianion 2. The use of a hindered base such as lithium 2,2,6,6-tetramethylpiperidide at -78°C led to decomposition of the starting material.



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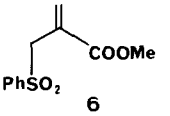

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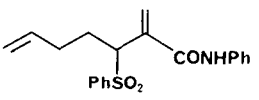
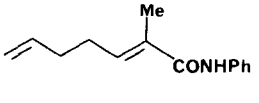
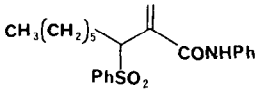
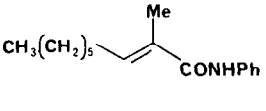
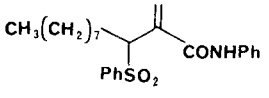
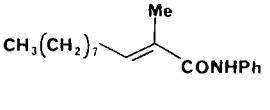
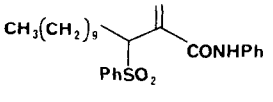
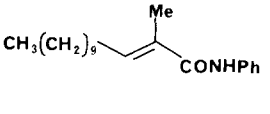
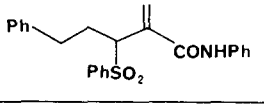
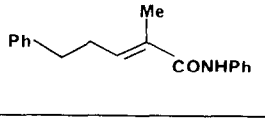
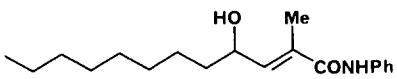
Reaction of the α-product 3c with 1.6 equiv of sodium borohydride in ethanol proceeded smoothly under very mild conditions (room temperature, 10 min) to furnish (*E*)-2-methyl-*N*-phenyl-2-undecenamide (4c)[5] in 79% yield (Table 1). The ^{1}H NMR analysis of 4c shows only one olefinic signal as a triplet of doublets at δ 6.38 ppm, consistent with *E*-geometry of the trisubstituted olefins. The spectrum of a mixture of (*E*)- and (*Z*)-2-methyl-*N*-phenyl-2-undecenamide prepared by the other method,[6] showed the olefinic protons at δ 5.53 ppm (*Z*-isomer) and at δ 6.38 ppm (*E*-isomer). The structure of 4c was further confirmed by hydrolysis to the corresponding methyl ester via the *N*-*t*-Boc derivative.[7] No detectable quantities of the *Z*-isomer were noted on ^{1}H NMR or GLC analysis of this ester. Under the same conditions, nonanal and

Table 1. Reaction of Dianion 2 with Alkyl Halides

Alkyl halide	Alkylation product (3)	Yield of 3	α,β-Unsaturated amide (4)	Yield of 4
CH_2=$CHCH_2CH_2Br$		(3a) 57%		(4a) 94%
$CH_3(CH_2)_5Br$		(3b) 64%		(4b) 88%
$CH_3(CH_2)_7I$		(3c) 78%		(4c) 79%
$CH_3(CH_2)_9I$		(3d) 84%		(4d) 95%
$PhCH_2CH_2Br$		(3e) 61%		(4e) 80%

decanal were stereoselectively converted to difunctional trisubstituted (*E*)-alkenes 7 and 8 in good yields.



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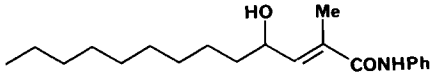

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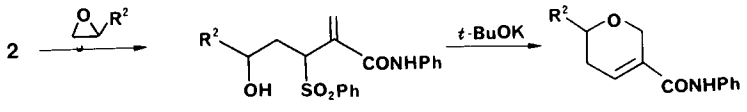
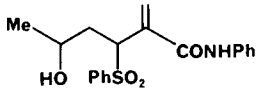
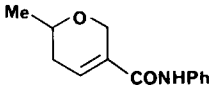
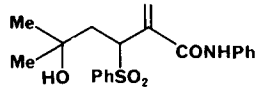
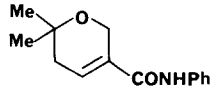
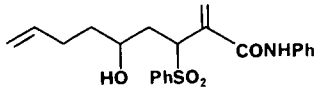
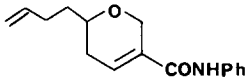
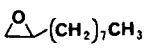
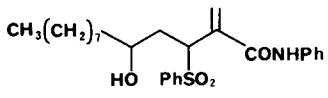
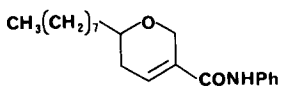
The high reactivity of the dianion 2 was demonstrated by the reaction with epoxides which proceeded without using a Lewis acid such as boron trifluoride etherate.[8] Thus, 1,2-epoxypropane was added at -78°C to a dianion solution,



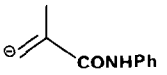
9 10

prepared from the amide 1 and 2.1 equiv of butyllithium in THF-HMPA-TMEDA (1:1:1). The mixture was stirred for 30 min, warmed to room temperature and stirred for 2 h. Extractive workup and column chromatography gave an adduct 9f in 68% yield.[9] Treatment of 9f with 2.5 equiv of potassium *t*-butoxide in THF-*t*-BuOH (3:1) at room temperature for 18 h gave 5,6-dihydro-2*H*-pyran 10f in 73% yield[10] as crystalline solids (Table 2).

Table 2. Reaction of Dianion 2 with Epoxides

Epoxide	Alkylation product (9)	Yield of 9	5,6-Dihydro-2H-pyran (10)	Yield of 10
		(9f) 68%		(10f) 73%
		(9g) 48%		(10g) 65%
		(9h) 63%		(10h) 68%
		(9i) 61%		(10i) 67%

The present method permits the introduction of a methacryloyl unit 11 into a variety of organic substances that might otherwise prove difficult to synthesize.[11]



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References and Notes

1. For reviews, see: a) K. Tanaka and A. Kaji, Sulfur Reports, 1, 97 (1980). b) E. M. Kaiser, J. P. Petty, and P. L. A. Knutson, Synthesis, 1977, 509. c) N. Petragnani and M. Yonashiro, Synthesis, 1982, 521.
2. a) A. Streitwieser, Jr., Acc. Chem. Res., 17, 353 (1984). b) D. Wilhelm, H. Dietrich, T. Clark, W. Mahdi, A. J. Kos, and P. v. R. Schleyer, J. Am. Chem. Soc., 106, 7279 (1984).
3. *N*-Phenyl-2-(phenylsulfonylmethyl)propenamide (2) was prepared by one-pot procedure from *N*-phenyl-2-(tributylstannylmethyl)propenamide, iodine, and sodium benzenesulfinate in 89% yield; mp 178-179°C.
4. Compound 3c: ^{1}H NMR ($CDCl_3$) δ 0.72-1.52 (m, 15H), 1.58-2.28 (m, 2H), 4.58 (dd, J = 11.6, 3.7 Hz, 1H), 5.67 (s, 1H), 6.16 (s, 1H), 6.92-7.92 (m, 10H), 8.40 (s, 1H). Anal. Calcd for $C_{24}H_{31}NO_3S$: C, 69.70; H, 7.56; N, 3.39. Found: C, 69.63; H, 7.60; N, 3.27.
5. Mp 58°C; ^{1}H NMR ($CDCl_3$) δ 0.72-1.62 (m, 15H), 1.87 (s, 3H), 1.94-2.26 (m, 2H), 6.38 (dt, J = 1.2, 7.2 Hz, 1H), 6.94-7.65 (m, 5H), 7.82 (s, 1H); IR (neat) 3225, 1655, 1595, 925, 900, 770, 700 cm^{-1}. Anal. Calcd for $C_{18}H_{27}NO$: C, 79.07; H, 9.96; N, 5.12. Found: C, 79.09; H, 9.91; N, 5.01.
6. Ethyl 2-methyl-2-undecenoate was prepared in 72% yield as a 61:39 mixture of *E*- and *Z*-isomer by the reported procedure. K. Tanaka, R. Tanikaga, and A. Kaji, Chem. Lett., 1976, 917.
Reaction of this ester with aniline in the presence of sodium methoxide in benzene gave a mixture of (*E*)- and (*Z*)-2-methyl-*N*-phenyl-2-undecenamide.
7. D. L. Flynn, R. E. Zelle, and P. A. Grieco, J. Org. Chem., 48, 2424 (1983).
8. M. J. Eis, J. E. Wrobel, and B. Ganem, J. Am. Chem. Soc., 106, 3693 (1984).
9. Mp 51-52°C; ^{1}H NMR ($CDCl_3$) δ 0.94-1.36 (m, 3H), 1.64-2.18 (m, 2H), 3.61-3.96 (m, 2H), 4.36-4.76 (m, 1H), 5.86 (s, 1H), 6.15 (s, 1H), 6.90-7.90 (m, 10H), 8.47 (s, 1H); IR (nujol) 3300, 1660, 1600, 780, 700 cm^{-1}. Anal. Calcd for $C_{19}H_{21}NO_4S$: C, 63.49; H, 5.89; N, 3.90. Found: C, 63.25; H, 6.00; N, 3.86.
10. Compound 10f: mp 150-150.5°C; ^{1}H NMR ($CDCl_3$) δ 1.21 (d, J = 6 Hz, 3H), 1.92-2.26 (m, 2H), 3.33-3.76 (m, 1H), 4.05-4.69 (m, 2H), 6.33-6.60 (m, 1H), 6.86-7.55 (m, 5H), 7.83 (s, 1H). Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.87; H, 6.96; N, 6.45. Found: C, 71.93; H, 6.96; N, 6.48.
11. a) M. Alderdice, C. P. Spino, and L. Weiler, Tetrahedron Lett., 25, 1643 (1984). b) T. Hiyama, A. Kanakura, H. Yamamoto, and H. Nozaki, Tetrahedron Lett., 1978, 3051.

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