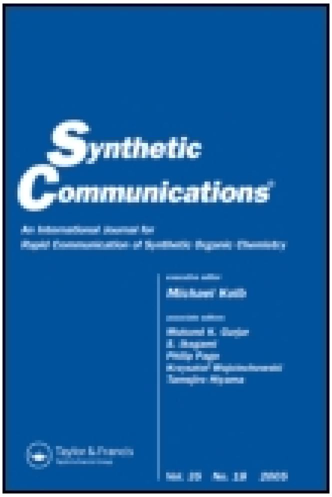


Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

The Reaction of 1-Nitro-4-(4-nitrophenylsulfonylmethyl)benzen with α,β-Unsaturated Esters

Yue Guoren [a] & Zhang Zheng [a]

[a] Department of Chemistry , Zhangye Teachers' College , 734000, Zhangye, Gansu, P.R. CHINA

[b] Department of Chemistry , Nanjing University , 210093, Nanjing, Jiangsu, P.R. CHINA

To cite this article: Yue Guoren & Zhang Zheng (1996) The Reaction of 1-Nitro-4-(4-nitrophenylsulfonylmethyl)benzene with α,β-Unsaturated Esters, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 26:10, 2003-2008, DOI: 10.1080/00397919608003555

To link to this article: http://dx.doi.org/10.1080/00397919608003555

SYNTHETIC COMMUNICATIONS, 26(10), 2003-2008 (1996)

THE REACTION OF 1-NITRO-4-(4-NITROPHENYLSULFONYL-METHYL)BENZENE WITH α,β-UNSATURATED ESTERS

Yue Guoren*
Department of Chemistry, Zhangye Teachers' College, 734000, Zhangye, Gansu, P.R.CHINA
Zhang Zheng
Department of Chemistry, Nanjing University, 210093, Nanjing, Jiangsu, P.R.CHINA

Abstract; Under solid-liquid PTC conditions, treatment of 1-nitro-4-(4-nitrophenylsulfonylmethyl)benzene(**1**) with α,β -unsaturated esters (**2**a-h) at 35 -75°C gave tandem addition-rearrangement products(**3**a-h). While at higher temperature(75°C), addition-rearrangement-addition products (**4**a-b) were obtained when acrylates were used. Finally a possible mechanism is proposed.

Keywords; Addition-rearrangement, Addition-rearrangement-addition, 1-Nitro-4-(4-nitrophenylsulfonylmethyl)benzene, α,β -Unsaturated esters

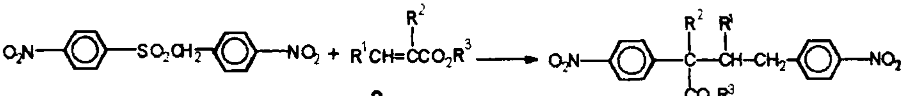
To date , many reports have appeared on using sulfur compounds for organic synthesis[1-5] , since Seebach and Corey[6] reported the utilization of 1,3 - dithiane for preparation aldehydes and ketones. In general, an organic sulfur compound can be used as a synthetic agent according to the following scheme, which consists of two processes: (1) formation of a C-C bond between a sulfur agent and an organic compound to afford an intermediate and (2) its desulfurization accompanied with creation of a new functional group to produce a desired product.

A novel type of tandem Michael addition-rearrangement reaction was found when p-nitrophenylsulfonylacetates[7] reacted with α,β -unsaturated esters in the system of K_2CO_3/DMF /TEBA, where the formation of C-C bonds and the elimination of sulfur dioxide proceeded at the same time in one pot. But if using the other arylsulfonylacetates[8] as Michael donors, only normal Michael addition was observed. As a new type of reaction, it should be applied widely. On this consideration, we have continuously investigated the reaction of 1-nitro-4-(4-nitrophenylsulfonylmethyl)benzene(**1**) with α,β -unsaturated esters(**2**). The reaction of 1-nitro-4-(4-nitrophenylsulfonylmethyl)benzene, except for the preparation[9] and physical properties such as spectra data[10], has not been reported. Alkylation[11], Knoevenagel reaction[12] and Michael addition[13] of the other arylsulfonylmethylbenzenes and their derivatives have appeared in the literature.

Our studies show that, under solid-liquid PTC conditions, treatment of 1-nitro-4-(4-nitrophenylsulfonylmethyl)benzene with α,β-unsaturated esters at 35 -75 °C gave tandem addition-rearrangement products . (Scheme 1)

---

* To whom correspondence should be addressed



1 **2a-h** **3a-h**

2a,3a R^1=H, R^2=H, R^3=CH_3,

2c,3c R^1=H, R^2=CH_3, R^3=CH_3,

2e,3e R^1=H, R^2=$CH_2CO_2CH_3$ R^3=CH_3,

2g,3g R^1=H, R^2=$CH_2CO_2C_3H_7$-n, R^3=C_3H_7-n

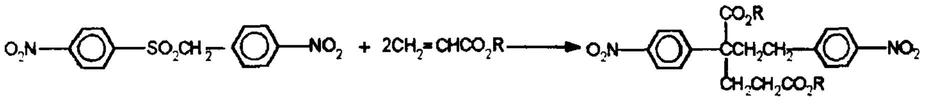
2b,3b R^1=H, R^2=H, R^3=C_2H_5

2d,3d R^1=H, R^2=CH_3. R^3=C_2H_5

2f,3f R^1=H, R^2=$CH_2CO_2CH(CH_3)_2$ R^3=$CH(CH_3)_2$

2h,3h R^1=CH_3, R^2=H. R^3=CH_3

Scheme 1



1 **2a-b** **4a-b**

2a,4a R=CH_3 2b, 4b R=C_2H_5

Scheme 2

While at higher temperature(75°C), tandem addition-rearrangement-addition products, which are 2-(4-nitrophenylethyl)-2-(4-nitrophenyl)glutarates, were obtained when acrylates were used (Scheme 2).

Results and Discussion

1; An addition-rearrangement reaction could easily occur when **1** reacted with α,β-unsaturated esters, which are acrylates, methacrylates, itaconates and crotonate, at 35-75 °C in the system of K_2CO_3/DMF/TEBA. Attempts to react with cinnamates failed* because of steric hindrance effects. Data from our studies(Table 1) reveal that the rate of acrylates was the fastest, followed by methacrylates, itaconates, and then crotonate.

2; The mechanism of addition-rearrangement reaction had been discussed for p-nitrophenylsulfonylacetates reacting with α,β- unsaturated esters[7]. Normal Michael addition products were not obtained in the reaction of **1** with α,β -unsaturated esters (**2**) under the conditions of K_2CO_3 /DMF/TEBA, which denotes that the rate of rearrangement is faster than addition.

3; At higher temperature(75°C), one equiv. of **1** reacted with two equiv. of acrylates (**4a-b**) to produce unexpected organic compounds such as **4a**, which has strong infrared absorption

---

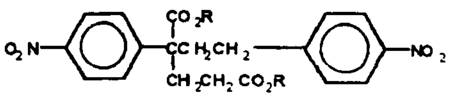
*Monitored by TLC, the reaction of 1 with ethyl cinnamate had not given product after 60 hours.

Table 1 Physical properties and data of elementary analylsis and MS for products

Prod. No.	Formula (M.W)	React. Time (h)*	Yield (%)	M.P. (°C)	Elementary analysis found (calcd.) C(%) H(%) N(%)	M/z (%)
3a	$C_{17}H_{16}N_2O_6$ (344.35)	5	95	93-94	59.25 4.75 7.94 (59.29) (4.69) (8.14)	344(M^+,0.1),314(0.9),195(100),163(29.7),150(9.0),136(11.6),106(11.6)
3b	$C_{18}H_{18}N_2O_6$ (358.38)	4	94	75-76	60.49 5.31 7.68 (60.32) (5.07) (7.82)	358(M^+,0.3),328(1.5),285(6.8),239(6.6),209(100),181(100),163(18.5),150(13.3),136(36.2),106(25.3)
3c	$C_{18}H_{18}N_2O_6$ (358.38)	5	92	101-102	60.51 5.19 7.68 (60.32) (5.07) (7.82)	342(0.5),328(0.6),299(3.2),269(1.2),253(1.5),209(100),177(32.3),163(6.0),150(23.0),136(27.5),106(15.1),
3d	$C_{19}H_{20}N_2O_6$ (372.41)	5	90	55-56	61.07 5.52 7.30 (61.27) (5.42) (7.52)	356(0.6),342(0.8),299(5.2),270(21.7),223(100),195(36.3),177(16.4),163(7.6),150(41.8),136(38.3),106(17.5).
3e	$C_{20}H_{20}N_2O_8$ (416.42)	6	91	108-109	57.69 5.10 6.61 (57.68) (4.85) (6.73)	385(0.5),267(16.4),235(100),207(48.7),150(3.3),136(10.1),106(4.0).
3f	$C_{24}H_{28}N_2O_8$ (472.54)	7	90	98-99	61.21 6.26 5.85 (61.00) (5.98) (5.93)	371(7.2),323(9.7),263(12.5),221(60.0),150(21.1),136(14.6),106(15.0).
3g	$C_{24}H_{28}N_2O_8$ (472.54)	8	90	90-91	61.08 6.12 5.81 (61.00) (5.98) (5.93)	472(M^+.0.1),442(0.7),413(1.4),371(5.8),343(5.8),323(15.1),263(61.5),221(100),193(35.4),150(5,5),136(18.2),106(12.8).
3h	$C_{18}H_{18}N_2O_6$ (358.38)	10	85	106-107	60.35 5.30 7.71 (60.32) (5.07) (7.82)	358(M^+,0.1),342(0.3),328(0.6),299(1.8),196(10.7),195(100),164(43.3)150(4.1),136(29.9),106(25.2).
4a	$C_{21}H_{22}N_2O_8$ (430.45)	1	93	138-139	58.42 5.32 6.39 (58.59) (5.16) (6.51)	430(M^+,0.2),415(0.2),400(6.1),399(1.5),398(2.2),371(14.7),370(9.0),341(5.7),311(6.8),281(100)249(56.2),221(26.7),150(42.3),136(3.0),106(4.5).
4b	$C_{23}H_{26}N_2O_8$ (458.51)	1	90	101-102	60.25 5.98 5.98 (60.25) (5.73) (6.11)	458(M^+,1.0),442(2.1),428(7.1),413(12.3),385(90.4),367(23.9),355(14.6),339(40.2),336(54.9),311(96.6),309(100),263(84.0),235(63.3),206(72.8),150(19.0),136(81.4),106(54.5).

* 3a-b were obtained at a temperature of 35°C and 3c-h and 4a-b obtained at 75°C

bands (in KBr pellet) at 1735, 1720cm^{-1} characterized to two carbonyl groups and at 1511, 1343cm^{-1} for two nitro groups. The ^{1} HNMR (in $CDCl_3$) spectra of **4a** recorded on an AM 500 ^{1}HNMR spectrometer has shown four symmetric doublets at 8.30, 8.20, 7.53, 7.37ppm characterized to two para-disubstituted phenyl groups, two singlets at 3.83, 3.73ppm for two methoxy groups and one multiple band at 2.70-2.03ppm (8H) for two ethene groups (figure 1). The stablest fragment in MS spectra (EI) of **4a** is 281(M^+-p-$O_2NC_6H_4CH{=}CH_2$, 100). We assert that the structures of **4** are as follows:



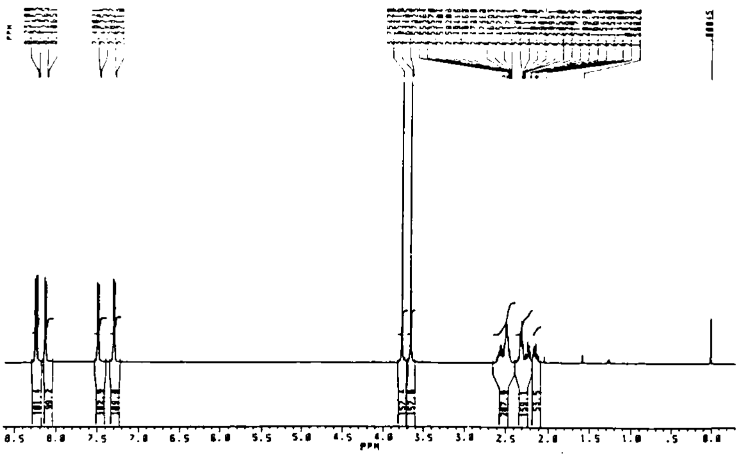
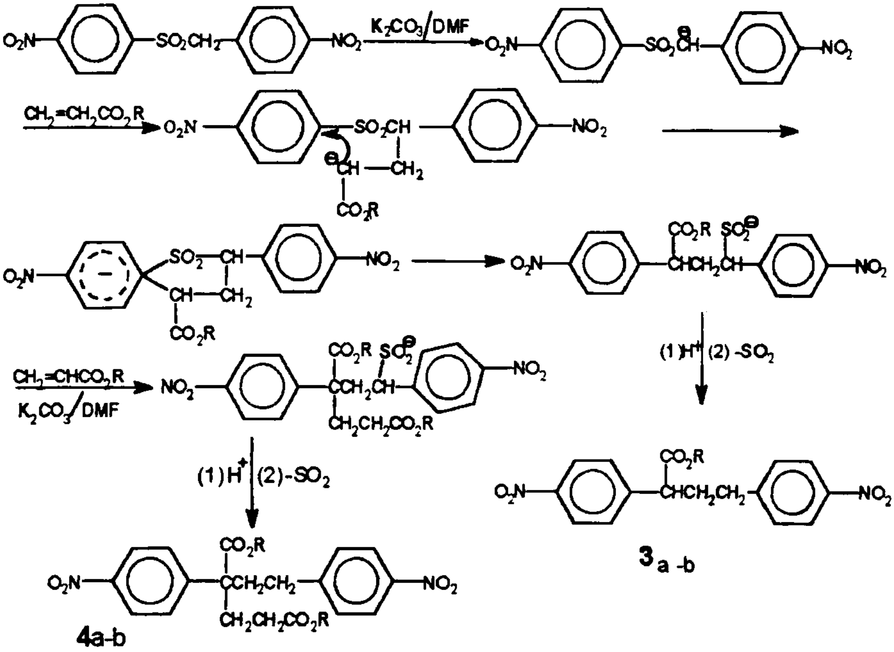


Figure 1



Scheme3

Table 2 Data of IR, ^{1}HNMR for products

Prod.	IR(cm^{-1})		^{1}HNMR* δ (ppm)
No.	C=O	NO$_2$	
3a	1722	1516 1346	8.23(2H, d, Ar-H, J=8.8Hz), 8.16(2H, d, Ar-H, J=8.5Hz), 7.48(2H, d, Ar-H, J=8.8Hz), 7.34(2H, d, Ar-H, J=8.5Hz), 3.70(3H, s, OCH_3), 3.68(1H, t, Ar-CH, J=8.0Hz), 2.97-2.00(4H, m, CH_2CH_2).
3b	1738	1519 1347	8.40(2H, d, Ar-H, J=8.8Hz), 8.20(2H. d, Ar-H, J=8.5Hz), 7.52(2H, d, Ar-H, J=8.8Hz), 7.40(2H, d, Ar-H, J=8.5Hz), 4.20(2H, q, OCH_2, J=7.0Hz), 3.66(1H, t, Ar-CH, J=8.0Hz), 2.97-2.00(4H, m, CH_2CH_2), 1.34(3H, t, CH_3, J=7.0Hz),
3c	1724	1516 1347	8.28(2H, d, Ar-H, J=8.8Hz), 8.18(2H. d, Ar-H, J=8.5Hz), 7.56(2H, d, Ar-H, J=8.8Hz), 7.37(2H. d, Ar-H, J=8.5Hz), 3.76(3H, s, OCH_3), 2.83-2.03(4H, m, CH_2CH_2), 1.76(3H, S, CCH_3).
3d	1728	1524 1349	8.17(2H, d, Ar-H, J=8.8Hz), 8.07(2H, d, Ar-H, J=8.5Hz), 7.50(2H, d, Ar-H, J=8.8Hz), 7.27(2H, d, Ar-H. J=8.5Hz), 4.16(2H, q, OCH_2, J=7.0Hz), 2.80-2.00(4H, m, CH_2CH_2), 1.63(3H, S, Ar-C-CH_3), 1.19(3H, t, O-C-CH_3, J=7.0Hz)
3e	1746 1729	1519 1346	8.22(2H, d, Ar-H, J=8.8Hz), 8.07(2H, d, Ar-H, J=8.5Hz), 7.50(2H, d, Ar-H, J=8.8Hz), 7.26(2H, d, Ar-H, J=8.5Hz), 3.70(3H, s, OCH_3), 3.59(3H, S, OCH_3), 3.16(2H, m, $COCH_2$), 2.50(4H, m, CH_2CH_2).
3f	1732 1720	1519 1346	8.20(2H, d, Ar-H, J=8.8Hz), 8.07(2H, d, Ar-H, J=8.5Hz), 7.50(2H, d, Ar-H, J=8.8Hz), 7.26(2H, d, Ar-H, J=8.5Hz), 5.00(2H, m, 2×OCH), 3.10(2H, m, $COCH_2$), 2.48(4H, m, CH_2CH_2), 1.16(12H, m, 4×C-CH_3)
3g	1736 1720	1517 1344	8.23(2H, d, Ar-H, J=8.8Hz), 8.09(2H, d, Ar-H, J=8.5Hz), 7.52(2H, d, Ar-H, J=8.8Hz), 7.30(2H, d, Ar-H, J=8.5Hz), 4.00(4H, t, 2×OCH_2, J=7.0Hz), 3.13(2H, m, $COCH_2$), 2.50(4H, m, CH_2CH_2Ar), 1.60(4H, m, O-C-CH_2), 0.83(6H, m, 2×CH_3)
3h	1733	1518 1348	8.22(2H, d, Ar-H, J=8.8Hz), 8.07(2H, d, Ar-H, J=8.5Hz). 7.53(2H, d, Ar-H, J=8.8Hz), 7.13(2H, d, Ar-H, J=8.5Hz), 3.60(3H, s, OCH_3), 3.42(1H. d, Ar-CH, J=8.5Hz), 2.66-2.00(3H, m, $CHCH_2$), 0.83(3H, d, C-CH_3, J=6.0Hz),
4a	1735 1720	1511 1343	8.30(2H, d, Ar-H, J=8.8Hz), 8.20(2H, d, Ar-H, J=8.5Hz), 7.53(2H, d, Ar-H, J=8.8Hz), 7.37(2H, d, Ar-H, J=8.5Hz), 3.83(3H, s, OCH_3), 3.73(3H, s, OCH_3), 2.70-2.03(8H, m, 2×CH_2CH_2)
4b	1734 1719	1516 1344	8.28(2H, d, Ar-H, J=8.8Hz), 8.16(2H. d, Ar-H, J=8.5Hz), 7.56(2H, d, Ar-H, J=8.8Hz), 7.37(2H, d, Ar-H, J=8.5Hz), 4.37(2H, q, OCH_2, J=7.0Hz), 4.20(2H. q. OCH_2, J=7.0Hz), 2.83-2.08(8H, m, 2×CH_2CH_2), 1.10(3H, t, O-C-CH_3, J=7.0Hz), 1.06(3H, t, O-C-CH_3, J=7.0Hz)

* A mixture of $CDCl_3$ and CCl_4 was used as the solvent

The results of elemental analysis of 4a were C; 58.42, H;, 5.32, N; 6.39, which are in agreement with the calculated values C; 58.59, H; 5.16, N; 6.51.

On the basis of experimental results, a possible mechanism via addition, rearrangement, and then addition is proposed (scheme 3).

Experimental Section

All reagents were of reagent grade and used without further purification. All melting points are uncorrected and measured with a Yancco MP-500 apparatus. Elemental analysis were performed using a Perkin-Elmer 240C instrument. IR spectra were recorded on a Nicolet FT-IR 170SX spectrometer, ^{1} HNMR spectra on a JEOL PMX 60 SI spectrometer and an Am 400 ^{1}HNMR spectrometer where using TMS as an internal standard , and Mass spectra on a ZAB-HS spectrometer.

1; 1-Nitro-4-(4-nitrophenylsulfonylmethyl)benzene (**1**) was prepared by the method described in the literature[14].

1.16g (4 mmol) of 1-nitro-4-(4-nitrophenylthiomethyl)benzene **1** was dissolved in 10 ml of glacial acetic acid at 55°C. 1.85g(4 mmol) of sodium perborate tetrahydrate was added in portions at 70 °C over a period of 1 hour . The mixture was continuously stirred for 5 hours. The solvent was removed under reduced pressure. The residue was treated with water. The precipitated product was collected, washed with water and recrystallized from glacial acetic acid to give 1.16g (91%) of analytical sample of **1** . M.P. 197 -198 °C. (Lit.[9] M.P.195 °C). IR (in KBr pellet): 1526, 1343 (NO_2), 1301, 1152 (SO_2)cm^{-1}, ^{1}HNMR(CD_3COCD_3): 8.47(2H,d,Ar-H,J=8.8Hz), 8.16 (2H,d,Ar-H, J=8.8Hz), 8.00(2H,d,Ar-H,J=8.5Hz), 7.53(2H,d, Ar-H,J=8.5Hz), 4.82 (2H,s,CH_2)ppm.

2: Methyl 2-methyl-2,4-bis(4-nitrophenyl)butanate(**3c**)

To a solution of 0.64 g (2 mmol) of **1** in 5 ml of DMF was added 0.55 g (4 mmol) of anhydrate potassium carbonate and 0.1g (0.44 mmol) of TEBA. The solution was stirred 15 minutes at room temperature before 0.61g(6mmol) of methyl methacrylates(**2c**) was added. The reaction progress was monitored by thin layer chromatography(TLC). After stirred at 75°C for 5 hours, the reaction mixture was cooled and poured into cold water. The mixture was added with 2N hydrochloric acid to PH=6.5 and extracted with dichloromethane(3×15ml). The combined organic phase was dried over anhydrate sodium sulfate and concentrated. The residue was chromatographyed on silica. Elution with a mixed solvent of petroleum ether and ethyl acetate (6:1) afforded 0.67g(92%) of **3c** as a pale yellow needle .M.P. 101-102°C.

3a-b,**3d-h** and **4a-b** were synthesized by the method similar to **3c**. Their principle reaction conditions and analytical data were listed in the table 1and table 2.

References

1. Ogura, K. *Pure and Appl. Chem.* **1987,** *59,* 1033;
2. Kocienski, P. *Phosphrous Sulfur* **1985,** *24,* 477;
3. Ottenheijm, H. C. J. *Phosphrous Sulfur* **1985,** *24,* 509;
4. Xu, C. Y. Liu, G. J. Zhang, Z. *Synth. Commun.* **1987,** *17,* 1839;
5. Posner, G. H. *Stud. Prog. Chem.* **1987,** *28,* 145;
6. Corey, E. J. and Seebach, D. *Angew. Chem. Intern. Ed. Engl.* **1965,** *4,* 1075;
7. Cheng,W.H. Zhang, Z. Xu, X. Q. *Gaodeng Xuexiao Huaxue Xuebao* **1995,** *16(9),*1410 ;
8. Zhang, Z. Liu, G. J. Xu, C. Y. Hu, L. B. *Youji Huaxue* **1990,** *10,* 422;
9. Waldron, W. R. and Reid, E. E. *J. Am. Chem. Soc.* **1923,** *45.* 2399;
10. Leandri, G. Mangini A. Passerini R. *J. Chem. Soc.* **1957,** 1386;
11. Prousek, J. *Collect. Czech. Chem. Commun.* **1988,** *53,* 851;
12. Makosza, M. and Tyraia, A. *Synth. Commun.* **1986,** *16,* 419;
13. Sanchez, I. H. and Aguilar, M. A. *Synthesis* **1981,** 55;
14. Xu, X. Q. Zhou, W. Q. Zhang, Z. *Nanjing Daxue Xuebao, Ziran Kexue* **1991,** *27.* 483;

(Received in the USA 11/11/95)