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REGULAR ARTICLE

Microwave-assisted rapid synthesis of arylazoxy sulfides

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Abstract. An efficient, fast, and straightforward procedure for the synthesis of arylazoxy sulfides can be achieved by coupling reaction between aryl nitrasocompounds and tribenzenesulphenamide under microwave irradiation. Using the present method, different kinds of aryl nitrasocompounds containing various dioxolane rings and various tribenzenesulphenamide derivatives were rapidly converted to the corresponding arylazoxy sulfides in good yield and short reaction time. The use of non-toxic solvent, simple and clean work-up, short reaction times and good yields are the advantages of this method.

Keywords. Aryl azoxy compounds; arylazoxy sulfides; arylazo sulfides; aryldiazonium salts; aryl azo sulfones; arylazoxy sulfones; calvatic acid.

1. Introduction

Aryl diazonium salts[1,2] have been considered as powerful intermediates in classical and modern organic synthesis due to their easy availability and high reactivity. Hence, there is always some scope to explore in the field of aromatic diazonium salts.

It was well known thing that aryldiazonium salts are unstable and explode at higher temperatures. Therefore a wide range of research work is going to synthesize diazonium salts with good stability and to store them safely and further use them into the synthesis of useful Building blocks. Aryldiazonium tetrafluoroborates,[3–5] aryldiazonium hexafluorophosphates,[6] and aryldiazoniumsulfonates[7,8] have been considered as excellent building blocks for aryldiazonium salts based transformations even in industrial level. Asymmetrically substituted azoxy compounds are known to possess potent biological properties. Macrozamin,[9,10] cycasin,[11,12] elaiomycin,[13] and calvatic acid[14,15] are some of them. Out of four first three were found to exhibit anti-cancer activity and the fourth one possesses antifungal, agricultural fungicide, anti-bacterial, and tuberculostatic properties. These aryl azoxy compounds also play a vital role in liquid crystal systems, polarizing plates.[16]

There are several synthetic routes for the synthesis of arylazo sulfides,[17] arylazo solfones[18] and arylazoxy sulfones[19,20] but up to best of our knowledge only one report is available for the synthesis of arylazoxy sulfides.[21,22] In 1974 Derek H R Barton *et al*[21,22] have reported the synthesis of aryl azoxy sulfides. This method has disadvantage of longer reaction times (approx. 6 h), lower yields (around 25%) and fewer number of derivatives (2 only). So the above disadvantages and the importance of aryl azoxy sulfides prompted us to develop a new synthetic method to overcome the disadvantages. In this letter we wish to report a rapid and high yielding synthesis of aryl azoxy sulfides by a coupling reaction between nitraso compounds and tribenzene sulphenamide under microwave irradiation (Scheme 1).

The nitraso derivatives were synthesized from corresponding nitro derivatives by using Zn/NH_4Cl as a

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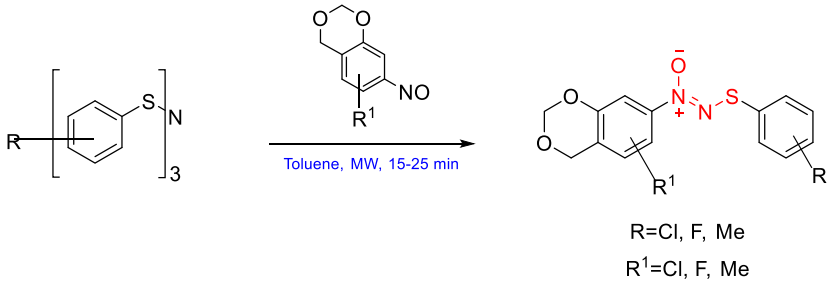
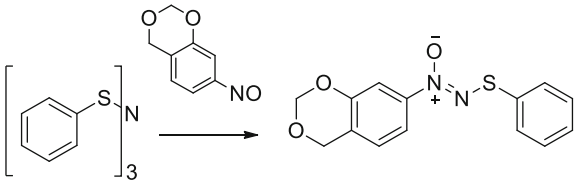


Scheme 1. General synthetic scheme for Arylazoxy sulfides.



Scheme 2. Reaction of unsubstituted tribenzene sulphenamide.

reducing agent and tribenzene sulphenamides were prepared by well-known method.[19] We have selected dioxolane ring because this framework resembles Calvatic acid derivative.[20–22]

2. Results and Discussion

In an initial experiment, we have carried out a reaction of unsubstituted tribenzene sulphenamide with equimolar quantity of nitraso compound in the absence of solvent at room temperature (scheme 2) in a conventional RB flask. Only trace amount of product formation was observed even at elevated temperatures. In order to achieve complete conversion, we have screened a variety of solvents like dichloromethane, dichloroethane, methanol, ethanol, and toluene.

We have seen only traces of product formation in polar protic solvents like methanol and ethanol (Table 1, entry 1 and 2) at room temperature and at 70 °C also. Then we have changed the solvents and performed in halogenated solvents like dichloromethane (Table 1, entry 3), at room temperature to 40 °C and observed only 10% of product formation. In dichloroethane (Table 1, entry 4) at room temperature the starting materials are intact and at 90 °C, we have seen 30% of product formation after 12 h. Based on the above results, we have changed the solvent to toluene (Table 1, entry 5) and performed a reaction at room temperature, observed no product formation and at 100 °C for about 12 h, observed 45% of product formation (Table 1, entry 6).

Table 1. Solvent screening.

Entry	Solvent	Yield	Temperature	Time (h)
1	Methanol	Traces	70 °C	12
2	Ethanol	Traces	70 °C	12
3	DCM	10	40 °C	12
4	DCE	30	90 °C	12
5	Toluene	–	rt	12
6	Toluene	45	100 °C	12

Table 2. Temperature screening for microwave condition.

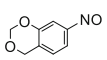
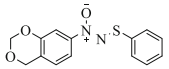
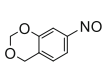
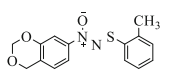
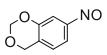
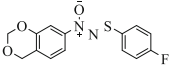
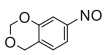
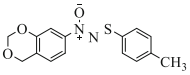
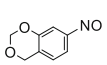
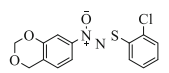
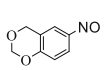
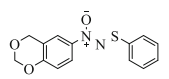
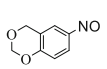
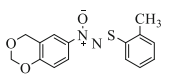
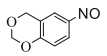
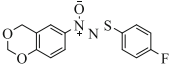
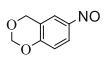
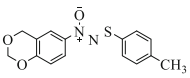
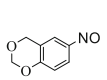
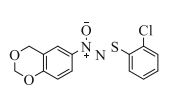
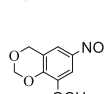
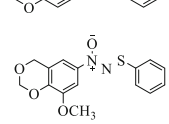
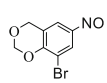
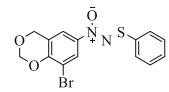
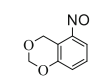
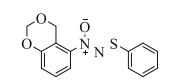
Entry	Temperature	Reaction time (min)	Yield (%)
1	40 °C	45	66
2	100 °C	15	83

Based on these observations, we have focused to reduce the reaction time and to improve the yields. Turned our attention to perform these reactions in microwave. Initially performed a reaction at 40 °C (Table 2, entry 1) and observed 66% of product formation after 45 min. To further reduce the reaction time, increased the temperature to 100 °C and observed 75% (Table 2, entry 2) of product formation within 15 min of time.

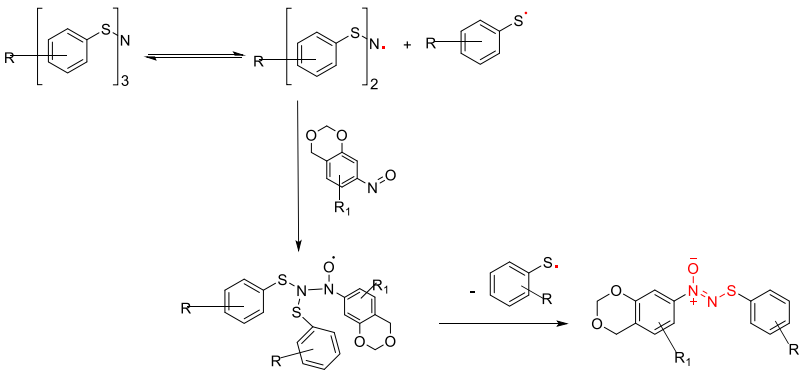
We have adopted the above developed reaction conditions and synthesized seventeen derivatives of aryl azoxy sulphides (Table 3).

We have screened the above conditions in presence of variety of substituents like –Cl, –Br, –F, $–OCH_3$ and Me. In all the cases the conversion was smooth with good yields. As seen from Table 3, the nature of the substituents in tribenzene sulfinamide slightly affected the reaction time and yield. For para substituted derivatives we have not seen any change in reaction

Table 3. Arylazoxysulfide derivatives.

S.NO	Sulphenamide derivative	Nitaso derivative	Product	Time (min)	Yeild(%)[a]
1				15	83
2[b]				25	75
3				15	70
4				15	73
5[b]				25	60
6				15	78
7[b]				25	65
8				15	73
9				15	78
10[b]				25	62
11				15	74
12				15	74
13				15	80
14[b]				25	62
15				15	72
16[b]				25	66
17				15	78

Reaction conditions: Sulphenamide derivative (1 mmol), nitraso derivative (1 mmol), toluene (10 vol), microwave, 15 min.
[a]Isolated yield.
[b]Reaction time 25 min.



Scheme 3. Possible mechanism.

time and yield but for ortho substituted derivatives (Table 3, entry nos. 2, 5, 7, 10, 14, and 16) the reaction time was increased from 15 min to 25 min to complete the conversion and the yields are bit lower than para-substituted derivatives.

The possible mechanism is shown as below (Scheme 3) and elaborated the mechanism.

Formation of aryl azoxy sulfides can be explained by free radical mechanism.[22] The first step of the mechanism is reversible and it is the dissociation of tribenzene sulphenamide into dibenzenesulphenamide radical and thiophenol radical. Further dibenzene-sulphenamide reacts with nitraso compound to form an intermediate from which elimination of one more thiophenol radical results our desired product.

3. Conclusions

In conclusion, we have demonstrated fast and high yielding method for the preparation of arylazoxy sulfides using aryl nitraso compounds and tribenzene-sulphenamide derivatives. Moreover the dioxolane ring on nitraso compounds resembles the frame work belongs to calvatic acid derivative. Hence our research work may useful in further development of arylazoxy sulfide related molecules and their biological activities. The disadvantage of this method is not scalable, further research work is going on in our laboratory to develop a scalable method.

4. Experimental section

Reagents were purchased from commercial sources and were used as received. ^{1}H NMR spectra were obtained on a Bruker AVANCE 300 spectrometer at 300 MHz with tetramethylsilane used as an internal reference. Thin-layer chromatography (TLC) was performed using Whatman No. 4500-101 (Diamond No. MK6F silica-gel 60 Å) plates. Visualization of TLC plates was performed using UV light (254 nm). The mass spectra were obtained on a Finnigan LCQ-DUO spectrometer using electrospray ionization.

4.1 *Genaral procedure for synthesis of Compounds* ***1–17***

A mixture of tribenzene sulphenamide derivative (1 mmol) and nitraso derivative (1 mmol) in toluene (10 vol) is microwave irradiated for 15–25 min. TLC analysis showed complete consumption of the starting material, the reaction mixture concentrated to get the residue, residue was purified by column chromatography using 20% EtOAc/*n*-hexanes as an eluent to afford aryl azoxy sulphides **1–17**.

1-(4H-benzo[d][1,3]dioxin-7-yl)-2-(phenylthio)diazene oxide(1): Off-white solid; yield: 83%;mp 125–126 °C; Rf = 0.5 (50% EtOAc/*n*-hexane);^{1}H NMR (300 MHz, $CDCl_3$,): δ 7.71–7.64 (m, 4H), 7.48–7.38 (m, 3H), 7.06 (d, J = 8.4 Hz, 1H), 5.28 (s,2H), 4.94 (s,2H)ppm.^{13}C NMR ($CDCl_3$): δ 158.3, 140.5, 139.9,135.0, 133.9, 132.6, 131.5, 130.2, 127.8, 126.6, 123.9, 115.3, 92.1, 68.5 ppm. Found, %: C 58.29; H 4.20; N 9.79; O 16.58; S 10.98 $C_{14}H_{12}N_2O_3S$. Calculated, %: C 58.32; H 4.20; N 9.72; O 16.65; S 11.12.

1-(4H-benzo[d][1,3]dioxin-7-yl)-2-(o-tolylthio)diazene oxide(2):Off-white solid; yield: 75%;mp 132–133 °C;Rf = 0.5 (50% EtOAc/*n*-hexane);^{1}H NMR (400 MHz, $CDCl_3$,): δ 7.75 (d, J = 4 Hz, 1H) 7.73–7.67 (m, 1H), 7.64 (d, J = 2 Hz, 1H),7.63–7.57 (m, 3H), 7.06 (d, J = 8.4 Hz, 1H), 5.27 (s,2H), 4.94 (s,2H),2.46 (s,3H) ppm. ^{13}C NMR ($CDCl_3$): δ 158.3, 147.6, 142.0,133.9, 132.1, 130.0, 128.8, 126.3, 125.5, 123.9, 119.5, 116.6, 93.1, 69.5, 18.0, ppm. Found, %: C 59.50; H 4.61; N 9.30; O 15.90; S 10.60. $C_{15}H_{14}N_2O_3S$. Calculated, %: C 59.57; H 4.62; N 9.27; O 15.88; S 10.63.

1-(4H-benzo[d][1,3]dioxin-7-yl)-2-((4-fluorophenyl)thio)-diazene oxide (3):Off-white solid; yield: 70%;mp 116–117 °C; Rf = 0.5 (50% EtOAc/*n*-hexane);^{1}H NMR

(400 MHz, $CDCl_3$,): δ 7.77–7.68 (m, 1H), 7.26 (t, J = 8 Hz, 2H), 7.06 (d, J = 8.4 Hz, 1H), 5.27 (s,2H), 4.94 (s,2H) ppm. ^{13}C NMR ($CDCl_3$): δ 164.2,159.6, 158.3,147.8, 142.0,134.2, 129.9, 128.8, 125.2,123.9, 119.5, 116.6, 93.1, 69.5, ppm. Found, %: C 53.88; H 3.60; F 6.20; N 8.98; O 15.70; S 10.47 $C_{14}H_{11}FN_2O_3S$. Calculated, %: C 54.90; H 3.60; F 6.22; N 9.15; O 15.69; S 10.47.

1-(4H-benzo[d][1,3]dioxin-7-yl)-2-(p-tolylthio)diazene oxide (4):Off-white solid; yield: 73%;mp 100–101 °C; Rf = 0.5 (50% EtOAc/*n*-hexane);^1H NMR (400 MHz, $CDCl_3$,): δ 7.68 (t, J = 8.4 Hz, 2H), 7.55 (d, J = 8 Hz, 2H), 7.26 (d, J = 8 Hz, 2H), 7.04 (d, J = 8.4 Hz, 1H), 5.27 (s,2H), 4.94 (s,2H),2.40 (s,3H) ppm. ^{13}C NMR ($CDCl_3$): δ 158.3, 147.6, 142.0,135.2, 132.2, 130.2, 130.0, 129.6, 128.8, 123.9, 119.5, 116.6, 93.1, 69.5, 25.8 ppm. Found, %: C 59.60; H, 4.65; N 9.20; O 16.00; S 10.62 $C_{15}H_{14}N_2O_3S$. Calculated, %: C 59.59; H, 4.67; N 9.30; O 15.90; S 10.61.

1-(4H-benzo[d][1,3]dioxin-7-yl)-2-((2-chlorophenyl)thio) diazene oxide (5):Off-white solid; yield: 60%;mp 130–131 °C; Rf = 0.5 (50% EtOAc/*n*-hexane);^1H NMR (400 MHz, $CDCl_3$,): δ 7.88 (d, J = 2 Hz, 1H), 7.86 (d, J = 2 Hz, 1H), 7.74–7.66 (m, 1H), 7.45–7.42 (m, 1H), 7.39–7.37 (m, 1H), 7.29–7.26 (m, 1H), 7.04 (d, J = 8.4 Hz, 1H), 5.29 (s,2H), 4.95 (s,2H) ppm. ^{13}C NMR ($CDCl_3$): δ 158.3, 147.8, 139.5,133.5, 131.9, 131.5, 128.8, 127.5, 127.4, 123.9, 119.5, 116.6, 93.1, 69.5 ppm. Found, %: C 52.12; H 3.43; Cl 10.94; N 8.72; O 14.85; S 9.92 $C_{14}H_{11}ClN_2O_3S$. Calculated, %: C 52.10; H 3.43; Cl 10.95; N 8.70; O 14.87; S 9.90.

1-(4H-benzo[d][1,3]dioxin-6-yl)-2-(phenylthio)diazene oxide (6):Off-white solid; yield: 78%;mp 88–89 °C;Rf = 0.5 (50% EtOAc/*n*-hexane);^1H NMR (300 MHz, $CDCl_3$,): δ 7.89–7.85 (m, 1H), 7.71 (s, 1H),7.59 (d, J = 7.2 Hz, 2H), 7.41–7.28 (m, 3H),6.87 (d, J = 9 Hz, 1H), 5.22 (s,2H), 4.87 (s,2H) ppm. ^{13}C NMR ($CDCl_3$): δ 158.3, 140.5, 139.9,133.0, 130.9, 130.6, 130.5, 130.2, 127.8, 126.6, 123.9, 115.3, 93.1, 69.5 ppm. Found, %: C 58.32; H 4.22; N 9.73; O 16.65; S 11.12; $C_{14}H_{12}N_2O_3S$. Calculated, %: C 58.30; H 4.21; N 9.72; O 16.63; S 11.10.

1-(4H-benzo[d][1,3]dioxin-6-yl)-2-(o-tolylthio)diazene oxide (7):Off-white solid; yield: 65%;mp 218–219°C;Rf = 0.5 (50% EtOAc/*n*-hexane);^1H NMR (300 MHz, $CDCl_3$,): δ 7.88–7.84 (m, 1H), 7.70–7.66 (m, 2H),7.24–7.19 (m, 4H), 6.86 (d, J = 9 Hz, 1H), 5.22 (s,2H), 4.87 (s,2H),2.39 (s,3H) ppm. ^{13}C NMR ($CDCl_3$): δ 158.3, 144.6, 140.5,134.6, 137.8, 131.5, 130.5, 128.2, 127.6, 127.5, 123.9, 115.3, 93.1, 69.5, 18.0 ppm. Found, %: C 59.59; H 4.67; N 9.22; O 15.84; S 10.59. $C_{15}H_{14}N_2O_3S$ Calculated, %: C 59.60; H 4.67; N 9.23; O 15.86; S 10.60.

1-(4H-benzo[d][1,3]dioxin-6-yl)-2-((4-fluorophenyl)thio)-diazene oxide (8):Off-white solid; yield: 73%;mp 112–113 °C; Rf = 0.5 (50% EtOAc/*n*-hexane).^1H NMR (400 MHz, $CDCl_3$,): δ 7.86–7.83 (m, 1H), 7.68 (d, J = 2 Hz, 1H), 7.58–7.54 (m, 1H), 7.10 (t, J = 8.4 Hz, 2H),6.86 (d, J = 8.8 Hz, 1H),5.22 (s,2H), 4.86 (s,2H) ppm. ^{13}C NMR ($CDCl_3$): δ 161.8, 158.3, 140.5, 132.6,131.6, 130.5, 129.6, 127.6, 123.9, 118.2, 118.1, 115.3, 93.1, 69.5 ppm. Found, %: C 54.90; H 3.60; F 6.21; N 9.15; O 15.65; S 10.45.

1-(4H-benzo[d][1,3]dioxin-6-yl)-2-(p-tolylthio)diazene oxide (9):Off-white solid; yield: 78%;mp 123–124 °C; Rf = 0.5 (50% EtOAc/*n*-hexane);^1H NMR (300 MHz, $CDCl_3$,): δ 7.86 (d, J =7.8 Hz, 1H), 7.69 (s,1H), 7.48 (d, J =7.5Hz, 2H), 7.20 (d, J =3.9 Hz, 2H), 6.85 (d, J =9 Hz, 1H), 5.21 (s,2H), 4.86 (s,2H),2.33 (s,3H) ppm. ^{13}C NMR ($CDCl_3$): δ 158.3, 140.5, 138.6,137.6, 133.1, 132.9, 132.8, 132.3, 131.9, 130.5, 127.6, 123.9, 115.3, 93.1, 69.5, 25.6 ppm. Found, %: C 59.60; H 4.69; N 9.27; O 15.90; S 10.60. $C_{15}H_{14}N_2O_3S$. Calculated, %: C 59.59; H 4.67; N 9.27; O 15.88; S 10.61.

1-(4H-benzo[d][1,3]dioxin-6-yl)-2-((2-chlorophenyl)thio) diazene oxide (10):Off-white solid; yield: 62%;mp 130–131 °C;Rf = 0.5 (50% EtOAc/*n*-hexane);^1H NMR (300 MHz, $CDCl_3$,): δ 7.91–7.73 (m, 3H), 7.38–7.18 (m, 3H), 6.88 (d, J =9 Hz, 1H),5.23 (s,2H), 4.89 (s,2H) ppm. ^{13}C NMR ($CDCl_3$): δ 158.4, 140.5, 134.0,133.6, 132.1, 131.1, 130.5, 129.6, 129.0, 127.6, 123.9, 115.3, 93.1, 69.5 ppm.Found, %: C 52.10; H 3.43; Cl 10.97; N 8.65; O 14.85; S 9.93:$C_{14}H_{11}ClN_2O_3S$. Calculated, %: C 52.11; H 3.44; Cl 10.98; N 8.67; O 14.85; S 9.90.

1-(8-methoxy-4H-benzo[d][1,3]dioxin-6-yl)-2-(pheny lthio)diazene oxide (11):Off-white solid; yield: 74%;mp 131–132 °C;Rf = 0.5 (50% EtOAc/*n*-hexane);^1H NMR (300 MHz, $CDCl_3$,): δ 8.02 (d, J =6 Hz, 2H), 7.67–7.63 (m, 5H), 5.30 (s,2H), 4.92 (s,2H), 3.92 (s,3H) ppm. ^{13}C NMR ($CDCl_3$): δ 151.0, 149.2, 133.9,137.6, 131.6, 131.5, 127.8, 126.3, 123.9, 123.8, 116.0, 116.6, 93.1, 69.5, 58.9 ppm. Found, %: C 56.60; H 4.43; N 8.82; O 20.11; S 10.06;$C_{15}H_{14}N_2O_4S$. Calculated, %: C 56.59; H 4.43; N 8.80; O 20.10; S 10.07.

1-(8-bromo-4H-benzo[d][1,3]dioxin-6-yl)-2-(phenylthio)-diazene oxide (12):Off-white solid; yield: 74%;mp 129–130 °C;Rf = 0.5 (50% EtOAc/*n*-hexane);^1H NMR (300 MHz, $CDCl_3$,): δ 8.22 (d, J =2.4 Hz, 1H), 7.75 (d, J =2.4 Hz, 1H), 7.66 (t, J =8.4 Hz, 2H),7.49–7.40 (m, 5H), 5.38 (s,2H), 4.94 (s,2H) ppm. ^{13}C NMR ($CDCl_3$): δ 155.2, 133.9, 133.6,131.6, 131.5, 131.2, 130.9, 130.0, 127.8, 125.0, 124.9, 113.6, 92.5, 68.0 ppm.Found, %: C 45.83; H 3.05; Br 21.79; N 7.61; O 13.06; S 8.73.$C_{14}H_{11}BrN_2O_3S$. Calculated, %: C 45.80; H 3.03; Br 21.77; N 7.62; O 13.06; S 8.73.

1-(4H-benzo[d][1,3]dioxin-5-yl)-2-(phenylthio)diazene oxide (13):Off-white solid; yield: 80%;mp 124–125 °C; Rf = 0.5 (50% EtOAc/*n*-hexane);^1H NMR (300 MHz, $CDCl_3$,): δ 7.64–7.56 (m, 3H), 7.54–7.41 (m, 4H),6.86 (d, J =4.2 Hz, 1H), 5.27 (s,2H), 5.17 (s,2H) ppm. ^{13}C NMR ($CDCl_3$): δ 158.3, 133.9, 133.6, 131.6, 131.4, 131.2, 131.0, 130.0, 127.8, 125.0, 124.9, 113.6, 92.5, 68.0 ppm.Found, %: 58.32; H 4.22; N 9.70; O 16.67; S 11.10. $C_{14}H_{12}N_2O_3S$. Calculated, %: C 58.32; H 4.20; N 9.72; O 16.65; S 11.12.

1-(4H-benzo[d][1,3]dioxin-5-yl)-2-(o-tolylthio)diazene oxide (14):Off-white solid; yield: 62%;mp 124–125 °C;Rf = 0.5 (50% EtOAc/*n*-hexane);^1H NMR (300 MHz,

$CDCl_3$,): δ 7.71 (t, J =1.8 Hz, 1H), 7.57 (d, J =7.5 Hz, 1H), 7.30–7.23 (m, 4H), 7.04 (d, J =8.4 Hz, 1H), 5.27 (s,2H), 5.15 (s,2H), 2.46 (s,3H) ppm. ^{13}C NMR ($CDCl_3$): δ 158.3, 144.6, 135.6, 131.4, 131.3, 130.5, 129.2, 128.2, 126.6, 124.2, 119.6, 115.3, 93.1, 61.9, 18.0 ppm.Found, %: C 59.60; H 4.66; N 9.30; O 15.85; S 10.60. $C_{15}H_{14}N_2O_3S$. Calculated, %: C 59.59; H 4.67; N 9.27; O 15.88; S 10.61.

1-(4H-benzo[d][1,3]dioxin-5-yl)-2-((4-fluorophenyl)thio)-diazene oxide (15):Off-white solid; yield: 72%;mp 129–130 °C;Rf = 0.5 (50% EtOAc/*n*-hexane);^{1}H NMR (300 MHz, $CDCl_3$,): δ 7.64–7.59 (m, 2H),7.56 (d, J =8.1 Hz, 1H), 7.28–7.23 (m, 2H), 7.18 (t, J =8.7 Hz, 2H), 7.04 (d, J =8.7 Hz, 1H), 5.26 (s,2H), 5.14 (s,2H) ppm. ^{13}C NMR ($CDCl_3$): δ 161.6, 158.3, 140.5, 132.6, 132.4, 130.5, 129.6, 127.6, 123.9, 118.2, 118.2, 115.3,93.1,69.5 ppm.Found, %: C 54.90; H 3.60; F 6.22; N 9.10; O 15.67; S 10.50. $C_{14}H_{11}FN_2O_3S$. Calculated, %: C 54.89; H 3.62; F 6.20; N 9.15; O 15.67; S 10.47.

1-(4H-benzo[d][1,3]dioxin-5-yl)-2-((2-chlorophenyl)thio) diazene oxide (16):Off-white solid; yield: 66%;mp 133–134°C;Rf = 0.5 (50% EtOAc/*n*-hexane);^{1}H NMR (300 MHz, $CDCl_3$,): δ 7.82–7.79 (m, 1H),7.60 (d, J =9 Hz, 1H), 7.47–7.44 (m, 1H), 7.39–7.32 (m, 3H),7.06 (d, J =8.4 Hz, 1H),5.29 (s,2H), 5.18 (s,2H) ppm. ^{13}C NMR ($CDCl_3$): δ 158.3, 140.5, 134.0, 133.6, 132.1, 131.1, 130.5, 129.6, 129.0, 127.6, 123.9, 115.3, 93.1, 69.5 ppm.Found, %: C 52.09; H 3.42; Cl 11.01; N 8.66; O 14.87; S 9.95.$C_{14}H_{11}ClN_2O_3S$. Calculated, %: C 52.10; H 3.44; Cl 10.98; N 8.68; O 14.87; S 9.93.

1-(4H-benzo[d][1,3]dioxin-5-yl)-2-(p-tolylthio)diazene oxide (17):Off-white solid; yield: 78%;mp 129–130 °C;Rf = 0.5 (50% EtOAc/*n*-hexane);^{1}H NMR (300 MHz, $CDCl_3$,): δ 7.58–7.50 (m, 3H), 7.27–7.23 (m, 3H),7.03 (d, J =8.4 Hz, 1H),5.26 (s,2H), 5.15 (s,2H), 2.40 (s,3H) ppm. ^{13}C NMR ($CDCl_3$): δ 158.3 140.5, 138.6, 137.6, 133.1, 132.9, 132.8, 132.6, 132.3, 130.5, 127.6, 123.9, 117.3, 93.1, 69.5, 22.8 ppm.Found, %: C 59.60; H 4.66; N 9.30; O 15.90; S 10.61.$C_{15}H_{14}N_2O_3S$. Calculated, %: C 59.59; H 4.67; N 9.27; O 15.88; S 10.61.

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