

Reactions of a Variety of Diazoalkanes with *o*-Sulfolobenzoic Anhydride

Takumi OSHIMA and Toshikazu NAGAI

Institute of Chemistry, College of General Education, Osaka University, Toyonaka, Osaka 560

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It was found that a number of diazoalkanes (I) bearing a relatively small substituent reacted with *o*-sulfolobenzoic anhydride (II) in acetonitrile at an ordinary temperature to give the *o*-(substituted glycoloyl)benzenesulfonic acid sultones (IV), which correspond formally to the products from the insertion into the C—O bond of II by the carbenes, while diaryldiazomethanes underwent decomposition under the same conditions to produce the corresponding tetraarylethylenes (V) instead of the inserted products (IV). The olefin formation reaction was very fast compared to the sultone formation and was considered to be the result of the acid-catalyzed decomposition caused by the contaminant *o*-sulfolobenzoic acid (III) which was derived from II. The kinetics and the mechanism of these reactions were discussed on the basis of the nature of diazoalkanes.

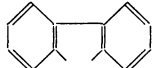
It is well known that diazoalkanes(I) undergo decomposition in the presence of protic acids,¹⁾ a variety of metallic halides,²⁾ or other Lewis acids³⁾—*e.g.*, ZnCl₂, Hg₂Cl₂, and BF₃—involving intermediate diazonium ions or carbenoids. However, the decomposition of I under the influence of an organic Lewis acid has not been widely investigated.⁴⁾ During our recent study of a mixed sulfonic carboxylic anhydride such as *o*-sulfolobenzoic anhydride(II), we found that II can act as an electron acceptor toward tertiary amines, thus giving rise to their radical cations.⁵⁾ This Lewis acid behavior of II led us to investigate the decomposition of diazoalkanes using it. We now wish to report that *o*-sulfolobenzoic anhydride(II) reacts under ordinary conditions with a variety of diazoalkanes(I) to afford the keto sultones(IV), and that, in the case of diaryldiazomethanes, a trace amount of contaminant *o*-sulfolobenzoic acid(III) rather than II preferentially causes the acid-catalyzed decomposition to yield the olefins(V).

Results and Discussion

The reactions of a variety of diazoalkanes(I) with II in dry acetonitrile gave the keto sultones(IV) or the tetraarylethylenes(V) depending on the nature of I (Scheme 1 and Table 1).

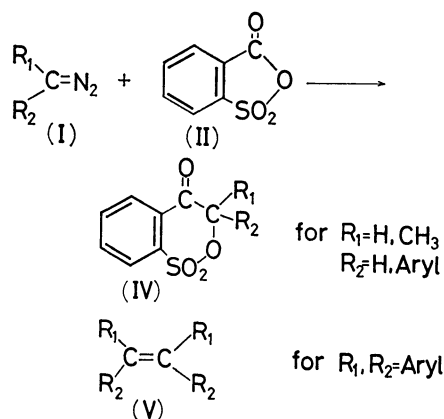
As may be seen in Table 1, the diazoalkanes (I-1—5) which bear a relatively small substituent, R₁, such as H or CH₃, gave the keto sultones(IV), while when the R₁ and R₂ substituents were both aryl rings (I-6—9), the olefins(V) were isolated instead of the keto sultones

TABLE 1. PRODUCT DISTRIBUTIONS FROM THE REACTIONS OF A NUMBER OF DIAZOALKANES(I) WITH *o*-SULFOLBENZOIC ANHYDRIDE(II) IN ACETONITRILE AT ROOM TEMPERATURE^{a)}

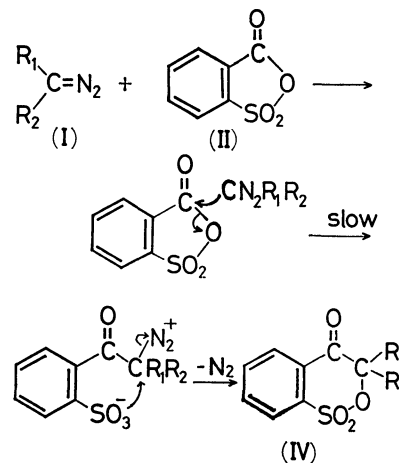
	R ₁	R ₂	Products (Yield ^{b)})
I-1	H	H	IV-1 (74) —
I-2	H	C ₆ H ₅	IV-2 (71) —
I-3	H	<i>p</i> -C ₆ H ₄ CH ₃	IV-3 (81) —
I-4	H	<i>p</i> -C ₆ H ₄ Cl	IV-4 (95) —
I-5	CH ₃	C ₆ H ₅	IV-5 (67) —
I-6	C ₆ H ₅	C ₆ H ₅	— V-6 (96)
I-7	C ₆ H ₅	<i>p</i> -C ₆ H ₄ CH ₃	— V-7 (97)
I-8	<i>p</i> -C ₆ H ₄ OCH ₃	<i>p</i> -C ₆ H ₄ OCH ₃	— V-8 (≈100)
I-9			— V-9 (75)

a) Reaction time: 1 h. b) The yield is in mol% based on the I used.

In the course of these reactions it was noticed that the disappearance of diazo-color and the evolution of nitrogen gas occurred very much more rapidly and vigorously in the case of the diaryldiazomethanes (I-6—9) than in the case of the monoaryldiazomethanes (I-2—5). The marked difference in the product distributions and the reaction velocities suggests that these reactions proceed by way of a different mechanism between the monoaryldiazomethanes and the diaryldiazomethanes.



Scheme 1.



Scheme 2.

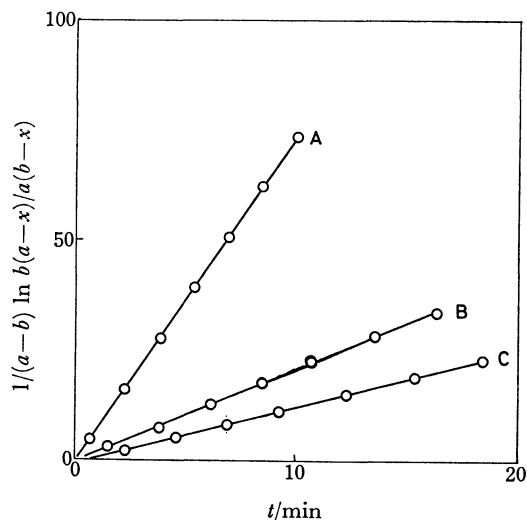


Fig. 1. Second-order kinetic behavior in the reactions of aryldiazomethanes with *o*-sulfobenzoic anhydride (II) in acetonitrile at 23 °C; a plot of the integrated form $[1/(a-b) \ln b(a-x)/a(b-x)]$ against time, where a and b are the initial concentrations of II and I respectively, x being the concentration of product IV.

A: *p*-Tolyldiazomethane (I-3); 2.71×10^{-2} M, II; 8.43×10^{-2} M, B: phenyldiazomethane (I-2); 2.54×10^{-2} M, II; 9.50×10^{-2} M, C: *p*-chlorophenyldiazomethane (I-4); 2.21×10^{-2} M, II; 9.00×10^{-2} M.

The kinetic measurements of these reactions provided some information about the mechanism. Keto sultone formation reactions obeyed a clean second order, as is shown in Fig. 1, suggesting a rate-determining nucleophilic attack of diazoalkanes at the carbonyl position of II (Scheme 2). This is also supported by the tendency for the rate constants to increase with the electron-donating ability of the aryl substituents of these monoaryldiazomethanes: $k=1.25$ ($1 \text{ mol}^{-1} \text{ min}^{-1}$) (*p*-Cl), $k=2.48$ (*p*-H), and $k=6.85$ (*p*-CH₃). Taking into account the fact that II is a good acylating reagent,⁶⁾ it is reasonable to account for this insertion reaction in terms of the nucleophilic attack of the diazo-carbon at the carbonyl position of II.

On the other hand, as Fig. 2 shows, the olefin-formation reactions progressed quickly even in the presence of a catalytic amount of II. Here, it is noteworthy that I-7, bearing an electron-donating *p*-substituent (CH₃), decomposes much faster than I-6. In addition, the IR spectra of equimolar I and II in acetonitrile showed no change in the two characteristic carbonyl absorptions at 1818 and 1836 cm⁻¹ of II after the reactions. These facts imply that the decomposition of diaryldiazomethanes does not consume II and that it proceeds through a catalytic mechanism.

Considering that II invariably contains a trace amount of free acid,^{7,8)} *o*-sulfobenzoic acid (III), it seems possible that this free acid induces the decomposition of diazoalkanes. The quantitative formation of the tetraarylethylenes in our present reaction is well consistent with that in the acid-catalyzed decompositions of diaryldiazomethanes in aprotic solvents with such strong acids as *p*-toluenesulfonic acid.^{1b,9,10,11)} Keeping this in mind, we examined the decompositions of I by

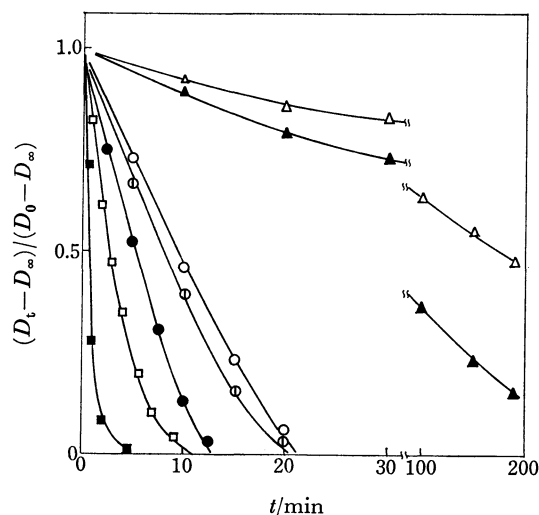


Fig. 2. Decay curves for aryl- and diaryldiazomethanes under the influence of *o*-sulfobenzoic anhydride (II) or *o*-sulfobenzoic acid (III) in acetonitrile. D_0 is the initial optical density, D_t and D_∞ being the values when the reaction time is t and when the reaction was complete respectively.

△: Phenyldiazomethane (I-2); 2.44×10^{-2} M, III; 1.15×10^{-3} M, 23 °C, ▲: *p*-tolyldiazomethane (I-3); 3.38×10^{-2} M, III; 1.15×10^{-3} M, 21 °C, ○: diphenyldiazomethane (I-6); 1.01×10^{-2} M, II; 2.10×10^{-4} M, 20 °C, ●: I-6; 1.01×10^{-2} M, III; 9.7×10^{-5} M, 20 °C, □: *p*-tolylphenyldiazomethane (I-7); 8.34×10^{-3} M, II; 2.10×10^{-4} M, 20 °C, ■: I-7; 8.34×10^{-3} M, III; 9.7×10^{-5} M, 20 °C, ⊙: I-6; 1.01×10^{-2} M, II; 2.1×10^{-4} M, 20 °C.

* *o*-Sulfobenzoic anhydride solution used here is identical to that used in the case of marked ○ but has been stood for 1 day in glass stoppered flask.

III, which had been prepared independently, and compared the decompositions with those by II (Fig. 2).

As for the reaction leading to V, the kinetic order by authentic III was very similar to that by II: the kinetic order was close to zero up to the final stage of the reaction, in analogy with that of the *p*-toluenesulfonic acid-catalyzed decomposition of diaryldiazomethanes in dry acetonitrile.¹²⁾ Furthermore, a rate acceleration was observed when we employed a solution of II which had been stored for one day (Fig. 2). This phenomenon is due to the partial transformation of II to III by the action of atmospheric moisture, as was confirmed by the UV spectra of II, as may be seen in Fig. 3. When the measurement was done one day later, the intensity in the UV spectrum of II (Curve b) decreased at $\lambda_{\text{max}}=286.5$ nm and had new absorption maxima at 237 and 278.5 nm instead of at 239 and 279 nm, with two isosbestic points at 254 and 284 nm. Therefore, it is apparent that the decomposition of diaryldiazomethanes was induced by the trace amount of III instead of by II.

As is well known, the acid-catalyzed reaction of diaryldiazomethanes, involving a rate-determining proton transfer and obeying a pseudo-first order, proceeds by way of intermediate diazonium ions^{1b,9,10,11)} (or carbonium ions derived from them). Bethell and Callister¹¹⁾ studied the decomposition of diphenyl-

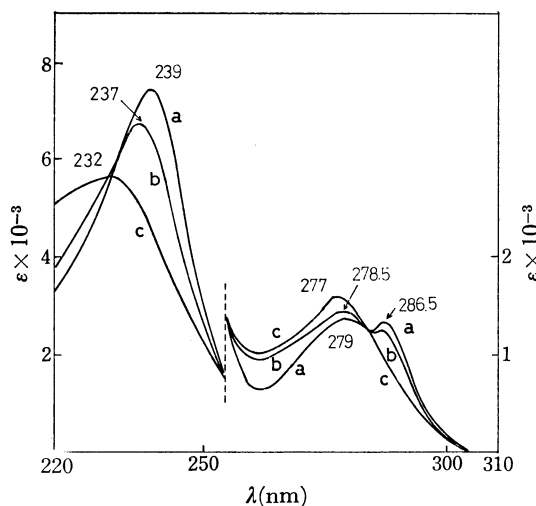
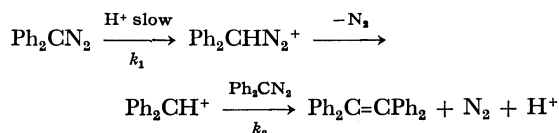


Fig. 3. UV spectra of II under the various conditions. a: Measured immediately after preparation, b: measured after 1 day, c: measured after hydrolysis.

diazomethane in dry acetonitrile with perchloric acid, which is fully ionized in this solvent,¹³⁾ and found the kinetic order to be pseudo-first, as is formulated in Scheme 3:

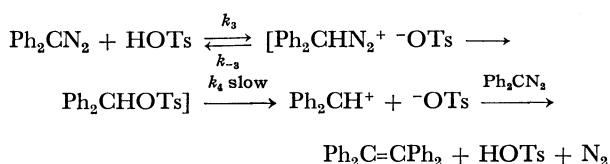


Kinetic equation:

$$\frac{-d[\text{Ph}_2\text{CN}_2]}{dt} = 2k_1[\text{H}^+][\text{Ph}_2\text{CN}_2] = k_1'[\text{Ph}_2\text{CN}_2]$$

Scheme 3.

However, at the same time they found that the kinetic order changes to zero when perchloric acid is replaced by *p*-toluenesulfonic acid, which reacts in an undissociated form in dry acetonitrile.¹²⁾ As to this zero order decomposition, they thought that the diphenyldiazomethane reacts first to form the benzhydryltoluenesulfonate intermediate, which subsequently undergoes a slow solvolysis to form tetraphenylethylene, as is formulated in Scheme 4:



Kinetic equation:

$$\text{if } (k_3/k_{-3})[\text{Ph}_2\text{CN}_2] \gg 1, \quad \frac{-d[\text{Ph}_2\text{CN}_2]}{dt} = k_4[\text{HOTs}]_{\text{st}}$$

$[\text{HOTs}]_{\text{st}}$: the stoichiometric acid concentration

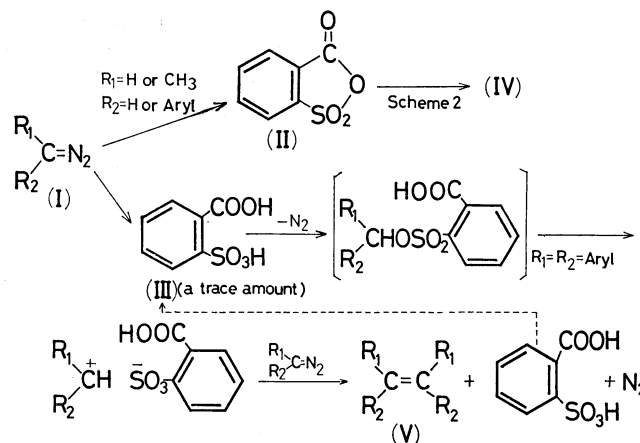
Scheme 4.

In the present system, *o*-sulfobenzoic acid (III) has both carboxyl and sulfo groups, and its behavior toward diazoalkanes can be regarded as being comparable to *p*-toluenesulfonic acid because the two acids similarly

bring about a quantitative olefin formation under zero order kinetics.

The decompositions of monoaryldiazomethanes by the action of III were quite slow compared with those of diaryldiazomethanes, even in the presence of about a ten-fold concentration of III (Fig. 2). This marked change in the decomposition rate between the monoaryldiazomethanes and the diaryl ones may be attributed to the differences in the stabilities of the intermediate sulfonates. The sulfonates derived from diaryldiazomethanes seem to be much more subject to solvolysis than the corresponding sulfonates from monoaryldiazomethanes.

Consequently, it is concluded that, in the cases of diazomethane and monoaryldiazomethanes, the insertion reaction is preferential because these diazoalkanes have an effective nucleophilicity toward II; even if the reaction could occur with a trace amount of III, it would essentially stop at the stage of the sulfonate formation because of its stability against solvolysis. On the other hand, in the cases of diaryldiazomethanes, the lesser nucleophilicity of the diazo-carbon atom toward II resulting from the conjugation with the two aromatic rings as well as the steric effects and the readier solvolysis of the sulfonates make the acid-catalyzed decomposition predominant. From these observations, the present decomposition reactions are formulated as follows (Scheme 5):



Scheme 5.

Experimental

The NMR spectra were obtained with a Varian EM-360 (60 MHz) instrument, with tetramethylsilane as the internal standard. The IR spectra were recorded on a Hitachi 215 Grating Infrared Spectrophotometer; a 0.1 mm NaCl cell was used for the measurement in solution. The UV spectra were taken with a Union SM-401 spectrophotometer.

Materials. The acetonitrile was purified by careful distillation from phosphorus pentoxide through a 10-in helix-packed column. The middle fractions were collected and stored in a glass-stoppered flask. The *o*-sulfobenzoic anhydride (II) was prepared by the method of Clarke and Dreger,¹⁴⁾ and recrystd from benzene; mp 126–127 °C, (lit.¹⁴⁾ 126–127 °C); IR (in CH₃CN): 1836 and 1818 (C=O), 1206, 996, 810 cm⁻¹. The anhyd *o*-sulfobenzoic acid (III) was given on the hydrolysis of II and was dried *in vacuo* above 105 °C; mp 140–141 °C; IR (Nujol): 3500–2500 (COOH

and SO_3H), 1720 ($\text{C}=\text{O}$), 1160 and 1020 cm^{-1} (SO_2). Because of moisture-sensitive substances, the anhydride and the acid, placed in a bottle fitted with a sealing cap, were stored in a desiccator, with silica gel as the desiccant. The diazomethane was prepared by the procedure in the literature,¹⁵ and its ethereal solution was dried over potassium hydroxide. The monoaryldiazomethanes and diaryldiazomethanes were synthesized by the methods of Closs and Moss¹⁶ and Smith and Howard¹⁷ respectively. $\lambda_{\text{max}}(\epsilon)$ in CH_3CN : 488 nm (25) for phenyldiazomethane (I-2), 495 (25) for *p*-tolyldiazomethane (I-3), 484 (32) for *p*-chlorophenyldiazomethane (I-4), 525 (95) for diphenyldiazomethane (I-6); these values are essentially identical with those in the literature.^{11,16}

p-Tolylphenyldiazomethane (I-7); mp 51–53 °C, reddish purple needles (from petroleum ether), (lit.¹⁸) 53–55 °C, $\lambda_{\text{max}}(\epsilon)$ in CH_3CN : 530 nm (98). Bis(*p*-methoxyphenyl)-diazomethane (I-8); mp 99 °C (dec), purple needles (from ether), (lit.¹¹) 99–100 °C (dec). 9-Diazofluorene (I-9); mp 94–95 °C (from EtOH), (lit.¹⁹) 94–95 °C. Because of the unstability of the diazo compounds, they were prepared just before use for the aryldiazomethanes and were purified before use by recrystallization for the diaryldiazomethanes.

Kinetic Measurements. The temperature during the measurements was not especially controlled, but its change was within ± 0.5 °C. As a rule, solutions of I, II, and III were made up separately just before use. The change in the optical density at the wavelength of the absorption maximum of I in the visible region was followed spectrophotometrically. The second order rate constants, k , were determined graphically from the plots of $1/(a-b) \ln b(a-x)/a(b-x)$ against the time.

General Procedure. To a three-necked flask (100 ml) equipped with a dropping funnel, a thermometer, and a drying tube of calcium chloride, we added II (5 m mol) in dry acetonitrile (25 ml), and then I (5 m mol) in dry acetonitrile (25 ml) was stirred in over a 10-min period. Stirring was then continued for 50 min. In the case of diazomethane, its excess in an ether solution dried over potassium hydroxide was dropped in. The addition of I caused the evolution of nitrogen gas. The removal of the solvent *in vacuo* gave oily reaction mixtures in the cases of I-1–5 or solid ones in the cases of I-6–9. The same procedure was used for the *o*-sulfobenzoic acid-catalyzed decomposition of diaryldiazomethanes (I-6–8) by employing a catalytic amount of III instead of II. These catalytic decompositions also gave almost quantitative olefins for I-6–8. These reaction mixtures were submitted to chromatography, using silica gel as the adsorbent. Elution with a petroleum ether–ether gave the olefins (V), while elution with chloroform gave the keto sultones (IV). The olefins, V-6, 8, were identified by comparison with authentic specimens,¹¹ while the V-7 and V-9 were confirmed by elemental analyses: V-7; Found: C, 93.11; H, 6.79%. Calcd for $\text{C}_{28}\text{H}_{24}$: C, 93.29; H, 6.71%. V-9; Found: C, 94.74; H, 5.11%. Calcd for $\text{C}_{26}\text{H}_{18}$: C, 95.09; H, 4.91%. 1,2-Di-*p*-tolyl-1,2-diphenylethylene (V-7) showed two kinds of methyl signals to the same extent, centered at δ 2.2 and due to the *cis* and *trans* isomers. The structures of the keto sultones (IV-1–5) were determined by means of elemental analyses and by measurements of the IR, NMR, and Mass spectra.

o-Glycolylbenzenesulfonic Acid Sultone (IV-1): Mp 93–94 °C, colorless needles (from CH_3OH), (lit.²⁰) 93–94 °C. IR (Nujol): 1700 ($\text{C}=\text{O}$), 1367 and 1195 cm^{-1} (SO_2). MS: $m/e=198$ (M^+). NMR (δ , CDCl_3): 7.7–8.2 (m, 4H), 5.25 (s, 2H). Found: C, 48.27; H, 3.17%. Calcd for $\text{C}_8\text{H}_6\text{O}_4\text{S}$: C, 48.49; H, 3.05%.

o-(Phenylglycolyl)benzenesulfonic Acid Sultone (IV-2): Mp

54–55 °C, colorless needles (from CH_3OH). IR (Nujol): 1703 ($\text{C}=\text{O}$), 1370 and 1195 cm^{-1} (SO_2). MS: $m/e=274$ (M^+). NMR (δ , CDCl_3): 7.67–8.17 (m, 4H), 7.40 (s, 5H), 6.38 (s, 1H). Found: C, 61.22; H, 3.77%. Calcd for $\text{C}_{14}\text{H}_{10}\text{O}_4\text{S}$: C, 61.32; H, 3.68%.

o-(Tolylglycolyl)benzenesulfonic Acid Sultone (IV-3): Mp 123–124 °C, pale yellow needles (from CH_3OH). IR (Nujol): 1700 ($\text{C}=\text{O}$), 1365 and 1195 cm^{-1} (SO_2). MS: $m/e=288$ (M^+). NMR (δ , CDCl_3): 7.67–8.17 (m, 4H), 7.25 (s, 4H), 6.37 (s, 1H), 2.37 (s, 3H). Found: C, 62.52; H, 4.23%. Calcd for $\text{C}_{15}\text{H}_{12}\text{O}_4\text{S}$: C, 62.50; H, 4.20%.

o-(*p*-Chlorophenylglycolyl)benzenesulfonic Acid Sultone (IV-4): Mp 89–90 °C, colorless needles (from CH_3OH). IR (Nujol): 1705 ($\text{C}=\text{O}$), 1360 and 1195 cm^{-1} (SO_2). MS: $m/e=308$, 310 (3:1) (M^+). NMR (δ , CDCl_3): 7.73–8.33 (m, 4H), 7.40 (s, 4H), 6.40 (s, 1H). Found: C, 54.21; H, 3.35%. Calcd for $\text{C}_{14}\text{H}_9\text{O}_4\text{SCl}$: C, 54.40; H, 3.01%.

o-(Methylphenylglycolyl)benzenesulfonic Acid Sultone (IV-5): Mp 80–81 °C. Colorless needles (from CH_3OH). IR (Nujol): 1700 ($\text{C}=\text{O}$), 1365 and 1194 cm^{-1} (SO_2). MS: $m/e=288$ (M^+). NMR (δ , CDCl_3): 7.67–8.07 (m, 4H), 7.27–7.57 (m, 5H), 2.28 (s, 3H). Found: C, 62.41; H, 4.59%. Calcd for $\text{C}_{15}\text{H}_{12}\text{O}_4\text{S}$: C, 62.50; H, 4.20%.

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