I. THE SYNTHESIS OF ESTER (*p*-TOLYLSULFONYL)HYDRAZONES AND THEIR DECOMPOSITION IN PROTIC SOLVENTS TO GIVE MIXED ACETALS

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ABSTRACT

Methyl benzoate (*p*-tolylsulfonyl)hydrazone (I) was prepared from the reaction between (*p*-tolylsulfonyl)hydrazide and either methyl benzimidate hydrochloride or methyl orthobenzoate. When the potassium or sodium salt of this hydrazone was decomposed, thermally or photochemically, in the presence of alcohols, benzaldehyde mixed acetals could be isolated in good yields and of high purity. When the decomposition was carried out in the presence of piperidine, there was produced 1-(α -methoxybenzyl)piperidine (II) and α, α -dipiperidinotoluene (III). The reaction products can be explained by assuming the initial formation of phenylmethoxydiazomethane.

INTRODUCTION

Diazo compounds have proved extremely useful in synthetic organic chemistry (1). There are, however, limited types of diazo compounds available, and as an extension to this useful class of reactants, an investigation into the possible synthesis of alkoxydiazoalkanes has been undertaken. Examination of the stabilities of known diazoalkanes (2) would lead one to predict that the alkoxydiazoalkanes may be unstable, thus only *in situ* synthesis may be possible. Such *in situ* generation of alkoxydiazoalkanes would in itself be of synthetic value and thus our initial investigations have been directed at the use of the Bamford-Stevens reaction (3) on ester (p-tolylsulfonyl)hydrazones.

Synthesis of Ester (p-Tolylsulfonyl)hydrazones

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Orthoesters have frequently been used to prepare imidate esters and Ainsworth (4) has produced ester semicarbazones from orthoesters and semicarbazide.



Upon refluxing an equimolar mixture of trimethyl orthobenzoate and (*p*-tolylsulfonyl)hydrazide in methanol, methyl benzoate (*p*-tolylsulfonyl)hydrazone (I) was isolated in a 72% yield. The product consisted of a mixture of *syn* and *anti* isomers as was indicated by the presence of two signals for the methoxy protons at τ 6.22 and 6.33 in the nuclear

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magnetic resonance (n.m.r.) spectrum. Upon further purification a pure isomer, m.p. 98–99°, with the signal for methoxy protons at τ 6.33, was produced.*

A second method of preparation was developed. Schmidt (6) has shown that imido esters react rapidly with hydrochloride salts of amines and hydrazines to give Schiff bases and hydrazones respectively. Methyl benzoate (p-tolylsulfonyl)hydrazone could be prepared in a 41% yield by adding a cold solution of methyl benzimidate in ethanol to a cold suspension of (p-toly|sulfony|) hydrazide hydrochloride. The product was again a mixture of syn and anti isomers. Both methods are of general applicability, the former being preferred because of the superior yields.

Decompositions in Protic Solvents

The sodium or potassium salt of I was prepared in good yield from solutions of I (mixture of isomers) and sodium or potassium ethoxide in dimethoxyethane. These salts are stable and can be isolated in a high degree of purity as indicated by their n.m.r. spectra. Thus they were used for the majority of the reactions investigated. When the sodium salt of I was refluxed in ethanol, a reaction took place that required a 67 h reflux

Na salt of I + ROH \rightarrow C₆H₅CH(OCH₃)OR + Na⁺-O₂SC₆H₄--CH₃(p) + N₂

period to complete. The only products found to be present were sodium p-toluenesulfinate and benzaldehyde methyl ethyl acetal. At higher temperatures the decomposition occurred much faster and in the presence of different alcohols fairly good yields of mixed acetals were obtained. A summary of these experiments is given in Table I.

The potassium salt of I decomposed photochemically in 2 h at room temperature to similarly produce benzaldehyde methyl ethyl acetal (70%).

R	Boiling point (°C (mm))	$C_{6}H_{5}$ OCH ₃ C H OR n_{D}^{25}	* Yield (%)	Conditions
C2H2-†	58-59 (2.5)	1,4831	37	Na salt, ethanol, 67 h at 78°
$C_2H_5-\dagger$	58-59 (2.5)	1.4831	70	Photochemical decomposition, eth- anol. 25°
n-C3H7-	67-68 (2.0)	1.4809	65	Na salt, 1-propanol, 23 h at 95°
(CH ₃) ₂ CH—CH ₂ -	66-67 (0.8)	1.4765	61	Na salt, 2-methyl-1-propanol, 7 h at 105°
$(C_{2}H_{5})_{2}CH-1$	87-88(1.0)	1.4796	35	K salt, 3-pentanol, 6 h at 116°
C ₆ H ₅ —CH ₂ -‡	116–117 (0.3)	1.5460	63	K salt, benzyl alcohol, 3.5 h at 116°

TABLE I Mixed acetals of benzaldehyde prepared by the thermal decomposition of salts of I

*The acetals were characterized by elemental analysis, n.m.r. spectra, and by the formation of the 2,4-dinitrophenylhydrazone of benzaldehyde upon treatment with a methanolic solution of 2,4-dinitrophenylhydrazine sulfate. †Reported (B. Władisław and A. M. J. Ayres, J. Org. Chem. 27, 281 (1962).) b.p. 205° (760), $n_{\rm D}$ ¹⁹ 1.4878. ‡1,2-Diethoxyethane was used as a solvent.

It seemed of interest to see whether the decomposition of methyl benzoate (p-tolylsulfonyl)hydrazone in the presence of secondary amines might give rise to compounds of the type represented by II. When the potassium salt of I was refluxed for 11 h in piperidine, the decomposition was complete. The only product that was isolated, in a 82% yield, was α, α -dipiperidinotoluene (III). It was believed that this product resulted from a reaction

*Studies by Karabatsos and Taller (5) on the n.m.r. spectra of phenylhydrazones would suggest that the isomer melting at 98–99° and having a signal at τ 6.33 should be assigned the syn configuration, using the convention outlined in ref. 5.

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between initially formed 1-(α -methoxybenzyl)piperidine (II) and piperidine. In order to test this assumption the decomposition was carried out photochemically at room temperature. When the reaction mixture was worked up, special care was taken that the temperature was kept as low as possible and II was isolated, in a yield of 30%. However



III was still the principal reaction product. The proof of structure of 1-(α -methoxybenzyl)piperidine (II) is based upon an elemental analysis, spectral data, and its conversion into α, α -dipiperidinotoluene upon heating with piperidine. Compound II is an unstable high-boiling liquid (b.p. 81–85° at 0.2 mm). Even at 0° it slowly decomposes and the smell of benzaldehyde becomes apparent. The infrared spectrum of a solution on standing also develops a carbonyl band at the same frequency as benzaldehyde (1 708 cm⁻¹). The n.m.r. spectrum shows singlets at τ 2.76, 5.33, and 6.66 ascribed to the aromatic protons, the methinyl hydrogen, and the methoxy hydrogens respectively, and broad bands at τ 7.3–7.8 and τ 8.3–8.8 ascribed respectively to the α - and β,γ -hydrogens of the piperidine ring. The ratio of integrated areas is the same as that predicted for II.

When the decomposition of the potassium salt of I was carried out in diglyme at 125– 130° in the presence of a trace of water, a 15% yield of a crystalline compound, melting at 147–149°, was isolated. The infrared spectrum showed a strong absorption at 1 619 cm⁻¹, which was attributed to a carbon–nitrogen double bond, and further strong bands at 1 165 cm⁻¹ and in the 1 300 – 1 350 cm⁻¹ region. These latter absorptions suggested the presence of a sulfonylamido group (7). The n.m.r. spectrum showed a complicated signal pattern of aromatic protons at τ 2.0–3.3 and singlets at τ 4.14, 6.23, 7.05, and 7.59 with relative areas 14:1:3:3:3. The compound was found to have a molecular weight of 440 and to fit the empirical formula C₂₃H₂₄N₂O₄S (molecular weight 424.5). The only structure that readily fits all the requirements is that of methyl benzoate (α -methoxybenzyl)-(ρ -tolylsulfonyl)hydrazone (IV).* When the experiment was repeated with a trace of



 D_2O instead of H_2O , the n.m.r. spectrum of IV showed that the singlet at τ 4.14 was present in only one-fifth of its original intensity, thus indicating that the proton responsible for this signal originates from the water. This type of product has recently been isolated by Nozaki *et al.* in an investigation of the reaction of phenylcarbene formed from benzaldehyde (*p*-tolylsulfonyl)hydrazone in various solvents (8).

*When an equimolar mixture of I and its potassium salt were heated in diglyme at 130° a 36% yield of IV was obtained.

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CONCLUSIONS

Salts of ester (*p*-tolylsulfonyl)hydrazones may be decomposed in protic solvents, both thermally and photochemically, to give rise to those products expected from alkoxydiazoalkanes. The results described herein are similar to those obtained by Bamford and Stevens (3) in the thermal decomposition (*p*-tolylsulfonyl)hydrazone salts of aromatic aldehydes and ketones. Therefore it seems reasonable to assume that the decomposition of an ester (*p*-tolylsulfonyl)hydrazone salt produces initially an alkoxydiazoalkane (V) which by virtue of its reactivity undergoes an immediate reaction with the solvent. However on basis of the present experiments alone the possibility of product formation via an intermediate such as VI can not be excluded.



EXPERIMENTAL

All melting points and boiling points are uncorrected.

The infrared spectra were obtained on a Perkin-Elmer Model 421 spectrophotometer equipped with grating optics. Nuclear magnetic resonance spectra were measured using a Varian Associates Model A-60 spectrometer, with tetramethylsilane as a reference. Ultraviolet spectra were obtained using a Cary Model 14M recording spectrophotometer.

Vapor phase chromatography was carried out with a Perkin-Elmer Model 154 vapor fractometer or a F. & M. Model 500 temperature-programmed gas chromatograph.

The photochemical decompositions were all carried out in a quartz reaction vessel, cooled by running tap water, with an internally situated 250 W Hanovia ultraviolet source.

The microanalyses were performed by Pascher Mikroanalytisches Laboratorium (Bonn, West Germany), Daessle Organic Microanalyses (Montreal), and the Microanalytical Laboratory of the Department of Chemistry, University of Alberta (Edmonton).

Methyl Benzimidate was prepared as described by Wheeler (9); yield, 90%; b.p. 73-74° (2.4 mm); n_D^{25} 1.5420. Reported b.p. 95-97° (14 mm).

Methyl Benzoate (p-Tolylsulfonyl)hydrazone (I) from Methyl Benzimidate

A solution of methyl benzimidate (12.2 g, 90.4 mmole) in 20 ml of absolute ethanol was added to a cold suspension of (*p*-tolylsulfonyl)hydrazide hydrochloride (20.0 g, 89.9 mmole) in 60 ml of absolute ethanol. Ammonium chloride precipitated slowly from the obtained homogeneous reaction mixture. After 3 h at room temperature the ammonium chloride was filtered off and most of the ethanol removed under reduced pressure. Diethyl ether and water were added to the residue. The ether solution was again washed with water and dried and the ether evaporated. The residue was dissolved in a mixture of 60 ml of benzene and 25 ml of *n*-hexane and cooled in the refrigerator for 2 days. The solid amounted to 8.2-11.2 g (30-41%). The n.m.r. spectrum showed that it was a mixture of the *syn* and *anti* isomer (methoxy signals at 6.23 and

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6.34 with an integration ratio of 1:4 respectively). Two additional recrystallizations from a benzene – nhexane mixture gave a product, m.p. 93-97°, consisting of only one isomer. However the crystals contained some benzene, as indicated by the n.m.r. spectrum and an analysis, which could not be readily removed. A pure product, believed to be the syn isomer, was obtained by recrystallization from diethyl ether; m.p. 98-99°.

Anal. Calcd. for C15H15N2O3S: C, 59.19; H, 5.30; N, 9.21; S, 10.54, Found; C, 58.87; H, 5.06; N, 9.41; S, 10.71.

When the product was heated for 0.5 h at 100-102°, a mixture of the two isomers was obtained (the integration ratio of the methoxy signals at 6.23 and 6.33 in the n.m.r. spectrum was 1:2 respectively).

Potassium Salt of Methyl Benzoate (p-Tolylsulfonyl)hydrazone

Methyl benzoate (p-tolylsulfonyl)hydrazone (10.0 g, 32.9 mmole) was added to a solution of potassium (1.3 g, 33.3 mg-atom) in a mixture of 6 ml of anhydrous ethanol and 70 ml of 1,2-dimethoxyethane. The solution was heated to its boiling point, then cooled. The potassium salt was filtered off and washed with ether. Yield 7.3 g (65%) of slightly yellow-colored salt which decomposes above 170°. The n.m.r. spectrum (in D_2O) indicated a complex signal pattern from the aromatic protons at 2.2-3.3, and sharp singlets at 6.55 and 8.25.

Methyl Benzoate (p-Tolylsulfonyl)hydrazone from Methyl Orthobenzoate

A solution of methyl orthobenzoate (10.0 g, 55 mmole, prepared by the method of McElvain and Venerable (10)) and (p-tolylsulfonyl)hydrazide (10.0 g, 54 mmole) in 60 ml of methanol was refluxed for 4 h. The solvent was removed under reduced pressure, the residual oil dissolved in 50 ml of benzene, and 25 ml of n-hexane added. The solution thus obtained was cooled for 2 days in the refrigerator before the crystals were filtered off. Yield, 12.2 g (73%) of white crystals, m.p. 85-95°. By an examination of the n.m.r. spectrum (in $CDCl_a$) it was clear that the solid consisted only of a mixture of the syn and anti isomer (apart from a small amount of benzene that could not be removed), as indicated by methoxy singlets at 6.22 and 6.33 (integration ratio 2:3 respectively) and aromatic methyl singlets at 7.58 and 7.63.

The Preparation of Benzaldehyde Acetals* from the Thermal or Photochemical Decomposition of Alkyl Benzoates (p-Tolylsulfonyl)hydrazones (Benzaldehyde Dimethyl Acetal)

Methyl benzoate (p-tolylsulfonyl)hydrazone (5.0 g, 16.4 mmole) and sodium methoxide (0.90 g, 16.6 mmole) were refluxed for 47 h in 35 ml of 1,2-dimethoxyethane. The solid (3.3 g) was collected by filtration and found to be a mixture of sodium p-toluenesulfinate and sodium methyl benzoate (p-tolylsulfonyl)hydrazone. The filtrate was concentrated and the residue was dissolved in ether, washed with water, and dried (MgSO₄). The liquid residue obtained after removal of the ether consisted of only benzaldehyde dimethyl acetal (as shown by n.m.r. spectroscopy); yield, 0.8 g (50%, based on 60% starting material that had reacted); b.p. 56-57° (3.5 mm). Reported (11) b.p. 207° at atmospheric pressure.

Benzaldehyde Methyl Ethyl Acetal

(a) Methyl benzoate (p-tolylsulfonyl)hydrazone (10.0 g, 32.9 mmole) was added to a solution of sodium (0.8 g, 34.8 mg-atom) in 50 ml of absolute ethanol and the mixture was refluxed for 67 h. Gas evolution took place very slowly. The ethanol was distilled off and the residue was taken up in ether, washed with water, and dried with anhydrous magnesium sulfate. A vacuum distillation of the residue, obtained after removal of the ether, gave 2.0 g (37%) of the acetal; b.p. $58-59^{\circ}$ (2.5 mm); n_{D}^{25} 1.4831. Reported (12) b.p. 205° (atmospheric pressure); n_D^{19} 1.4878. Anal. Calcd. for C₁₀H₁₄O₂: C, 72.26; H, 8.49. Found: C, 72.48; H, 8.40.

(b) Potassium methyl benzoate (p-tolylsulfonyl)hydrazone (9.0 g, 26.3 mmole) was suspended in 180 ml of absolute ethanol and irradiated at room temperature. Gas evolution took place rapidly and the potassium salt slowly dissolved. After 2 h the gas evolution ceased (calcd. amount of nitrogen at 25° and 700 mm: 693 ml; observed: 695 ml). The solution was treated as described above and yielded 3.1 g (70%) benzaldehyde methyl ethyl acetal; b.p. 60-61° (2.6 mm); $n_{\rm D}^{25}$ 1.4832.

Benzaldehyde Methyl n-Propyl Acetal

Methyl benzoate (p-tolylsulfonyl)hydrazone (10.0 g, 32.9 mmole) was added to a solution of sodium (0.8 g, 34.8 mg-atom) in 40 ml of 1-propanol, and the mixture was refluxed for 23 h, at which time the nitrogen evolution had ceased. Part of the sodium p-toluenesulfinate (4.5 g, 77%; its infrared and n.m.r. spectra were identical with those of an authentic sample) crystallized out upon cooling and was filtered off. The 1-propanol was distilled off and the residue was taken up in ether, washed with water, and dried. Removal of the ether and a vacuum distillation of the residue yielded 3.85 g (65%) of the acetal; b.p. 67-68° (2.0 mm); n_D²⁵ 1.4809. Anal. Calcd. for C₁₁H₁₆O₂: C, 73.29; H, 8.95. Found: C, 73.72; H, 8.57.

Benzaldehyde Methyl Isobutyl Acetal

The same procedure as described above was used except that 40 ml of isobutyl alcohol was used as

*All the acetals prepared reacted with a methanolic 2,4-dinitrophenylhydrazine sulfate solution to give benzaldehyde 2,4-dinitrophenylhydrazone, m.p. 241-242°.

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solvent and a reflux time of only 7 h was required to effect complete decomposition. Yield, 3.9 g (61%); b.p. 77-78° (2.4 mm); n_D^{25} 1.4769.

Anal. Calcd. for C₁₂H₁₈O₂: C, 74.20; H, 9.34. Found: C, 75.24; H, 9.45.

Benzaldehyde Methyl 3-Pentyl Acetal

Potassium (1.3 g, 33.3 mg-atom) was added to a mixture of 3-pentanol (10.0 g, 0.114 mole) and 50 ml of 1,2-diethoxyethane. Methyl benzoate (*p*-tolylsulfonyl)hydrazone (10.0 g, 32.9 mmole) was added and the mixture was refluxed for 6 h. The solvent was removed under reduced pressure and the residue was taken up in ether, washed with water, and dried. The residue, obtained after removal of the solvent, was distilled *in vacuo* to give 2.4 g (35%) of the acetal; b.p. 87-88° (1.0 mm); n_D^{25} 1.4796.

Anal. Calcd. for C₁₃H₂₀O₂: C, 74.96; H, 9.68. Found: C, 75.18; H, 9.77.

Benzaldehyde Methyl Benzyl Acetal

Methyl benzoate (*p*-tolylsulfonyl)hydrazone (10.0 g, 32.9 mmole) was added to a solution of potassium (1.3 g, 33.3 mg-atom) in benzyl alcohol (10.0 g, 92.6 mmole) and 1,2-diethoxyethane (50 ml). The mixture was refluxed for 3.5 h and cooled, potassium *p*-toluenesulfinate (6.15 g, 97%) was filtered off and the solvent removed under reduced pressure. The residue was fractionally distilled *in vacuo* to yield 4.7 g (63%) of the product; b.p. 116–117° (0.3 mm); n_D^{25} 1.5460.

Anal. Calcd. for C₁₅H₁₆O₂: C, 78.91; H, 7.06. Found: C, 78.67; H, 6.91.

The Thermal Decomposition of Potassium Methyl Benzoate (p-Tolylsulfonyl)hydrazone in Diglyme in the Presence of a Trace of Water to Produce IV

Potassium methyl benzoate (p-tolylsulfonyl)hydrazone (2.0 g, 5.8 mmole) was heated for 1 h at 125–130° in 20 ml of diglyme, to which a small amount of water (0.100 g, 5.5 mmole) had been added. The reaction mixture was cooled and filtered. Addition of 50 ml of water and 75 ml benzene followed. The benzene layer was separated, after vigorous shaking, washed twice with water, and dried with magnesium sulfate. The benzene was removed and pentane was added to the residue. Upon cooling, methyl benzoate (α -methoxybenzyl)(p-tolylsulfonyl)hydrazone (IV) (0.18 g, 15%) slowly crystallized. The product was recrystallized from a 5:1 *n*-hexane – benzene mixture, to give white prisms, m.p. 147–149°.

Anal. Calcd. for C₂₃H₂₄N₂O₄S (molecular weight 424.5): C, 65.07; H, 5.70; N, 6.60; S, 7.55. Found: C, 65.35; H, 5.76; N, 6.72; S, 7.71. Molecular weight (osmometric), 440.

The experiment was repeated using D₂O (0.093 g, 4.6 mmole) instead of H₂O. Investigation of the n.m.r. spectrum of the methyl benzoate (α -methoxybenzyl)(*p*-tolylsulfonyl)hydrazone (0.12 g, 10%; m.p. 146–148°) thus obtained revealed that the singlet at 4.14 was present in only one-fifth of its original intensity, indicating that the proton responsible for this signal had originated from the water.

The Thermal Decomposition of Potassium Methyl Benzoate (p-Tolylsulfonyl)hydrazone in Piperidine

The potassium salt (10.0 g, 29.2 mmole) was refluxed for 11 h in 50 ml of predistilled piperidine (b.p. 103-105°), at which time the gas evolution had ceased. The reaction mixture was cooled, potassium *p*-toluenesulfinate (5.5 g, 97%) was filtered off, and the solvent removed under reduced pressure. The residue was dissolved in ether, washed with water, and dried with magnesium sulfate. Removal of the ether left 6.2 g (82%), α,α -dipiperidinotoluene (III) that slowly solidified, m.p. 76-79°. Recrystallization from acetone produced white needles, m.p. 81-83°. Reported (13) m.p. 80-81°; mixture m.p. 81-83°. The infrared spectrum was also identical with that of an authentic sample.

The Photochemical Decomposition of Potassium Methyl Benzoate(p-Tolylsulfonyl)hydrazone in the Presence of Piperidine

A suspension of the potassium salt of I (9.2 g, 26.9 mmole) in a mixture of 150 ml of 1,2-dimethoxyethane and 30 ml of piperidine was irradiated for 7.5 h. The solution was filtered, the solvent mixture removed under reduced pressure and the residue taken up in ether and dried. The liquid residue obtained after removal of the ether was distilled *in vacuo* to give 1.6 g distillate, b.p. 85-100° (0.25 mm). A high-boiling residue (3.0 g) solidified upon cooling and a n.m.r. spectrum showed that it consisted mainly of α, α -dipiperidinotoluene. The distillate was almost pure 1-(α -methoxybenzyl)piperidine (II), and only a small amount of benzaldehyde dimethyl acetal was present as impurity, as was shown by n.m.r. spectroscopy. Redistillation afforded pure α, α -dipiperidinotoluene; b.p. 81-85° (0.2 mm); n_D^{25} 1.5202.

Anal. Calcd. for C13H19ON: C, 76.05; H, 9.33; N, 6.82. Found: C, 76.02; H, 9.13; N, 7.01.

A small amount of 1-(α -methoxybenzyl)piperidine (0.19 g) was dissolved in 3 ml of piperidine, heated to the boiling point of the solution, and then immediately cooled. Removal of the solvent yielded 0.24 g of a solid, m.p. 75–78°, identical in all respects with α, α -dipiperidinotoluene.

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