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N-ARYL SULFONYL HYDRAZIMIDATES - HYDRAZONES OF ESTERS

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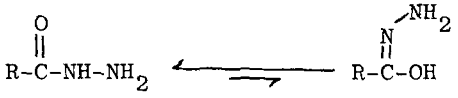
Abstract: The ease of preparation and the potential synthetic utility of the N-aryl sulfonyl hydrazimidates is described and the stereochemistry of one of these compounds is unambiguously assigned by X-ray crystallography.

Although facile tautomerization of the hydrazide **1** to the hydrazimidic acid **2** appears possible, evidence exists documenting only the hydrazide tautomer **1**.[1] This equilibrium is analogous to the amide **3** to imidic acid **4** interconversion. However, a considerable body of information has accumulated concerning both the preparations and the reactions of imidate esters **5**.[2] Equilibration of **5** (R'= alkyl) to the N-alkyl amide is not observed under mild conditions due to a strong covalent bond to oxygen. Under forcing conditions though even the O-alkyl and especially the O-aryl imidates (**5** R'=alkyl or aryl) are known to isomerize to the corresponding N-substituted amides via a reaction known as the Chapman rearrangement.[3]

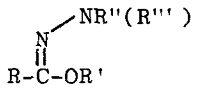
(1)



$R{-}\overset{\overset{O}{\|}}{C}{-}NH{-}NH_2 \rightleftharpoons R{-}\overset{\overset{N{-}NH_2}{\|}}{C}{-}OH$

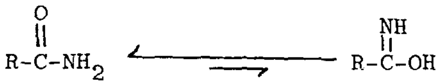
(2)

(6)



$R{-}\overset{\overset{N{-}NR''(R''')}{\|}}{C}{-}OR'$

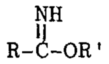
(3)



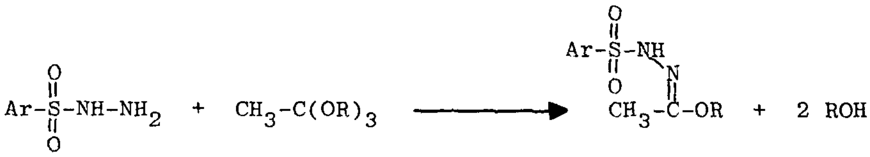
$R{-}\overset{\overset{O}{\|}}{C}{-}NH_2 \rightleftharpoons R{-}\overset{\overset{NH}{\|}}{C}{-}OH$

(4)

(5)



$R{-}\overset{\overset{NH}{\|}}{C}{-}OR'$

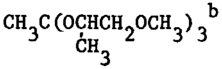


$Ar{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}{-}NH{-}NH_2 + CH_3{-}C(OR)_3 \longrightarrow CH_3{-}\overset{\overset{Ar{-}SO_2{-}NH{-}N}{\|}}{C}{-}OR + 2\ ROH$

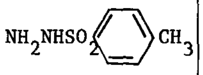
(7)

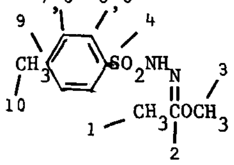
Table I

$CH_3C(OCH_3)_3$ $CH_3C(OCH_2CH_3)_3$ $CH_3C(OCH_2CH_2OCH_2CH_3)_3$[a]



$CH_3C(OCHCH_2OCH_3)_3$[b] with CH_3 on CH





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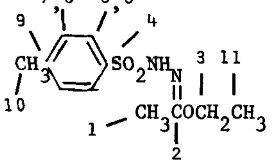

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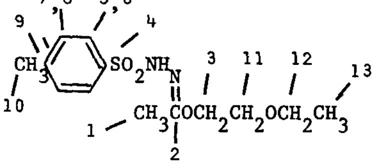

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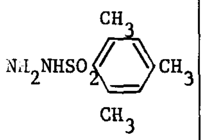

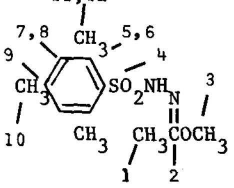

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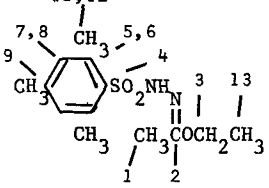

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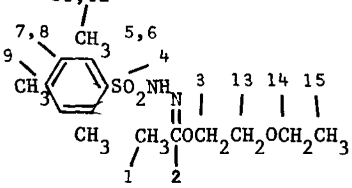

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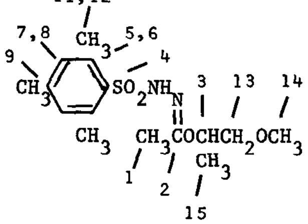

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Compound	C-1	C-2	C-3	C-4	C-5,6	C-7,8	C-9	C-10	C-11,12	C-13	C-14	C-15	Solvent[e]
11	15.1	165.2	53.8	143.6	129.5	128.7	136.8	21.3	—	—	—	—	DMSO
12	15.6	152.0	64.1	142.7	129.2	127.5	136.6	20.9	14.8	—	—	—	DMSO
13	15.0	166.4	68.2	143.8	129.3	128.3	135.2	21.4	66.6 66.0	—	—	—	$CDCL_3$
14	15.0	163.4	53.4	141.7	139.9	131.4	133.0	20.5	23.1	—	—	—	DMSO
15	15.2	163.0	61.7	142.0	139.8	131.4	133.2	20.4	23.0	14.0	—	—	DMSO
10	15.3	164.8	68.5	142.9	140.5	131.9	133.8	20.8	23.4	66.6	64.0	15.0	Acetone
16	15.6	162.3	71.1	142.4	140.5	131.9	133.8	20.7	23.3	74.8	58.6	16.2	DMSO

Compound	11	12	13	14	15	10	16
Melting Point	147-149^{o}C	145-147^{o}C	94-97^{o}C	136-137^{o}C	165-167^{o}C	84-86^{o}C	135-138^{o}C
Yields	51%[c]	62%[c]	66%[c]	58%[c]	83%[d]	48%[c]	94%[d]

[a]Kuryla, W.C. and Leis, D.G. J. Org.Chem. 1964 29 p.2773. [b]Ibid., p.2773. [c]Yield after chromatography or recrystallization. [d]Crude yield. [e]TMS was used as internal standard

A much less well investigated functionality is that of the hydrazimidate ester **6**.[4] We have recently prepared a variety of N-aryl sulfonyl derivatives of **6**. In this paper we wish to report the preparations and physical properties of some of these compounds.

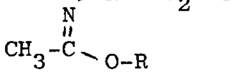
A most straightforward preparation of the N-aryl sulfonyl hydrazimidates **6** (R'=alkyl, R"= H, R'"-SO$_2$aryl) is effected simply by dissolution of an appropriately substituted aryl sulfonyl hydrazine in an excess of trialkyl orthoacetate. Occasionally a little gentle warning is required to obtain a completely homogenous solution. After stirring the reaction at room temperature for approximately one half to one and one half hours a high yield of the N-aryl sulfonyl hydrazimidate **7** is obtained by filtration of the precipitated product from the excess ortho ester.

Table I lists the different hydrazimidate esters that we have prepared by this procedure. In addition the ^{13}C-NMR spectra and the yields of purified compounds are given. An important conclusion which we drew from the ^{13}C-NMR spectra of the purified compounds is that they can be obtained exclusively as a single isomer. It was not possible to determine spectrally whether the two heteroatoms exist in the Z- or E- orientation (**8** or **9**) with respect to one another about the carbon nitrogen double bond. Hence we undertook an X-ray crystal structure determination to answer this question.

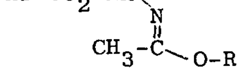
The mesitylene sulfonyl hydrazimidate **10** derived from tri(2-ethoxyethyl) orthoacetate crystallized from hexanes/ethyl acetate in the monoclinic space group $P2_1/n$. The measured cell constants of a=7.690(1) Å, b=15.375(2) Å, c=14.862(1) Å and β=97.91(1)° produced a calculated density of 1.25 g/cm^3 for four molecules in the unit cell. The reflection data were collected on a Syntex diffractometer using the ω-scan collection technique and CuK$_\alpha$ radiation (λ=1.5418Å). Before Lorentz-polarization corrections, 1946 of 2468 unique reflections (79%) with $2\theta \leq 114°$ were judged observed. No absorption correction was made. The structure was solved by the MULTAN programs.[5] Thermal anisotropic full matrix least squares refinement was applied to all non-hydrogen atoms. The positions of all hydrogens were calculated and refined by full-matrix least squares to a final R factor of 0.057.[6] An ORTEP diagram of the hydrazimidate **10** appears on the following page with all non-hydrogen atoms shown. This analysis unambiguously shows that crystalline hydrazimidate **10** exists exclusively in the **E** configuration.

Based upon the similarity of the chemical shifts of the set of carbon atoms which exists in all of the hydrazimidates found in Table I, we believe that all of our purified compounds in Table I exist as E isomers. We are continuing to investigate some reactions of these novel esters with the hope of successfully applying some recent modifications of the Bamford-Stevens reaction to these derivatives.

(8)

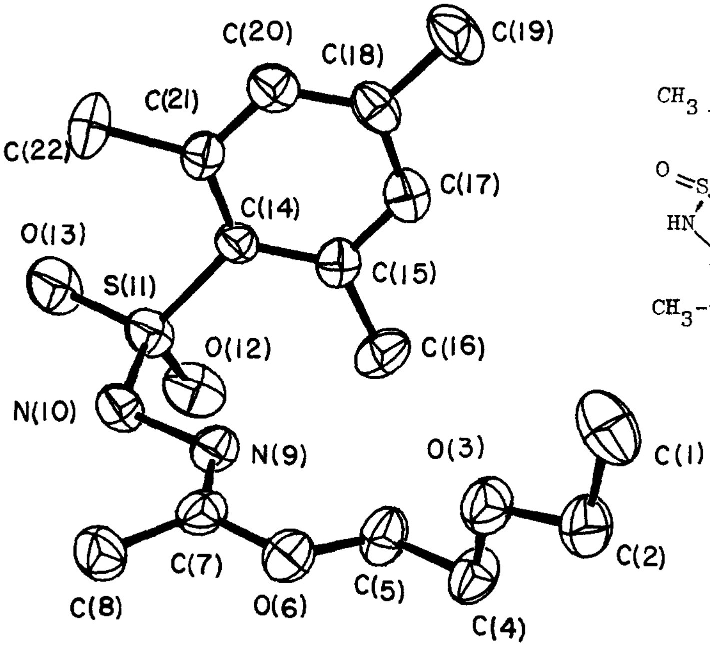


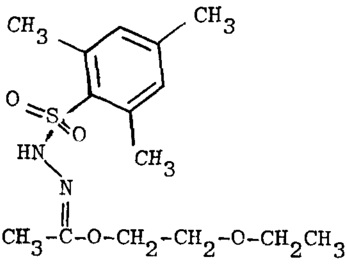
Z-isomer



(9)

E-isomer





(10)

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References and Notes

1. See, H. Paulsen and D. Stoye in "The Chemistry of Amides", ed. J. Zabicky, J. Wiley & Sons, NY, 1970, pp 515-600.

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