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β-(α-Benzenesulfonamidobenzal)hydrazine 및 그 유도체의 합성

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Synthesis of β-(α-Benzenesulfonamidobenzal)hydrazine and Its Derivatives

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요 약. N-Arylsulfonylbenzimidoyl chloride를 출발물질로 사용하여 다음과 같은 7가지 새로운 히드라진 유도체들을 합성하였다.

β-(α-Benzenesulfonamidobenzal)hydrazine (II)
β-(α-Benzenesulfonamidobenzal)dimethylmethylenehydrazine (III)
β-(α-Benzenesulfonamidobenzal)phenylhydrazine (VII)
β-(α-Benzenesulfonamidobenzal)-4-nitrophenylhydrazine (VIII)
β-(α-Benzenesulfonamidobenzal)-2, 4-dinitrophenylhydrazine (IX)
β-(α-Benzenesulfonamidobenzal)dimethylhydrazine (X)
β-(α-Benzenesulfonamidobenzal)-*p*-methylphenylhydrazine (XI)

이 유도체들의 구조를 원소분석, ir, nmr, mass 스펙트럼 및 기타 화학적인 방법을 통해서 확인하였다.

일반적으로 이 치환반응은 극성인 용매에서, 그리고 친핵체인 페닐히드라진 유도체에 전자를 끄는기가 있을때 수득율이 높았다.

ABSTRACT. Seven new hydrazine derivatives were prepared from N-Aryllsufonylbenzimidoyl chloride. These were:

β-(α-Benzenesulfonamidobenzal)hydrazine (II)
β-(α-Benzenesulfonamidobenzal)dimethylmethylenehydrazine (III)
β-(α-Benzenesulfonamidobenzal)phenylhydrazine (VII)
β-(α-Benzenesulfonamidobenzal)-4-nitrophenylhydrazine (VIII)

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β-(α-Benzenesulfonamidobenzal)-2, 4-dinitrophenylhydrazine (IX)

β-(α-Benzenesulfonamidobenzal)dimethylhydrazine (X)

β-(α-Benzenesulfonamidobenzal)-p-methylphenylhydrazine (XI)

The structure of these derivatives were identified by elemental analysis, spectral data and other chemical methods. In general, it was found that the yields of these reactions were significantly improved in polar solvent and by the electron attracting substituents in phenylhydrazine.

INTRODUCTION

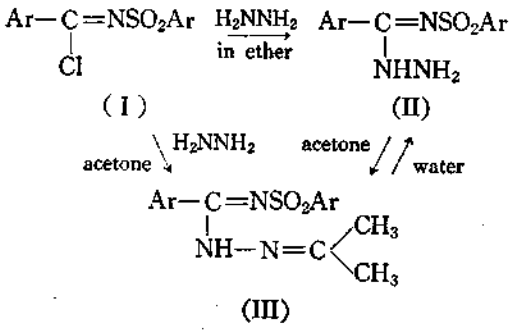
The most characteristic reaction of the imidoyl chlorides, which shows many similarities to the acyl chlorides, is substitution of halogen by a nucleophile and its application to organic synthesis has been reported[1]. Busch and Ruppenthal[2] synthesized its derivatives by reacting benzimidoyl chloride with phenylhydrazine. Behringer and Fischer[3] were reported to have synthesized N-[5-phenyl-tetrazoyl-(1)] benzimidhydrazine from N-[5-phenyl-tetrazoyl-(1)]-benzimid chloride. Eilingsfeld, Seefelder, Weidinger[4], Goedeler[5] prepared ester, thioester, thionester, alkyl chloride, ketone and imidoyl isocyanate derivatives from benzimidoyl chloride.

Ugi, Beck and Fetzer[6] determined the rate of hydrolysis of imidoyl chlorides and elucidated their mechanisms. However, not much work has been done on N-arylsulfonylbenzimidoyl chloride. N-Arylsulfonyl benzimidoyl chloride was first synthesized from benzenesulfonamide and benzotrichloride by Dubina and Burmistrov[7] in 1966. Thereafter syntheses of amine[8], ester and thioester derivatives[9] and the kinetic studies[10] for the hydrolysis of ester and thioester derivatives has been reported.

The purpose of this investigation is to synthesize the hydrazine derivatives from N-arylsulfonylbenzimidoyl chloride as a part of studies on the nucleophilic substitution reaction of N-arylsulfonyl benzimidoyl chloride.

RESULTS AND DISCUSSION

When N-Arylsulfonylbenzimidoyl chloride (I) was reacted with hydrazine (NH_2NH_2, where R_1=H, R_2=H), different products were obtained depending on the solvents used. In ether, the product must be (II).



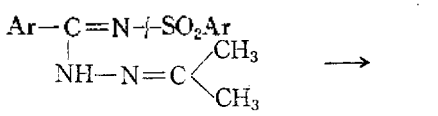
(I) (II) (III)

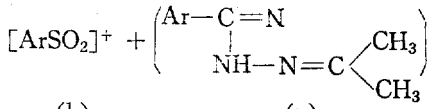
The ir spectrum of compound (II) shows NH_2, NH and C=N absorptions at 3, 500 (doublet), 3, 300 and 1, 600cm^{-1} respectively. However, when (I) was reacted with hydrazine in acetone, white crystal was obtained. It shows NH and C=N absorptions at 3, 300 and 1, 600 cm^{-1}.

The nmr spectrum of this compound is shown in *Fig.* 1. The nmr peaks at δ=7. 5 and 2. 0 ppm are assigned to the protons on the benzene ring and methyl groups. It should be mentioned that the methyl peak is doublet because the two methyl groups are not equivalent.

The mass spectrum of this compound shows molecular weight of 315. From the elemental analysis data and above results, the structure must be (III). Intense peaks at *m/e* 141 and

174 actually arise from fragment (a) and (b).

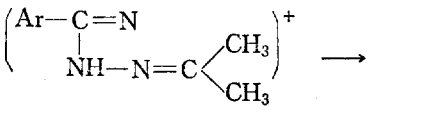


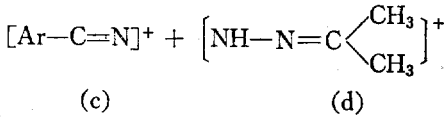


(b) (a)

Fragment (a) decompose to $[Ar—C=N]^+$ (c) and $\left[-NH—N=C\begin{matrix}CH_3\\CH_3\end{matrix}\right]^+$ (d).

They show secondary characteristic peaks at *m/e* 103 and 71.





(c) (d)

Intense peaks at *m/e* 77 and 238 are due to fragments $[C_6H_5]^+$ (e) and $[p-(C_6H_5)]^+$ (f) respectively.

Melting point and ir spectrum of the substance which was obtained from the reaction between (II) and acetone were the same as those of (III). (III) returned to (II) upon hydrolysis. Therefore it is highly probable that (I) reacts with hydrazine to form (II), which subsequently reacts with acetone to form (III).

N-Arylsulfonylbenzimidoyl chloride (I) was reacted with hydrazine derivatives (IV) in ether and acetone. But the products (VII)~(XI) in both solvents were the same. Acetone was used exclusively because the yields were favored in it. In these reactions, the following products (Va) or (Vb) are expected to result.

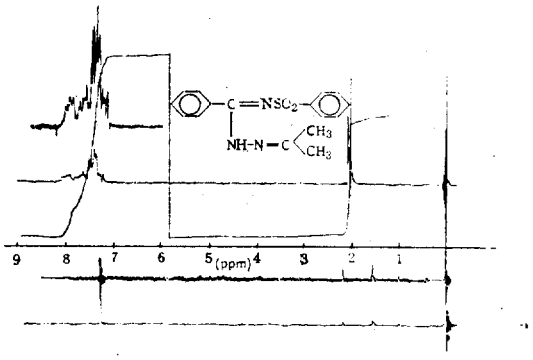


Fig. 1. nmr Spectrum of β-(α-benzenesulfonamidobenzal)-dimethylmethylenehydrazine (III)

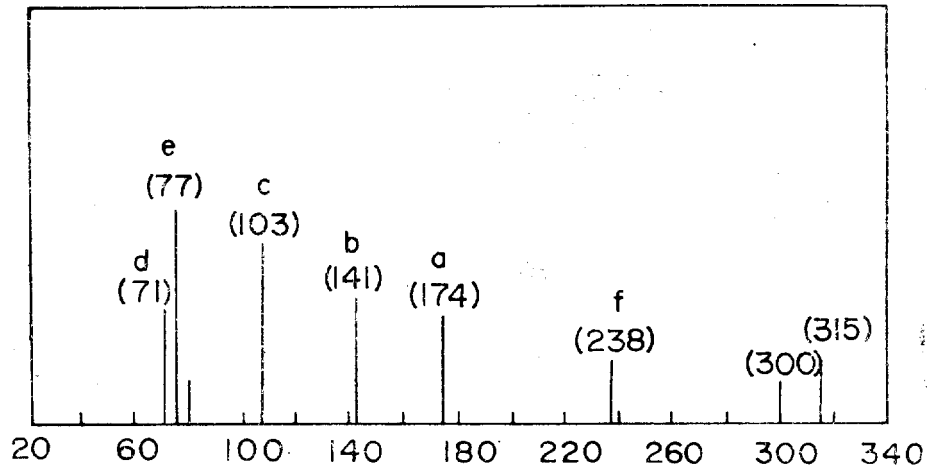
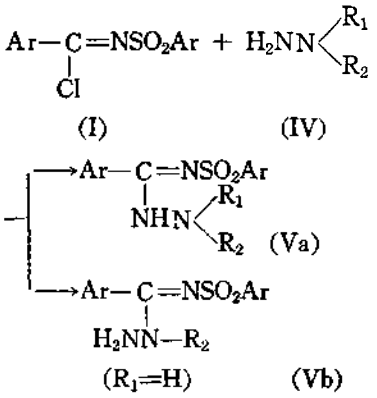


Fig. 2. Mass spectrum of β-(α-Benzenesulfonamidobenzal)dimethylmethylenehydrazine (III).



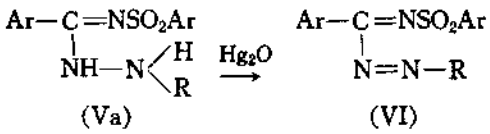
(I) (IV)

(Va)

(Vb)

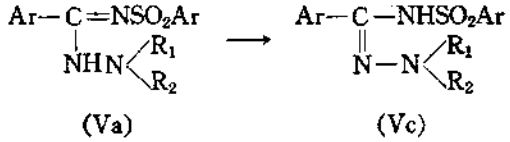
The ir specta of these compounds shows NH and C=N absorptions at 3,300 and 1,600cm^{-1} respectively. If the structure of the reaction products were the same as (Vb), it is expected that the products react with benzaldehyde to form hydrazine derivatives[2]. However, no further reaction was observed. Therefore the structure (Vb) whose carbon is attached to the α-nitrogen of hydrazine derivatives should be ruled out.

If the reaction products had the same structure as (Va), they would react with weak oxidizing agent such as Hg_2O [11] to form azo compounds (VI).

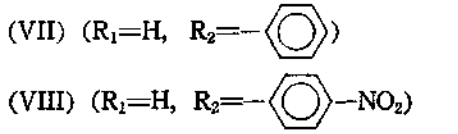


(Va) (VI)

However, the products were stable to Hg_2O. It seems that the reaction proceeds *via* intermediate (Va) to compounds (Vc, VII~XI).



(Va) (Vc)



(VII) (R_1=H, R_2=—C$_6$H$_5$)

(VIII) (R_1=H, R_2=—C$_6$H$_4$—NO_2)

(IX) (R_1=H, R_2=—C$_6$H$_3$(NO_2)$_2$)

(X) (R_1=CH_3, R_2=CH_3)

(XI) (R_1=H, R_2=—C$_6$H$_4$—CH_3)

One of the experimental results supporting this speculation is that the products are easily soluble in NaOH solution and returns to original states by adding acids. It means that acidic protons exist in the compounds. Therefore the structure (VII)~(XI) is more favorable than (Va).

Fig. 3 shows the nmr spectrum of β-(α-benzenesulfonamidobenzal)phenylhydrazine. The complex peaks at δ=6.8~8.0 ppm are due to protons on the benzene ring and -NH group.

Table 1 shows that the yields of these reactions were significantly improved by the electon attracting substituents in the phenylhydrazine(IV).

EXPERIMENTAL

Synthesis of N-Arylsulfonylbenzimidoyl Chloride (I). The mixture of 15.7 g (0.1 mole)

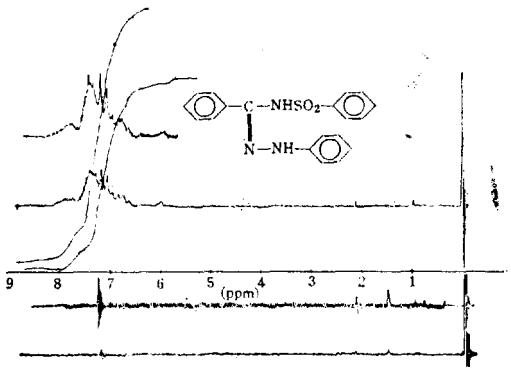


Fig. 3. nmr Spectrum of β-(α-benzenesulfonamidobenzal)-phenylhydrazine (VII)

Table 1. Physical and analytical data of β-(α-Benzenesulfonamidobenzal)hydrazine derivatives.

Number of Compounds	Hydrazine derivatives $Ar-C(=N-N<^{R_1}_{R_2})-NHSO_2Ar$	Melting Point (°C)	Elemental analysis		Yield (%)
			Calc. (%)	Found (%)	
II	$R_1=H$, $R_2=H$ ($C_{13}N_3SO_2H_{13}$)	108	C 41.38 H 6.40 N 20.69	40.27 6.75 21.48	21.4
III	$R_1, R_2 = C(CH_3)_2$ ($C_{16}N_3SO_2H_{17}$)	98	C 60.95 H 5.39 N 13.33	60.25 4.85 12.87	61.3
VII	$R_1=H$, $R_2=-C_6H_5$ ($C_{19}N_3SO_2H_{17}$)	136~138	C 64.95 H 4.84 N 11.96	64.80 5.11 11.16	68.1
VIII	$R_1=H$, $R_2=-C_6H_4-NO_2$ ($C_{19}N_4SO_4H_{16}$)	187~189	C 57.57 H 4.04 N 14.14	57.30 4.21 14.26	80.2
IX	$R_1=H$, $R_2=-C_6H_3(NO_2)_2$ ($C_{19}N_5SO_6H_{15}$)	196~198	C 51.70 H 3.41 N 15.82	49.80 3.61 15.45	84.8
X	$R_1=CH_3$, $R_2=CH_3$ ($C_{15}N_3SO_2H_{17}$)	82	C 59.41 H 5.61 N 13.86	58.74 5.46 13.27	59.8
XI	$R_1=H$, $R_2=-C_6H_4-CH_3$ ($C_{20}N_3SO_2H_{20}$)	157	C 65.57 H 5.46 N 11.47	64.67 4.98 12.36	53.9

of benzenesulfonamide and an equivalent amout of anhydrous aluminium chloride was dissolved in 400 m*l* of methylene chloride and cooled to 30~35 °C. To this solution 9.5 g (0.1 mole) of benzotrichloride was added dropwise. After standing overnight at room temperature, the reaction mixture was poured into ice cold hydrochloric acid solution. Recrystallization from ether gave (I) melting at 81°C (*lit.*[7] 81°C).

Synthesis of β-(α-Benzenesulfonamidobenzal)hydrazine (II). N-Arylsulfonylbenzimidoyl chloride (I) (5.0 g, 0.018 mole) was dissolved in 200 m*l* of ether. To this 4 m*l* of hydrazine (100 %) was added dropwise over a 30 min period. After standing overnight, the mixture was distilled. After removal of ether, precipitate was formed. The precipitate was washed with benzene. Recrystallization from methanol gave 0.98 g (20%) of white crystal (II) melting at 108 °C.

Synthesis of β-(α-Benzenesulfonamidobenzal)dimethylmethylenehydrazine (III). N-Arylsulfonylbenzimidoyl chloride (I) (5 g, 0.018 mole was dissolved in 50m*l* of acetone. To this 4 m*l* of hydrazine was added dropwise over a 30 min period. After standing 1 hour, product was separated on diluting with water. Recrytallization from methanol gave 3.46 g (61.3%) of white crystal (III) melting at 98 °C.

The Reaction between β-(α-Benzenesulfonamidobenzal)hydrazine (II) and Acetone. β-(α-Benzenesulfonamidobenzal)hydrazine (II) (1.2 g, 0.004 mole) was dissolved in acetone and reaction was allowed to continue for 1 hour at room temperature. On diluting with water, precipitate was formed. Recrystallization from methanol gave 1.0 g (80%) of white crystal melting at 98°C. The ir spectrum of this compound was identical with that of the compound (III).

Hydrolysis of β-(α-Benzenesulfonamidobenzal) dimethylmethylenehydrazine (III). Hydrazine derivative (III) (1.3 g, 0.004 mole) was suspended in 50 m*l* of water and the mixture was refluxed for 1 hour. After standing overnight, product was crystallized. Recrystallization from methanol gave 1.2 g (90 %) of β-(α-Benzenesulfonamidobenzal)hydrazine (II). The ir spectrum of this compound was identical with that of the compound (II).

Synthesis of β-(α-Benzenesulfonamidobenzal)phenylhydrazine (VII). Arylsulfonylbenzimioyl chloride (I) (5.0 g, 0.018 mole) was dissolved in acetone. To this 4 m*l* of phenylhydrazine was added dropwise over a 30 min period at 0 °C. After 1 hour of standing, product was separated on diluting with water. Recrystallization from methanol gave 4.28 g (68.1%) of (VII) melting at 136~138 °C.

Synthesis of β-(α-Benzenesulfonamidobenzal)dimethylhydrazine (X). N-Arylsulfonylbenzimidoyl chloride (I) (5.0 g, 0.018 mole) was dissolved in acetone. To this 4 m*l* of 1, 1-dimethylhydrazine was added dropwise over a 30 min period at 0 °C. After 1 hour of standing, oily substance was separated on diluting with water. After standing overnight it crystallized. Recrystallization from methanol gave 3.25 g (59.8 %) of white crystal (X) melting at 82 °C.

Oxidation of β-(α-Benzenesulfonamidobenzal)phenylhydrazine Derivatives (VII, VIII, IX, XI). Hydrazine derivative (0.5 g) was dissolved in 10 m*l* of ethanol. To this 1 g of mercurous oxide was added and refluxed for 1 hour. The mixture was cooled and filtered. On standing, perecipitate was formed from the solution. The precipitate was filtered and recrystallized from methanol. The ir spectra of the crystals were identical with those of derivatives (VII, VIII, IX, XI).

The Reaction between β-(α-Benzenesulfonamidobenzal)phenylhydrazine Derivatives (VII, VIII, IX, XI) and Benzaldehyde. Hydrazine derivatives (0.5 g) was dissolved in 10 m*l* of ethanol. To this 0.5 g of benzaldehyde was added and allowed to stand overnight. On standing, precipitate was formed from the solution. The precipitate was filtered and recrystallized from methanol. The ir spectra were identical with those of derivatives (VII, VIII, IX, XI).

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