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SYNTHESIS AND REACTION OF NEW TYPE I-N YLIDE,
N-TOSYLIMINOIODINANE

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(Diacetoxyiodo)arene reacts with p-toluenesulfonamide in the presence of base to give the new type I-N ylide, N-tosyliminoaryliodinane.$^{1)}$ In the decomposition of this ylide, the nitrene intermediate is proposed to be formed and react with nucleophiles to afford the imine compounds.

(Diacetoxyiodo)benzene has been used as an oxidizing reagent, exemplified in the reaction with primary aromatic amine to give the corresponding azo compounds.$^{2)}$ However, (diacetoxyiodo)benzene reacts with the compounds bearing active methylene group in the presence of base to give the iodonium ylide (1), which was investigated in detail by Neilands and his coworkers.$^{3)}$ Recently, Hayashi et al. reported that the iodonium ylide decomposed to give the product via carbene intermediate.$^{4)}$

$$C_6H_5I(OAc)_2 \quad + \quad CH_2{<}^{R}_{R'} \longrightarrow C_6H_5\overset{+}{I}-\overset{-}{C}{<}^{R}_{R'} \quad + \quad 2AcOH$$

(1)

For the iodonium ylide that is known, an isoelectronic iodine-nitrogen compound (iminoiodinane) has not yet been found.

We have found the formation of new type I-N ylide, N-tosyliminoaryliodinane (2), in the reaction of (diacetoxyiodo)arene with p-toluenesulfonamide.

$$ArI(OAc)_2 \quad + \quad p\text{-}CH_3C_6H_4SO_2NH_2 \longrightarrow ArI{=}NSO_2C_6H_4CH_3(p) \quad + \quad 2AcOH$$

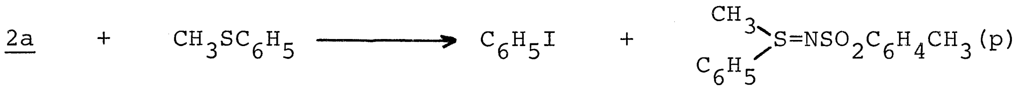
(2)

(Ar = C_6H_5-, p-$CH_3C_6H_4$-, p-ClC_6H_4-)

(Diacetoxyiodo)benzene (3.20 g, 10 mmol) was added to a stirred mixture of p-toluenesulfonamide (1.71 g, 10 mmol), potassium hydroxide (1.40 g, 25 mmol) and methanol (40 ml) below 10 °C. The resulting yellow colored homogeneous solution was stirred for three hours at room temperature. After the reaction, the reaction mixture was poured into water to precipitate a yellow colored solid on standing overnight, which was recrystallized from methanol to give N-tosyliminophenyliodinane (2a) in 69.7 % yield, mp 102-104 °C (dec.) : nmr (DMSO-d_6), δ 2.30 (s,3H,CH_3) and 7.00-7.80 ppm (m,9H,aromatic protons). In a similar manner, p-(diacetoxyiodo)-toluene and p-(diacetoxyiodo)chlorobenzene were allowed to react with p-toluenesulfonamide affording N-tosylimino-p-tolyliodinane (2b, mp 100-102 °C, yield 88.0 %) and N-tosylimino-p-chlorophenyliodinane$^{5)}$ (2c, mp 113-114 °C, yield 88.5 %), respectively. In the ir spectrum of 2a, the characteristic absorption appears at 1235 ($\nu_{as}SO_2$) and 1135 cm^{-1} ($\nu_{s}SO_2$), which are situated in the lower region than that of p-toluenesulfonamide ($\nu_{as}SO_2$: 1305; $\nu_{s}SO_2$: 1155 cm^{-1}). It indicates that the ylide form (2a') is present. This product is stable in the atmosphere.

$$\underset{(\ 2a\ )}{C_6H_5I{=}NSO_2C_6H_4CH_3(p)} \longleftrightarrow \underset{(\ 2a'\ )}{C_6H_5I^{+}{-}N^{-}SO_2C_6H_4CH_3(p)}$$

Compound 2a reacted with thioanisole at 100 °C to give iodobenzene and N-tosyliminomethylphenylsulfurane in 49.4 % yield.



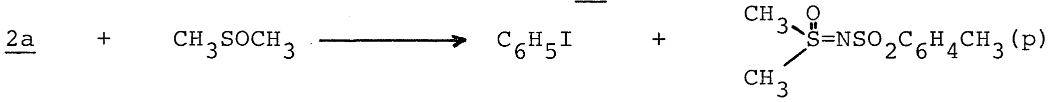
$$2a \quad + \quad CH_3SC_6H_5 \longrightarrow C_6H_5I \quad + \quad (CH_3)(C_6H_5)S{=}NSO_2C_6H_4CH_3(p)$$

In a simialr manner, 2a reacted with triphenylphosphine at 100 °C affording iodobenzene and N-tosyliminotriphenylphosphorane in 68.6 % yield.

$$2a \quad + \quad (C_6H_5)_3P \longrightarrow C_6H_5I \quad + \quad (C_6H_5)_3P{=}NSO_2C_6H_4CH_3(p)$$

These results indicate that the intermediate generated from 2a possesses the electrophilic character. The reaction is proposed to proceed via sulfonyl nitrene intermediate.

Compound 2a reacted with DMSO at room temperature to give iodobenzene and N-tosyliminodimethylsulfurane oxide quantitatively. As 2a does not decompose at room temperature, the reaction is not proposed to proceed via nitrene intermediate but via substitution reaction on the nitrogen of 2a.



$$2a \quad + \quad CH_3SOCH_3 \longrightarrow C_6H_5I \quad + \quad (CH_3)_2\overset{O}{\overset{\|}{S}}{=}NSO_2C_6H_4CH_3(p)$$

REFERENCES AND NOTES

1) This was named in an analogous manner to iminophosphorane and iminosulfurane.

2) K.H.Pausacker, J. Chem. Soc., 1989 (1953).

3) B.Karele and O.Neilands, Zh. Org. Khim., 4, 1818 (1968) and references cited therein.

4) Y.Hayashi, T.Okada, and M.Kawanishi, Bull. Chem. Soc. Japan, 43, 2505 (1970).

5) In this reaction sodium methylate was used as a base.

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