BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 2932—2934 (1972)

Reactions between Acyl Halides and Silver Hyponitrite

Masatsugu Sekiguchi, Michio Kobayashi, and Hiroshi Minato
Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Fukazawa, Setagaya, Tokyo

(Received March 31, 1972)

Organic esters of hyponitrous acid (HON=NOH) have not been studied extensively, the only examples reported being ethyl,[1] benzyl,[2] and *t*-butyl[3] esters. In connection with the generation of sulfonyloxy radicals, disulfonyl hyponitrites appear to be of interest as a possible source of sulfonyloxy radicals. The reaction between silver hyponitrite and *p*-toluenesulfonyl bromide and that between silver hyponitrite and benzoyl chloride have been investigated, and the results are given in this paper.

Results and Discussion

Since silver hyponitrite decomposes slowly upon irradiation of light, the reactions were carried out in its absence. Silver hyponitrite is hardly soluble in any organic solvent (including DMF, HMPA, and DMSO), and the reactions were carried out in heterogeneous media in the presence of excess hyponitrite.

When *p*-toluenesulfonyl bromide was let to react with silver hyponitrite in various solvents at room temperature or lower temperatures (0 to −30°C), di-*p*-toluenesulfonyl hyponitrite was not formed and nitrous oxide and nitrogen evolved. The results of the products analyses are given in Table 1.

---

[1] J. R. Partington and C. C. Shah, *J. Chem. Soc.*, **1932**, 2589.

[2] J. B. Sousa and S. K. Ho, *ibid.*, **1961**, 1788; *Nature*, **186**, 776 (1960); N. H. Ray, *J. Chem. Soc.*, **1960**, 4023.

[3] H. Kiefer and T. G. Traylor, *Tetrahedron Lett.*, **1966**, 6163; R. L. Huang, T. W. Lee, and S. H. Ong, *J. Chem. Soc., C*, **1969**, 40; R. C. Neuman and R. J. Bussey, *J. Amer. Chem. Soc.*, **92**, 2440 (1970).

Table 1. Products of reactions between *p*-toluenesulfonyl bromide (TsBr) and silver hyponitrite

Reactants (mmol)		Solvent	Time[a)] (hr)	Products (mol/mol TsBr Used)				Ts% Accounted For	(N_2+N_2O) mol/200 molTsBr
TsBr	$Ag_2N_2O_2$			TsOTs	TsOAg	N_2O	N_2		
2.00	5.0	$C_2H_4Cl_2$	3 (3)	0.391	trace	0.156	1.114	78.2	54
2.00	4.0	$C_2H_4Cl_2$	15 (3)	0.431	0.153	0.086	0.035	100	24
16.00	40.0	$C_2H_4Cl_2$	48 (48)	0.388	0.234	(b)	(b)	100	80[b)]
12.00	11.1	$C_2H_4Cl_2$	20 (20)	0.239	0.447	0.096	0.159	92.5	54
2.00	3.4	CH_2Cl_2	15 (3)	0.401	0.156	0.146	0.042	95.8	38
2.00	5.0	C_6H_6	15 (2)	0.350	0.135	0.125	9.004	83.5	26
2.00	2.5	CH_3CN	15 (0.5)	—	0.840	0.304	0.002	84.0	62

a) Products were analyzed after the time shown, except for gaseous products which were analyzed when the reaction appeared essentially complete; the time which elapsed before the analyses of gas is shown in parentheses.

b) The amount of total gas was determined with a gas buret.

No *p*-toluenesulfonic anhydride was found in acetonitrile. Silver *p*-toluenesulfonate is soluble in acetonitrile, but not in other solvents in which it covers the surface of silver hyponitrite hindering the reaction between silver hyponitrite and *p*-toluenesulfonic anhydride in solution. Silver *p*-toluenesulfonate does not behave thus in acetonitrile, and *p*-toluenesulfonic anhydride is smoothly converted into silver *p*-toluenesulfonate by the reaction with silver hyponitrite. By a separate experiment, it was confirmed that *p*-toluenesulfonic anhydride reacts with silver hyponitrite, forming silver *p*-toluenesulfonate.

Since the reaction took place between the solid salt and *p*-tosyl bromide in solution and the solubility of the salt differed with the solvent, the results of the reaction varied with solvent. In 1,2-dichloroethane, considerable amounts of nitrogen were evolved. This indicates that the following homolysis takes place to some extent in 1,2-dichloroethane.

$$\mathrm{AgON{=}NOAg + 2TsBr \xrightarrow{-2AgBr} TsON{=}NOTs \longrightarrow 2TsO\cdot + N_2} \qquad (1)$$

In order to obtain further evidence for the formation of *p*-tosyloxy radicals, the reaction was carried out in benzene, which is expected to be substituted by *p*-tosyloxy radical. However, it was found that in benzene almost all the gas evolved was not nitrogen but nitrous oxide, and thus the homolysis shown above must be a very minor reaction in benzene.

As for the reaction responsible for evolution of nitrous oxide, the following two processes are possible.

$$\mathrm{AgON{=}NOAg + 2TsBr \xrightarrow{-2AgBr} TsON{=}NOTs \longrightarrow TsOTs + N_2O} \qquad (2)$$

$$\mathrm{AgON{=}ONAg + TsBr \xrightarrow{-AgBr} TsON{=}NOAg \longrightarrow TsOAg + N_2O} \qquad (3)$$

Silver *p*-tosylate can be converted into *p*-toluenesulfonic anhydride, and *vice versa*, depending upon the reaction conditions; the reaction between silver *p*-tosylate and *p*-tosyl bromide yields *p*-toluenesulfonic anhydride, and that between *p*-toluenesulfonic anhydride and silver hyponitrite yields silver *p*-tosylate.

$$\begin{tikzcd}\mathrm{TsOAg + TsBr} \arrow[r, "-\mathrm{AgBr}"] & \mathrm{TsOTs} \arrow[l, bend left, "+\mathrm{AgON{=}NOAg}", "-\mathrm{N_2O}"']\end{tikzcd}$$

It was reported that a mixture of benzoyl halides and silver hyponitrite initiates polymerization of ethylene.[4] However, products and the mechanism of the reaction were not described. In order to ascertain whether or not free radicals are produced from these reactants, the reaction was studied in some detail. The results are given in Table 2.

The major component of the gas evolved was nitrous oxide. Thus homolysis (4) should be a minor reaction, Nitrous oxide was evolved either by reaction (5) or (6).

$$\mathrm{AgON{=}NOAg + 2BzCl \xrightarrow{-2AgCl} BzON{=}NOBz \longrightarrow 2BzO\cdot + N_2} \qquad (4)$$

$$\mathrm{AgON{=}NOAg + 2BzCl \xrightarrow{-2AgCl} BzON{=}NOBz \longrightarrow BzOBz + N_2O} \qquad (5)$$

$$\mathrm{AgON{=}NOAg + BzCl \xrightarrow{-AgCl} BzON{=}NOAg \longrightarrow BzOAg + N_2O} \qquad (6)$$

Chlorodiphenyls and nitrodiphenyls were formed in small yields from the reactions in chlorobenzene and nitrobenzene, respectively. In order to clarify the nature of this phenylation, the isomer distributions of the substituted diphenyls were studied by gas chromatography. The isomer distribution of chlorodiphenyls is *o*- 59.8, *m*- 23.3, and *p*- 16.9%; that of nitrodiphenyls is *o*- 53.5, *m*- 12.5, and *p*- 33.9%. They are similar to the isomer distributions found in free radical phenylation with benzoyl peroxide or *N*-nitrosoacetanilide. This also supports the idea that homolysis (4) takes place to a small extent.

In summary, the reactions between *p*-tosyl bromide and silver hyponitrite yield both nitrogen and nitrous oxide, the former probably being a product of the homolysis of di-*p*-tosyl hyponitrite formed as an intermediate, and the latter a product of ionic reactions.

---

[4] G. Scott and L. Seed, Brit. 839884 (1960); U. S. 2946776 (1960); A Mercer and D. A. Scott, Brit. 848492 (1960); *Chem. Abstr.*, **55**, 5346 (1961).

TABLE 2. PRODUCTS OF REACTIONS BETWEEN BENZOYL CHLORIDE AND SILVER HYPONITRITE

Reactants (mmol)		Solvent	Products (mol/mol BzCl Used)					Ph % Accounted For	(N_2+N_2O) mol/200 mol BzCl
BzCl	$Ag_2N_2O_2$		Bz_2O	BzOH	Substituted Diphenyls	N_2O	N_2		
4.00	4.00	PhCl	0.416	0.072	0.0088	0.290	0.02	91.3	61.0
4.00	4.00	$PhNO_2$	0.335	0.135	0.0085	(a)	(a)	95.4	59.6

a) not determined.

The reactions between benzoyl chloride and silver hyponitrite were essentially similar.

Experimental

Materials. Silver hyponitrite was prepared by the reduction of silver nitrate with sodium amalgam.[5] *p*-Toluenesulfonyl bromide was synthesized by the reaction of sodium *p*-toluenesulfinate and bromine.[6] Solvents were purified by conventional procedures.[7]

Reactions between Silver Hyponitrite and p-*Toluenesulfonyl Bromide.* In a helium atmosphere, well-dried powder of silver hyponitrite (1.380 g, 5 mmol) was slowly added for about 1 hr to a stirred solution of *p*-toluenesulfonyl bromide (0.470 g, 2 mmol) in 1,2-dichloroethane (6 m*l*) at room temperature. After stirring was continued for 3 hr, the gas evolved was collected in a sampling tube and subjected to gas-chromatographic analysis (a Shimadzu Gas Chromatograph GC3AH, helium 60 m*l*/min, 35°C, a 1 m silica gel column; retention time, O_2 and N_2, 0.30 min, N_2O, 4.2 min). The possibility of contamination of nitrogen from air was checked by observing the amount of oxygen in the gas (a 1 m molecular sieve 5A column, helium 120 m*l*/min, 35°C; retention time, O_2, 0.45 min, N_2, 0.55 min). The identity of nitrous oxide and nitrogen was further confirmed by use of a mass spectrometer. The mass spectrum of the gas evolved showed peaks at 44 (N_2O), 30 (NO), and 28 (N_2). By comparison with the mass spectra of pure N_2O (at 70 eV, N_2O 100, NO 25.6, N_2 11.0) and pure N_2, the presence and the amounts of N_2O and N_2 in the gas evolved were determined.

The reaction mixture was filtered, and the residue was washed with 1,2-dichloroethane. When the filtrate and washings were combined and evaporated under reduced pressure, white solids of *p*-toluenesulfonic anhydride (0.309 g) were obtained (IR, 1400, 1200, and 1180 cm^{-1}). The identity of *p*-toluenesulfonic anhydride was further checked by the reaction with aniline; from 100 mg of the anhydride, 67 mg of $PhNH_3^+OTs^-$ and 88 mg of PhNHTs were obtained. When a similar reaction mixture was allowed to stand overnight at room temperature, the amount of the anhydride decreased (0.281 g, 0.862 mmol) and a considerable amount of silver *p*-tosylate was found (0.085 g, 0.305 mmol). The amount of silver *p*-tosylate was determined by converting it into *S*-benzylisothiuronium *p*-tosylate by the reaction with *S*-benzylisothiourea hydrochloride.

Reactions in dichloromethane, benzene, and acetonitrile were carried out in a similar manner.

Reactions between Silver Hyponitrite and Benzoyl Chloride. In a helium atmosphere, well-dried powder of silver hyponitrite (1.104 g, 4.0 mmol) was slowly added for about 1 hr to a stirred solution of benzoyl chloride (0.560 g, 4.0 mmol) in chlorobenzene (11.26 g). After 3.5 hr, the gas collected was analyzed as described above.

The reaction mixture was filtered, the filtrate and washings were combined and extracted with a saturated $NaHCO_3$ solution. From the alkaline extracts, 35 mg (0.287 mmol) of benzoic acid was obtained. Benzoic anhydride contained in the organic layer was converted into PhCONHPh by the reaction with aniline; 0.337 g (1.71 mmol).

For determination of the amounts of chlorodiphenyls, a similar reaction mixture was prepared by a separate experiment, and concentrated. Benzoic anhydride was decomposed by refluxing with a 10% NaOH solution (10 m*l*) and ethanol (10 m*l*). The mixture was extracted with ether, the ethereal extracts were dried over anhydrous magnesium sulfate, and then concentrated. The amounts of *o*-, *m*-, and *p*-chlorodiphenyl in the residue were determined by gas chromatography (a Hitachi K-53 Gas Chromatograph, a 5 m Apiezon grease L column, 190°C; internal standard, dibenzyl).

Grateful acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

---

5) A. Hantzsch and L. Kaufmann, *Ann.*, **292**, 320, 323 (1896); G. Brauer, "Handbook of Preparative Inorganic Chemistry," Vol. 1, Academic Press Inc., New York (1963), p. 493; R. C. Newman and R. J. Bussey, Ref. 3.

6) F. C. Whitmore and F. H. Hamilton, "Organic Syntheses," Coll. Vol. I, p. 492 (1941).

7) W. Weissberger, "Organic Solvents," Interscience Publishers, Inc., New York (1955).