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REACTIONS OF 9-NITROANTHRACENE WITH THIOLS IN LIQUID AMMONIA

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Anthrylsulfides were obtained in high yields in the reactions of 9-nitroanthracene 1 with thiols. The reactions with thiolates resulted in the formation of aci-9,9'-dinitro-10,10'-dihydro-10,10'-bianthryl 2 via a 9-nitroanthracene anion radical.

We have shown in a previous paper1) that the reaction of 9-nitroanthracene 1 with sodium hydrogensulfide in liquid ammonia at a relatively high temperature such as 100°C gave ms-dianthryldisulfide 3, although the mechanism of this reaction has not been fully understood. In this paper, we wish to report the results of the reactions of 1 with sodium hydrogensulfide, thiols, and their thiolates at low temperatures in liquid ammonia.

The reaction of 1 with sodium hydrogensulfide in liquid ammonia in a titanium autoclave under nitrogen atmosphere gave a dimer 2,2) the disulfide 3, anthracene 4, and anthraquinone 5. The products were isolated by column chromatography on silica gel using benzene-hexane(1/1 volume ratio) as an eluent. The results of this reaction are shown in Table 1. Characteristic feature of the data in Table 1 are the following: (1) the dimer 2 is formed under relatively mild conditions, as illustrated in run 1-3, (2) at relatively high temperatures such as 80 and 100°C, the disulfide 3, anthracene 4, and anthraquinone 5 are obtained as the reaction products(run 4-6), (3) in the reaction in DMF, the dimer 2 is not obtained(run 7 and 8), and (4) the reaction of the dimer 2 with sodium hydrogensulfide(run 9) gives a similar result with that of 1 with sodium hydrogensulfide at 100°C(run 6).

Anthrylsulfides were obtained in high yields in the reactions with aliphatic thiols such as butanethiol, hexanethiol, and phenylmethanethiol, and in addition, small amounts of disulfides corresponding to those thiols were obtained in these reactions, while benzenethiol was found to react with 1, affording 9-anthrylphenylsulfide besides such products as the dimer 2, anthraquinone 5, 9,10-dithiophenoxyanthracene, and diphenyldisulfide. On the other hand, in the reactions with the thiolates, the dimer 2 and disulfides corresponding to those thiolates were obtained. Thus, the reactions with the thiols and the thiolates in liquid ammonia gave the different types of products. The results of the reactions of 1 with the thiols and the thiolates are shown in Table 2.

The dimer 2 was obtained only in the reaction with ionic nucleophiles, i.e., sodium hydrogensulfide and the thiolates, and with such nucleophiles as hydrogensulfide and benzenethiol which are easily dissociable in liquid ammonia. Ishitani and Nagakura3) showed that 1 is a good electron acceptor. Landolt and Snyder4) observed the formation of an anion radical of 1 in the reaction of 1 with sodium cyanide in DMF by ESR. Accordingly, it could be reasonably assumed that an ionic intermediate (C) was formed by dimerization of a 9-nitroanthracene anion radical (A). The dimer 2 decomposes gradually to 1 in atmosphere. As the transformation of the dimer 2 to 1 was confirmed by NMR in DMF-d_7 at 35°C, it was natural that the dimer 2 was not obtained in the

Table 1. Reactions of 9-nitroanthracene 1 with NaSH in liquid ammonia[a]

Run	Temp. (°C)	Time (hr)	NaSH (mmol)	Products(%)			
				2	3	4	5
1	40	3	5.0	85	trace	0	0
2	40	24	5.0	74	13	0	0
3	60	5	2.5	55	28	0	0
4	80	5	2.5	0	67	2	8
5	100	1	2.5	0	53	12	15
6	100	1	5.0	0	71	13	5
7[b]	60	3	5.0	0	75	11	0
8[b]	80	3	5.0	0	67	11	0
9[c]	100	1	5.0	0	63	14	5
10	40	5	5.0[d]	85	2	0	0

a) 9-Nitroanthracene 1 : 2.5 mmol, liq.NH_3 : 20 ml. b) DMF : 20 ml.
c) Dimer 2 : 2.5 mmol. d) H_2S : 5.0 mmol.

Table 2. Reactions of 9-nitroanthracene 1 with RSH and RSNa in liquid ammonia[a]

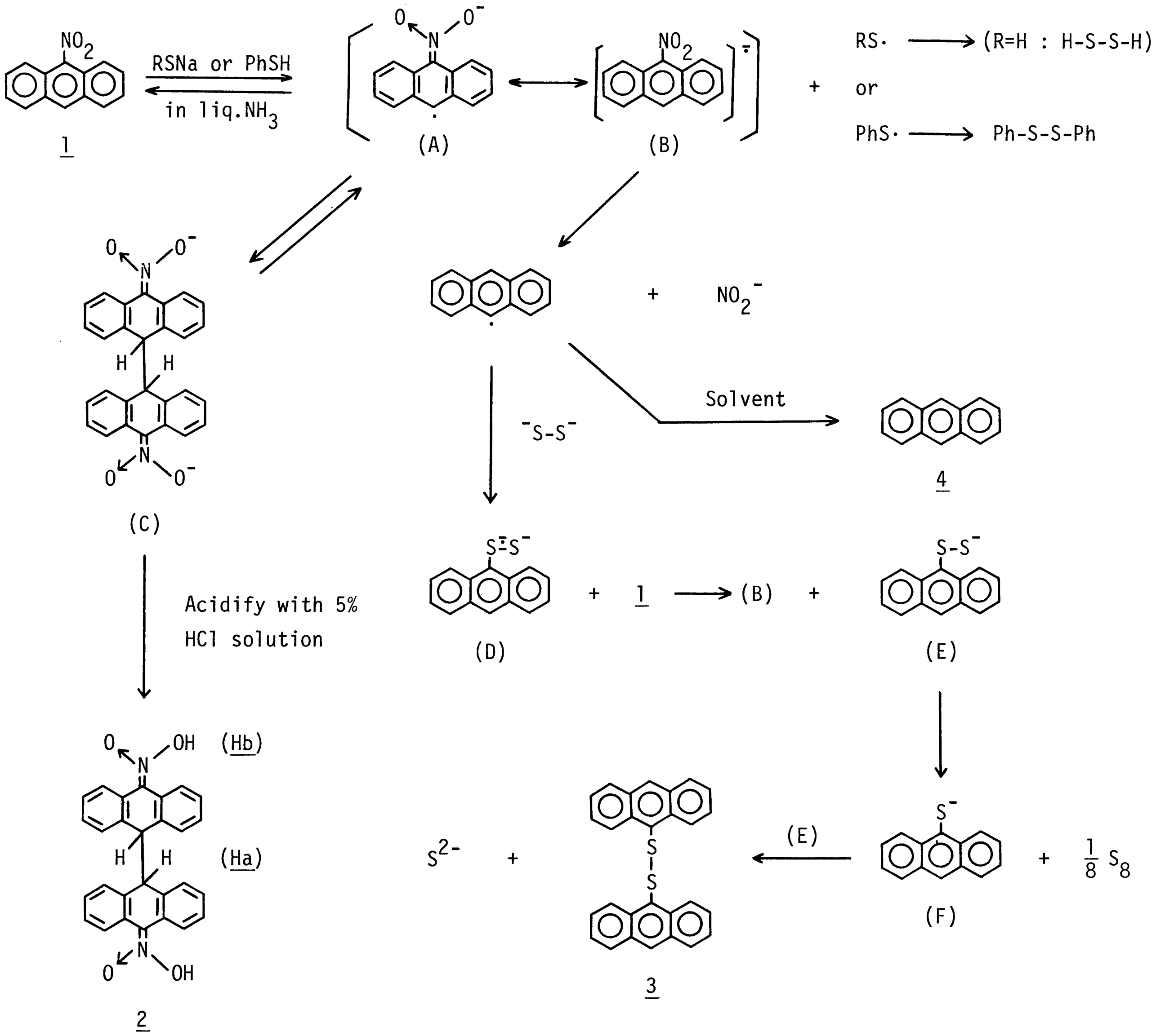
Run	Substituent R	Temp. (°C)	Time (hr)	pKa[b]	Products(%)		Mp (°C)	MS (m/e)
					2	Anthrylsulfide		
1	C_4H_9	60	5	11.5	0	94	oily matter	266(M^+)
2	C_6H_{13}	60	5	13.5	0	63	oily matter	294(M^+)
3	$PhCH_2$	40	5	11.8	0	86	100.5-101.0	300(M^+)
4	$PhCH_2$	60	5	11.8	0	91	100.5-101.0	300(M^+)
5[c]	Ph	60	5	7.5	10	24	101.0-101.5	286(M^+)
6	C_4H_9 (Na)	40	3		75	0		
7	C_6H_{13} (Na)	40	3		70	0		
8	$PhCH_2$ (Na)	40	3		71	0		

a) 9-Nitroanthracene 1 : 2.5 mmol, RSH : 2.5 mmol, RSNa : 5.0 mmol, liq.NH_3 : 20 ml.
The disulfides corresponding to the thiols and the thiolates were obtained in all runs.
b) The pKa value in H_2O. c) Other products : anthraquinone 5 (8%), diphenyldisulfide (58%), and 9,10-dithiophenoxyanthracene (2%, mp : 209-210°C, MS(m/e) : 394(M^+)).

reactions in DMF, as shown in run 7 and 8 of Table 1. Perhaps the ionic intermediate (C) was stabilized by the solvation in such dipolar protic solvents as liquid ammonia.

Meanwhile, if the reaction with sodium hydrogensulfide in liquid ammonia proceeds by the direct nucleophilic substitution of a nitro group of 1 by HS^-, 9-mercaptoanthracene should be obtained.[5] In this reaction, however, no 9-mercaptoanthracene was formed, but the disulfide 3 was obtained. Moreover, the dimer 2, which was formed via the 9-nitroanthracene anion radical (A), was obtained quantitatively by the reaction with sodium hydrogensulfide under such mild reaction condition as 40°C for 3 hours and the disulfide 3 was hardly formed under this reaction condition. Accordingly, it is reasonable that the disulfide 3 is formed via the one electron transfer reaction as shown in the following Scheme.[6]

Scheme



The initiation step is an electron transfer to 1 from an electron-donor species as sodium hydrogensulfdie in liquid ammonia, and the subsequent scission of the C-NO_2 bond in the 9-nitroanthracene anion radical (B) generates an anthracene radical and a nitrite ion. The anthracene radical then combines with $^-S-S^-$ to form a radical anion intermediate (D), which quickly transfers an electron to 1 to generate the intermediate (B) and a disulfanide (E). The disulfanide (E) eliminates an elemental sulfur to form anthracenethiolate (F), which reacts with the disulfanide (E) to give the disulfide 3.7) Meanwhile, the anthracene radical abstracts a hydrogen atom from the solvent to afford anthracene 4.

Since the disulfide 3, anthracene 4, and anthraquinone 5 are also formed by the reaction of the dimer 2 with sodium hydrogensulfide(run 9 of Table 1), it appears that the dimer 2 is in equilibrium with the 9-nitroanthracene anion radical.6) The reaction with sodium hydrogensulfide would involve a slow elimination of a nitrite ion from the 9-nitroanthracene anion radical (B), because the dimer 2 was only obtained at a low temperature, as illustrated in run 1 of Table 1. Moreover, the formations of the dimer 2 and a large amount of diphenyldisulfide in the reaction of 1 with benzenethiol in liquid ammonia would support the reaction Scheme.

On the other hand, in the reactions with the aliphatic thiols, the products suggesting one electron transfer reaction such as the dimer 2, anthracene 4, and anthraquinone 5 were hardly obtained, and the corresponding anthrylsulfides were obtained in high yields. Therefore, most of the formation of the anthrylsulfides in the reactions with such aliphatic thiols as butanethiol, hexanethiol, and phenylmethanethiol in liquid ammonia would be due to the direct nucleophilic substitution of the nitro group of 1 by the thiol groups. The low yield of 9-anthrylhexylsulfide in the reaction with hexanethiol may be ascribed to a steric hindrance between hexanethiol and the 1,8-hydrogen atoms in 1. Both one electron transfer and nucleophilic substitution reaction would occur in the reaction with benzenethiol. Since a relatively large amount of diphenydisulfide was formed via the one electron transfer reaction, 9-anthrylphenylsulfide was formed only in low yields (24%), as shown in run 5 of Table 2. In conclusion, it was found that the reactions of 1 with the thiolates involve the radical anion intermediates and the electron transfer steps in liquid ammonia, which can stabilize a solvated electron.8) Moreover, the results of the reactions with the thiols suggest a facile synthesis of the arylalkylsulfides by the reactions of the aromatic nitro compounds with alkanethiols in liquid ammonia.9)

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2) Aci-9,9'-dinitro-10,10'-dihydro-10,10'-bianthryl 2 : mp 135°C (dec.), Found : C 74.80, H 4.55, N 6.74% ; Calcd. for $C_{28}H_{20}N_2O_4$: C 74.99, H 4.49, N 6.25% ; IR (KBr) : 2710 (νOH), 1635 cm^{-1} (νC=N) ; NMR (DMF-d_7) : δ 3.80 (s, 2H, Ha), 7.35 (s, 2H, Hb).

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