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Phenalenones. III. The Anomalous Diazotization of 3-Substituted 2-Aminophenalenones

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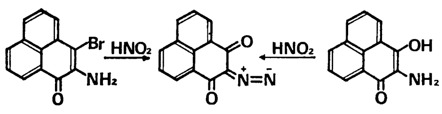
(Received July 9, 1980)

Synopsis. The diazotization of 3-substituted 2-amino-1*H*-phenalen-1-ones (substituents=Cl, Br, PhS, or OH) gave 2-diazo-1*H*-phenalene-1,3(2*H*)-dione. It is most probable that the reaction involves the intramolecular rearrangement of a transient diazohydroxide intermediate and the consequent elimination of the substituent at the 3-position.

When 2-amino-3-bromo-1*H*-phenalen-1-one (**1a**) was treated with nitrous acid in concentrated hydrochloric acid, 2-diazo-1*H*-phenalen-1,3(2*H*)-dione (**2**) was unexpectedly obtained. Although the diazo diketone **2** had previously been prepared by the diazotization of 2-amino-3-hydroxy-1*H*-phenalen-1-one (**1e**),[1] the reaction of **1a** seemed to be different from that of **1e**. A bromine atom at the 3-position of **1a** is replaced by a carbonyl oxygen, whereas a hydrogen atom of the hydroxyl group is apparently eliminated in the case of **1e**. However, the reaction of **1e** may be understood similarly, if the hydroxyl group is considered to be a leaving group.



1a **2** **1e**

Scheme 1.

In order to clarify this, the diazotization of several 3-substituted 2-amino-1*H*-phenalen-1-ones was investigated.

Results and Discussion

The treatment of the amine **1a** with nitrous acid gave no clear solution, and no nitrogen gas evolved on the addition of phosphinic acid to the reaction mixture. In accordance with these observations, the reaction product was not the 3-bromo-1*H*-phenalen-1-one expected for a usual reductive deamination, but, rather, was diazo diketone **2**. The yields of **2** were independent of the presence of phosphinic acid.

Similarly, other 3-substituted 2-amino-1*H*-phenalen-1-ones (**1b**—**1e**) afforded the corresponding diazo diketones in good yields (Table 1).

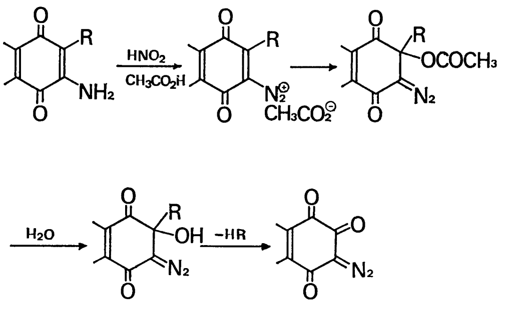
Table 1. Yields of **2a** and **2d**

	1		2	
	R^1	R^2	R^2	Yield/%
a	Br	H	H	96
b	Cl	H	H	62
c	SPh	H	H	44
d	Br	Br	Br	97
e	OH	H	H	74
f	H	H	H	0

Eistert *et al.*[1] carried out the diazotization of the 3-hydroxy derivative **1e** by using nitrosyl hydrogensulfate in a homogeneous solution. The present reactions proceeded sufficiently in a suspension of the amines in hydrochloric acid.

An exceptional case was the reaction of 2-amino-1*H*-phenalen-1-one (**1f**) (R^1=H), which gave an unworkable polymer (mp>330 °C, partly soluble in an aqueous sodium carbonate solution). The treatment of the diazotized solution with phosphinic acid led to a partial decomposition to give a small amount of phenalenone, although the main product was a complicatedly polymerized mass. The formation of phenalenone indicates that normal diazotization occurred in part.

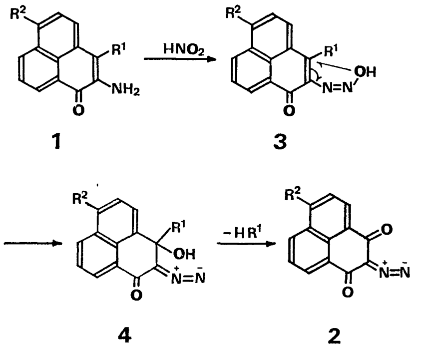
These reactions resemble those of 3-substituted 2-amino-1,4-naphthoquinones. Cajipe *et al.*[2] found that the diazotization of the amino quinones in acetic acid gave 3-diazo-1,2,4(3*H*)-naphthalenetrione. They postulated a reaction mechanism involving the nucleophilic attack of the acetate ion at the 3-position, followed by hydrolysis and the elimination of RH (R=Cl, CH_3O, N_3, and PhS), as is shown in Scheme 2.



Scheme 2.

However, the application of Cajipe's mechanism to the present reaction seems to be less probable, since we did not use acetic acid as a solvent, and even if the nucleophile is the hydroxide ion, the concentration of the hydroxide ion could be extremely low in concentrated hydrochloric acid.

For our reactions, the participation of the diazohydroxide intermediate **3** and a sequent intramolecular rearrangement seem probable, as is outlined in Scheme 3. The existence of a diazohydroxide compound as a transient intermediate has been widely accepted in the diazotization of primary amines.[3] The hydroxyl group of **3** migrates to the 3-position of the phenalene ring, then HR^1 is released to give the diazo diketone **2**. Consistently with the reaction sequences benzenethiol was obtained as another reaction product in the reaction of **1c**. On the same basis, it is understandable that the unsubstituted 2-amino-1*H*-phenalen-



Scheme 3.

1-one **1f** did not give **2**, since the hydroxyl group of the intermediate **3f** can migrate only with difficulty because of the less positive nature of the carbon atom at the 3-position. In addition, even if migration occurs, the intermediate **4f** can not be converted to **2** unless dehydrogenation takes place. There is no possibility of dehydrogenation under the present reaction conditions.

The authers are grateful to Mr. Toshikatsu Sekine and Mr. Minoru Matsuzawa for their technical support.

Experimental

All the melting points are uncorrected. The IR spectra were taken on a JASCO IRA-1 spectrophotometer, while the UV spectrum was recorded on a Hitachi EPS-3T spectrophotometer. The NMR spectra were recorded with a JEOL JNM-PS-100 spectrometer (100 MHz), with TMS as the internal standard. The mass spectra were obtained at 70 eV using a Hitachi RMU-7M spectrometer.

*2-Amino-3-bromo-1*H*-phenalen-1-one (**1a**)* (mp 187—188.5 °C) and *2-amino-3,6-dibromo-1*H*-phenalen-1-one (**1d**)* (mp 213—215 °C) were prepared by the methods described in a previous paper.[4)]

*2-Amino-3-chloro-1*H*-phenalen-1-one (**1b**).* Into 30 ml of a vigorously stirred solution of 2-amino-1*H*-phenalen-1-one[4)] (0.50 g) in chlorobenzene we added, portion by portion, a chlorine solution in carbon tetrachloride containing 0.20 g of chlorine at 50 °C. After 30 min, a yellow precipitate was collected and washed with carbon tetrachloride. The free base was obtained by the treatment of the solid salt with a sodium carbonate aqueous solution. Red crystals of mp 214 °C (methanol) was obtained in a 36% yield. IR (KBr) 3467, 3347 (N-H) and 1622 cm^{-1} (C=O); NMR (DMSO-d_6) δ=7.95—7.52 (4H, m), 8.32 (1H, d, J=8 Hz), 8.46 (1H, d, J=8 Hz). Found: C, 67.76; H, 3.49; N, 6.12; Cl, 15.82%. Calcd for $C_{13}H_8ONCl$: C, 67.98; H, 3.51; N, 6.10; Cl, 15.44%.

*2-Amino-3-(phenylthio)-1*H*-phenalen-1-one (**1c**).* The solution of 2-amino-3-bromo-1*H*-phenalen-1-one (1.37 g) in 80 ml of an ethanol–dioxane mixture (2:1) was added by an ethanolic solution of sodium benzenethiolate which had been prepared from 1.10 g of benzenethiol and sodium methoxide; the mixture was then refluxed for 4 h. After the removal of a small amount of dark powder by filtration, the solution was concentrated to give 0.96 g of reddish brown crystals (63%); mp 147.5—149 °C. MS *m/e* 303 (M$^+$); IR (KBr) 3470, 3360 (N-H), and 1635 cm^{-1} (C=O); NMR (DMSO-d_6) δ=7.07—7.14 (5H, m), 7.48 (1H, t, J=7 Hz), 7.77 (1H, t, J=6 Hz), 7.82 (1H, d, J=6 Hz), 7.98 (1H, d, J=6 Hz), 8.32 (1H, d, J=7 Hz), and 8.51 (1H, d, J=7 Hz).

Found: C, 75.68; H, 4.31; N, 4.54; S, 10.32%. Calcd for $C_{19}H_{13}ONS$: C, 75.22; H, 4.32; N, 4.62; S, 10.57%.

*2-Diazo-1*H*-phenalene-1,3(2*H*)-dione (**2**).* Finely ground 2-amino-3-bromo-1*H*-phenalen-1-one (2.00 g) was added, portion by portion, to 20 ml of concentrated hydrochloric acid, after which we added 2.00 g of sodium nitrite dissolved in minimum volume of water; the mixture was then stirred at 5 °C for 1 h and allowed stand overnight. A yellow-brown solid was collected and washed with dilute aqueous ammonia and then with water. Recrystallization from benzene gave 1.05 g (65%) of **2** as pale yellow crystals of mp 197—199 °C dec. (lit,[1)] mp 191—195 °C). MS *m/e* 222.0434 (M$^+$, Δ=0.5 m mass unit), 194.0041 (M$^+$−28, −N$_2$), and 166.0418 (M$^+$−56, -CO) IR (KBr) 2230, 2160 (N$_2$), and 1635 cm^{-1} (C=O); NMR (CDCl$_3$) δ=7.66 (2H, t, J=7 Hz), 8.12 (2H, d, J=7 Hz), 8.48 (2H, d, J=7 Hz); UV ($\lambda_{\max}^{\mathrm{EtOH}}$, nm, log ε) 235.5 (4.82), 298 (4.08), and 338 (4.05). Found: C, 69.91 H, 2.55; N, 12.11%. Calcd for $C_{13}H_6O_2N_2$: C, 70.27; H, 2.72; N, 12.61%.

Similar reactions on **1b**, **1c**, and **1e** afforded **2**, as is shown in Table 1. The addition of the diazotized reaction mixture to phosphinic acid did not affect the yields of diazo diketone.

In a run of the reactions on **1c**, benzenethiol was obtained besides **2**. The reaction mixture was filtered and washed with diethyl ether. The filtrate and washings were combined, and the solution was extracted with diethyl ether. The subsequent removal of the solvent left an oil, which was determined to be benzenethiol by a comparison of its IR and GLC with those of an authentic specimen (15% crude yield).

*6-Bromo-2-diazo-1*H*-phenalene-1,3(2*H*)-dione (**2d**).* Orange yellow crystals (benzene); mp 194—195.5 °C dec; MS *m/e* 302 (M$^+$); IR (KBr) 2230, 2150 (N$_2$), and 1644 cm^{-1} (C=O); NMR (pyridine-d_5) δ=7.81 (1H, t, J=9 Hz), 8.07 (1H, d, J=9 Hz), 8.39 (1H, d, J=9 Hz), 8.50 (1H, d, J=8 Hz), and 8.56 (1H, d, J=8 Hz). Found: C, 51.53; H, 1.67; N, 9.01; Br, 25.95%. Calcd for $C_{13}H_5O_2N_2Br$: C, 51.85; H, 1.67; N, 9.31; Br, 26.54%.

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