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THE PREPARATION OF SOME 1,2,4-TRIAMINOANTHRAQUINONES BY THE SMILES REARRANGEMENT OF 2-ALKOXY-1,4-DIAMINOANTHRAQUINONES

M.S.Simon and J.F.Downey, Jr.
Polaroid Corporation, Cambridge, Massachusetts 02139

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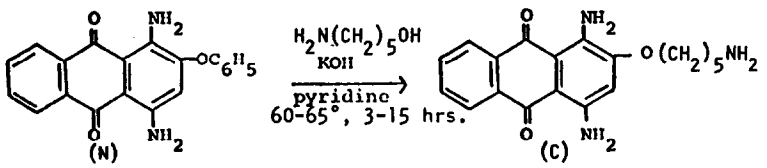
1,4-Diamino-2-alkoxyanthraquinones are formed by the treatment of 1,4-diamino-2-phenoxyanthraquinone (N) with alkoxide ions ([1]). We have made a series of aminoalkoxy derivatives (A-H in Table) by this route. The twin absorption peaks which are characteristic of the



1,4-diaminoanthraquinone system are shifted from 540 and 580 nm to 536 and 574 nm, a change which is readily apparent, since the human eye is very sensitive to this region of the spectrum.

Reacting β-methylaminoethanol with (N) gave an unexpected product, absorbing at 550 and 591 nm, which proved to be 1,4-diamino-2-(N-methyl-β-hydroxyethylamino)anthraquinone (J). This result is noteworthy for two reasons. Under the reaction conditions (N) is wholly unreactive to secondary amines, even with prolonged treatment at higher temperatures. Furthermore, the 1,2,4-triaminoanthraquinones are almost unknown (2).

Reaction or β-methylaminoethanol with (N) at lower temperatures (40-45°) showed that the 2-alkoxy product was formed initially, and could be isolated,(H), but rearranged rapidly to (J) when the reaction was continued.

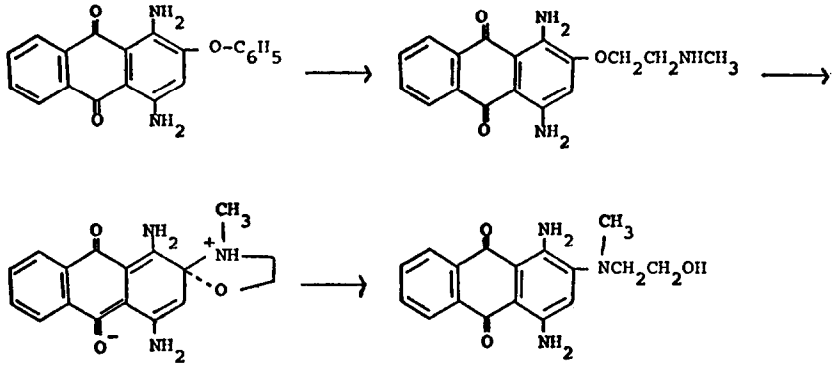
We interpret these results as being due to a Smiles rearrangement (3,4,5) of the 1,4-diamino-2-β-alkylaminoethoxyanthraquinone. The 2-position is activated by the suitably located carbonyl group of the anthraquinone system. Such activation had previously been observed by Smiles (6). Under the basic conditions of the reaction the alkoxide is the better leaving

TABLE

Compound	Name	m.p.	λmax	ε	λmax	ε	sho.	ε	Solvent
A	1,4-diamino-2-β-aminoethoxyanthraquinone	214-5.5°	537		576		504		MC
B	1,4-diamino-2-γ-aminopropoxyanthraquinone	213-4°	537	16,000	575	17,000	505	8,600	iPROH
C	1,4-diamino-2-ε-aminopentoxyanthraquinone[7]	213-5°	536	15,600	574	16,000	503	8,700	MC
D	1,4-diamino-2-θ-aminooctyloxyanthraquinone[7,8]	145-8°	534	13,400	573	14,300	500	7,500	EtOH
E	1,4-diamino-2-β-aminobutoxyanthraquinone	241-2°	535		575		505		MC
F	1,4-diamino-2-β-tert.butylaminoethoxy-anthraquinone[7]	211-2°	536	15,400	575	16,700	506	8,300	iPROH
G	1,4-diamino-2-β-anilinoethoxyanthraquinone[7]	228-30°	537	15,300	577	16,200	505	8,460	MC
H	1,4-diamino-2-β-methylaminoethoxyanthraquinone[7]	180-2°	538	14,900	577	15,600	505	8,000	MC
J	1,4-diamino-2-(N-methyl-β-hydroxyethylamino)-anthraquinone[7]	213-4°	550	16,800	591	18,600	514	8,600	MC
K	1-amino-2-(N-methyl-β-acetoxyethylamino)-4-acetamidoanthraquinone[7]	157-7.5°	536		500(sho.)		568(sho.)		MC
L	1-amino-2-(N-methyl-β-acetamidoethoxy)-4-acetamidoanthraquinone[7]	231-2.5°	520	13,600	485(sho)	9,300	550(sho)	10,900	MC
M	1,4-diamino-2-bis(β-hydroxyethyl)amino-anthraquinone[7]	192.5-4°	554	17,400	596	19,800	524	9,400	iPROH
N	1,4-diamino-2-phenoxyanthraquinone[7]	190-3°	542	11,000	581	10,600	510	6,600	MC

MC= 2-methoxyethanol iPROH= isopropanol EtOH= ethanol

group in the charged intermediate shown below, leading to the rearranged product.



We obtained rearranged products with β-ethylaminoethanol, diethanolamine, di-β-hydroxypropylamine as well, but not with β-aminoethanol, β-aminobutanol, nor β-anilinoethanol. We conclude that these amines are not sufficiently nucleophilic to eliminate the alkoxy substituent. On the other hand, the failure of β-tert.butylaminoethanol to give a rearranged product is probably a case of steric hindrance to the formation of the charged intermediate.

References and Notes

1) P.Nawiasky, B.Stein, A.Krause, U.S.Patent 1,943,876 (January 16, 1934).
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7) Compound has been characterized by elemental analyses, NMR, IR and UV-visible region spectra.
8) Compound prepared by J.N.Pentikis.