Synthesis and Infrared Studies of Some Anils

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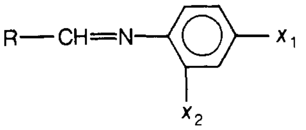
A series of new anils derived from 9-anthracene glyoxal hydrate and primary aromatic amines is prepared. Their corresponding derivatives such as 2,4-dinitrophenyl hydrazones, semicarbazones, and oximes are also discussed. Various important functional groups and linkages are ascertained by ir spectral studies.

Several Schiff bases derived from glyoxal and aromatic amines have not been fully investigated. Although a few references are available on these anils, the only anil worthy of mention is the *p*-dimethyl amino anil of phenyl glyoxal which was condensed by Krohnke and Gross (*2*) to evaluate the bathochromic effect in the compounds in the presence of silica gel and Lewis acids.

Recently, anils derived from phenyl glyoxal hydrate, methyl glyoxal, β-naphthyl glyoxal hydrate, and primary aromatic amines have been reported by many workers (*1, 4, 5, 6, 9, 11*).

The present communication describes the synthesis of new anils derived from 9-anthracene glyoxal hydrate and primary aromatic amines with the general formula:



where R = $C_{15}H_{19}O$; x_1 = Cl, CH_3, NO_2, OCH_3, $N(CH_3)_2{}^{3-}$ and x_2 = H, CH_3, NO_2, Cl, OCH_3. The method recommended by many authors for preparation was employed. But in the case of the *p*-dimethyl amino anil of 9-anthracene glyoxal hydrate, a different method was adopted (*3*).

All these Schiff bases were characterized by the formation of derivatives such as 2,4-dinitrophenyl hydrazones, semicarbazones, oximes, and also by chemical analysis. Ir spectral studies (*7, 10*) were successful in ascertaining the various functional groups and linkages.

Experimental

Chemicals of high purity and Analar grade were used throughout. Infrared spectra of these anils (or Schiff bases) were recorded on a Perkin-Elmer infrared Model-137 in KBr pellets, whereas the spectra in the far infrared region (16–40 μ) were recorded on a Beckman IR SA spectrophotometer fitted with CsBr prism using nujol mull as solvent.

Elemental analyses (particularly nitrogen) in agreement

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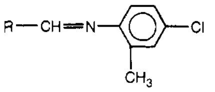
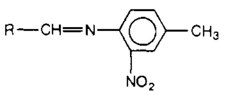
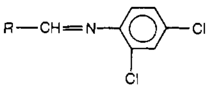
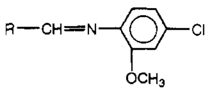
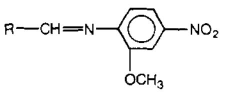
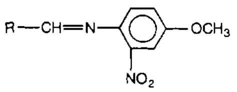
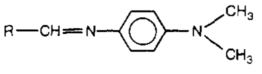
Table I. Characteristic Melting Points of Anils and Their Derivatives

SN	Anils: Formula^a	Anils: Mp, °C	Corresponding derivatives: 2,4-Dinitrophenyl hydrazone, mp, °C	Corresponding derivatives: Semicarbazone, mp, °C	Corresponding derivatives: Oxime, mp, °C
1		120	280	185	195
2		115	240	175	180
3		117	165	215	144
4		125	175	190	155
5		180	200	165	150
6		150	212	195	180
7		227	208	217	158

^{a} Where R = $C_{15}H_{19}O$.

with theoretical values for all the anils and their characteristic derivatives were obtained and submitted for review.

Preparation of p-dimethyl amino anil of 9-anthracene glyoxal and other anils of this series. Into a 500-ml round-bottom flask, 2.12 grams of 9-acetyl anthracene was placed, and 5.0 ml of glacial acetic acid, 1.1 gram of selenium dioxide (*8*), and 1–2 ml of water were added. The mixture was heated to reflux for nearly 2 hr. After refluxing it was poured in 500 ml of boiling water, warmed for 10–15 min, then cooled, and filtered. Yellowish red-colored crystals of 9-anthracene glyoxal thus obtained were condensed with *p*-dimethyl amino aniline (*12*) in an alcoholic medium in equimolar quantities. After mixing, it was stirred with a glass rod. A few drops of water were added. The mixture was allowed to stand for an hour and filtered. Crystals of *p*-dimethyl amino anil of 9-anthracene glyoxal thus obtained were recrystallized with ethyl methyl ketone, mp 224° ± 2°C.

The other anils listed in Table I were prepared by refluxing in a water bath with equimolar quantities of 9-anthracene glyoxal hydrate and the corresponding amine in ethanol.

Preparation of derivatives. The corresponding derivatives such as 2,4-dinitrophenyl hydrazones, semicarbazones, and oximes were prepared by the usual methods (*12*). All these derivatives were crystallized from hot ethanol. The characteristic melting points of these derivatives are recorded in Table I.

Infrared Studies

A very strong band around 1700 cm^{-1} characteristic of a keto group was found in the spectra of all of the prepared anils. Further, inductive, mesomeric steric effects and conjugation of the keto group with respect to the anthracyl skeleton lowers this frequency, which is frequently noted (*7*).

The presence of C—Cl, $C—CH_3$, $O—CH_3$, $O—NO_2$ groups in different compounds was confirmed by the presence of stretching frequencies (*7*). There is also a sharp peak around 1600 cm^{-1} in the spectra of all of the prepared compounds which shows the presence of the azomethine group —CH═N. A doublet around 830 cm^{-1} (*10*) represents a para distribution. The stretching frequencies of —C═C— in anthracene are obtained in the range 1625 cm^{-1}, respectively, and are also found in the spectra of the prepared anils, thus revealing the presence of the anthracene nucleus.

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