

ISOLATION AND CHARACTERIZATION OF A SUBSTITUTED BENZPYRIDONE FROM
DARIUS CRUDE

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Abstract - Heavy ends of petroleum are becoming important contributors to future petroleum requirements. A knowledge of the composition of these materials is, therefore, necessary for their efficient processing and use. Isolation and characterisation of a substituted benzpyridone from 300-470°C fraction of Darius crude is presented.

INTRODUCTION

The nitrogen and oxygen compounds, besides those of sulphur, are among the important non-hydrocarbon constituents of petroleum. Because of their reactivity they act as sensitive indicators of the physico-chemical environment of petroleum during its long storage underground. Their importance to the petroleum technologists lies in the deleterious effects e.g. poisoning of the refining catalysts and the formation of deposits in the finished products. These compounds get mainly concentrated in the higher boiling fractions of petroleum which represent a fairly large portion of the original crude. With proper selection of techniques these heavy ends of petroleum could be transformed into more useful products, thus becoming important contributors for future petroleum requirements. Good knowledge of distribution of major structural and functional groups in the heavy ends of petroleum is, therefore, necessary for developing the basic compositional data needed for efficient processing and use of these materials. By 1967, application of the classical techniques had resulted in the isolation and identification of a large number of individual nitrogen and oxygen compounds¹⁻⁷ from the lower boiling fractions. Attempts to understand the nature of these compounds in the higher boiling fractions have however been limited.

During our work on sulphur compounds from the high boiling (300-470°C) fraction of Darius crude, it has been possible to isolate an N-alkyl benzpyridone; present paper deals with the structure elucidation of this compound.

ISOLATION

Darius crude fraction (300-470°C, S:2.6%) was subjected to elution chromatography on silica gel (Fig.1). Benzene eluted a material (S:9.66%), which was adsorbed on a column of alumina. Elution of the column with hexane-benzene (1:1) was carried out till six well defined coloured zones were developed. One of the zones afforded a product with 16.92% of sulphur.

Inverse dry-column chromatography of this residue on silica gel with diisopropyl ether - isooctane (1:19) and ethyl acetate - isooctane - pyridine (50:50:3) resulted in the recovery of fractions B₁-B₁₄ and B₁₅-B₁₉ respectively. Elution of the latter fractions from the column of silica gel with diisopropyl ether, methanol and chloroform yielded fractions D₁₆-D₂₀ with the first solvent. These fractions were further subjected to elution chromatography on silica gel. Elution with heptane containing various proportions of diisopropyl ether and mixing of fractions similar in behaviour on TLC, led to the isolation of two series of compounds, one series with blue fluorescence and the other yellow fluorescence under UV light. The compound discussed in the present paper was among the latter series.

STRUCTURE ELUCIDATION

The UV spectrum of the compound in cyclohexane showed $\lambda_{\max}$ at 212, 222 and 286 nm. The presence of a primary amino group in the molecule was suggested by the bands at 3374 and 3299 cm^{-1} in its IR spectrum. The broadness of the band could be due to the association of the amino group. The IR spectrum also showed 2963 to 2862 cm^{-1} bands of the alkyl group vibration, a medium to strong band at 1724 cm^{-1} of the carbonyl of cyclic lactam and the bands between 1628-1600 cm^{-1} and two weak bands at 1600 and 1580 cm^{-1} of aromatic nucleus. That the aromatic ring was ortho-disubstituted was suggested by the weak bands between 1200-1170 cm^{-1} . A medium band between 1260 and 1270 cm^{-1} was attributed to C-N stretching vibration of an aromatic tertiary amine⁸⁻¹².

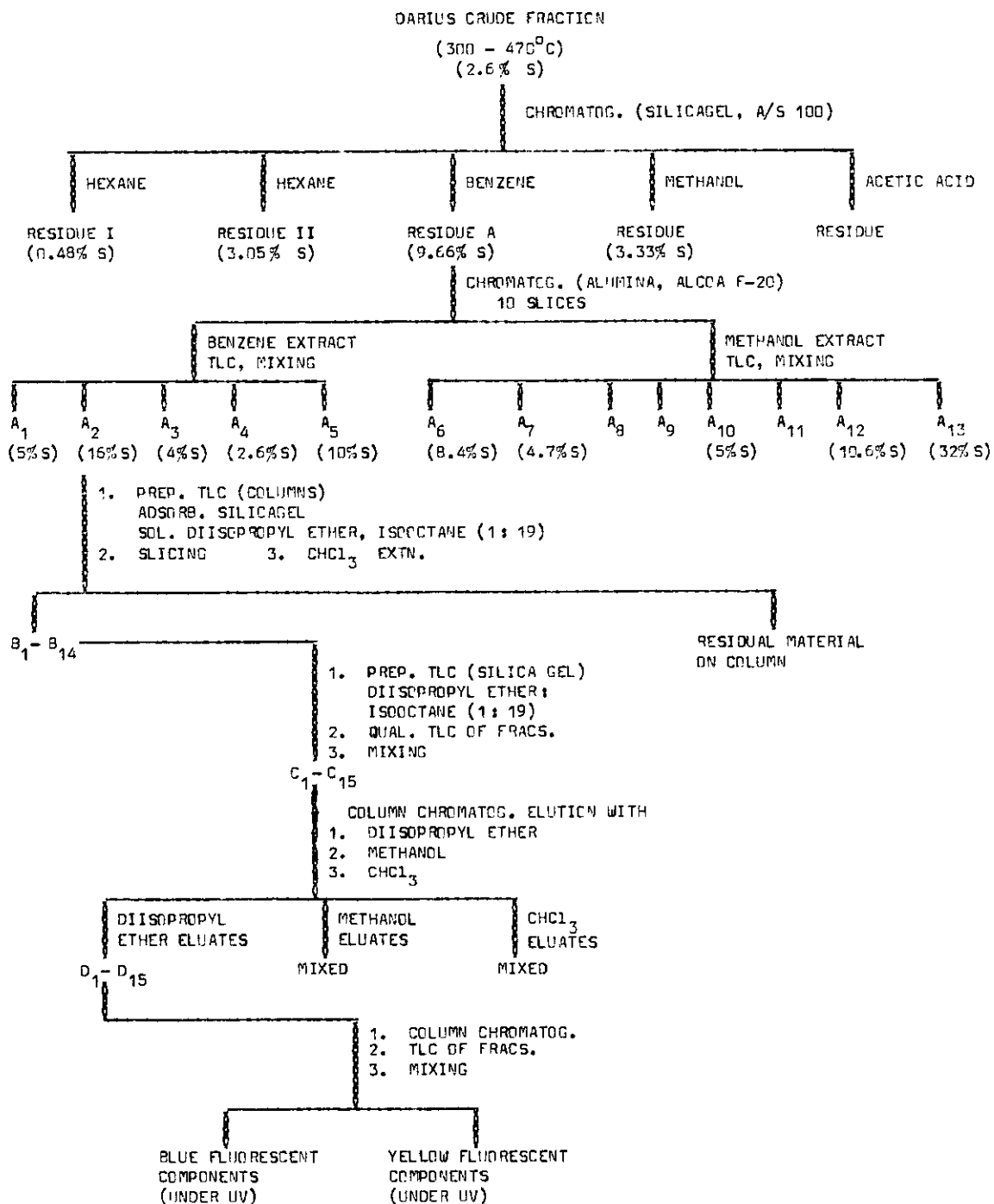
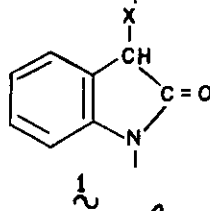


FIG - 1

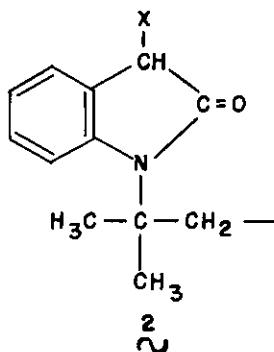
The NMR spectrum (Fig.2) of the compound showed (i) an ill-resolved multiplet centered at 7.64δ , integrating for four aromatic protons, (ii) a multiplet centered at 4.20δ , integrating for one-CH proton between aromatic and an electronegative group, (iii) a multiplet centered at 1.74δ , integrating for eight protons β - to nitrogen and (iv) two multiplets between $1.10 - 1.48\delta$ and $0.90 - 1.10\delta$, integrating for 22 and 15 protons, respectively of $-\text{CH}_2$ and $-\text{CH}_3$ groups.
10,11,13,14

The UV, IR and NMR spectra of the compound suggested that the molecule had an ortho-disubstituted aromatic ring, a methine proton CH-E, a five membered lactam ring either fused to the aromatic ring or in the side chain.

The above information could be best explained by the partial formula (1) :



The NMR spectrum showed either protons β - to nitrogen suggesting that the nitrogen of the lactam ring carried a $-\text{C}(\text{CH}_3)_2\text{CH}_2-$ group. Hence, the partial structure (1) could be modified as (2):



The mass spectrum (Fig.3) of the compound showed parent and base ion peaks at m/e 442 and 149 respectively. The even mass number of the parent ion peak suggested that the molecule contained two nitrogen atoms. From the groups shown by IR and the number of protons in the NMR, the molecular formula assigned to the compound for a mass of 442 was $\text{C}_{29}\text{H}_{50}\text{N}_2\text{O}$; the number of unsaturations being six.

As all these unsaturations were accounted for in structure (2), it could be concluded that the side chain was saturated. The amino group could either be on the ring system or in the side chain. The base peak at m/e 149 in the mass

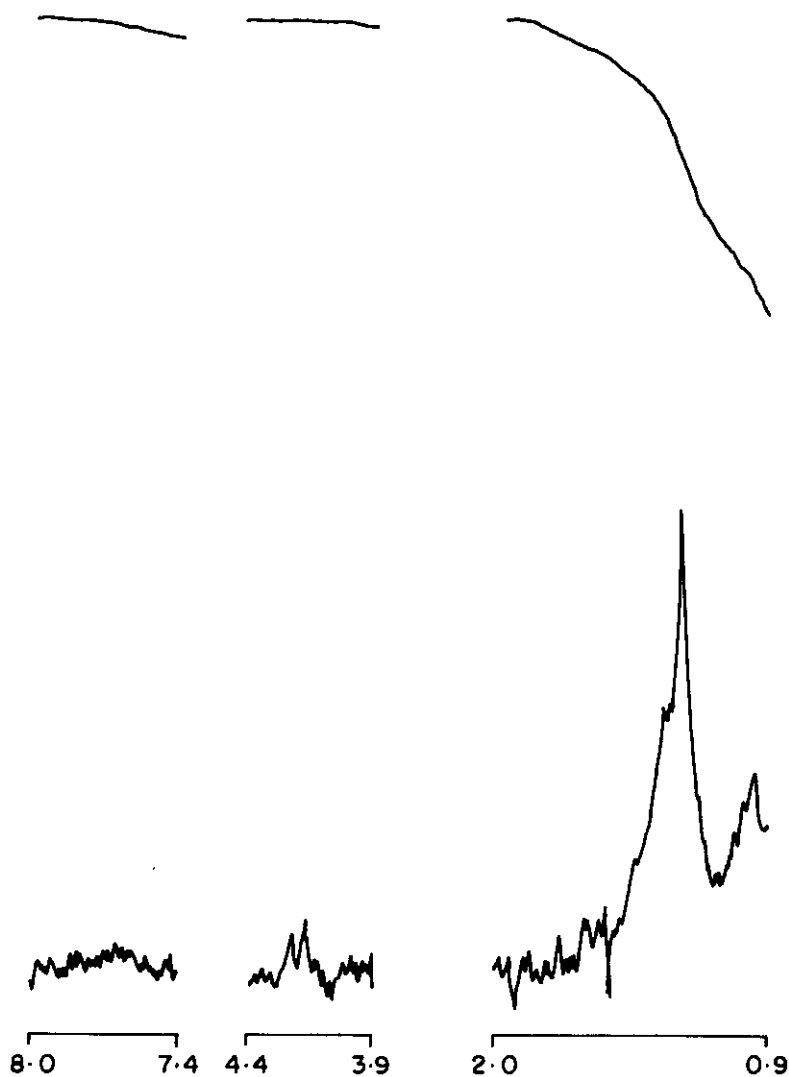


FIG. - 2 : NMR SPECTRUM (IN CCl_4)

MASS SPECTRUM
OF THE COMPOUND

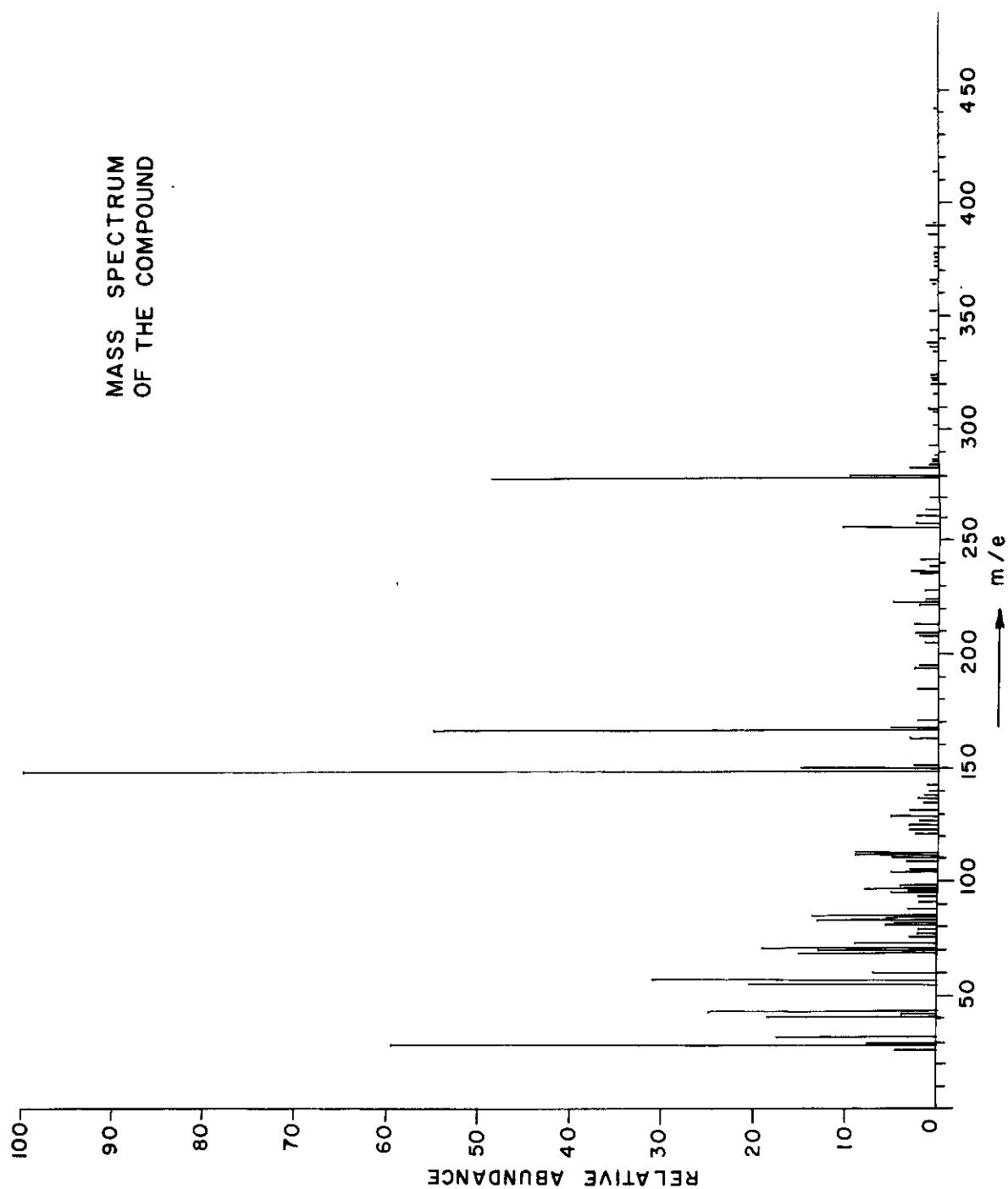
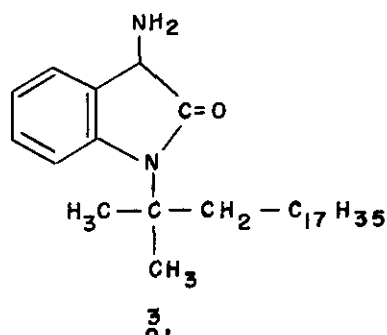


FIG. - 3

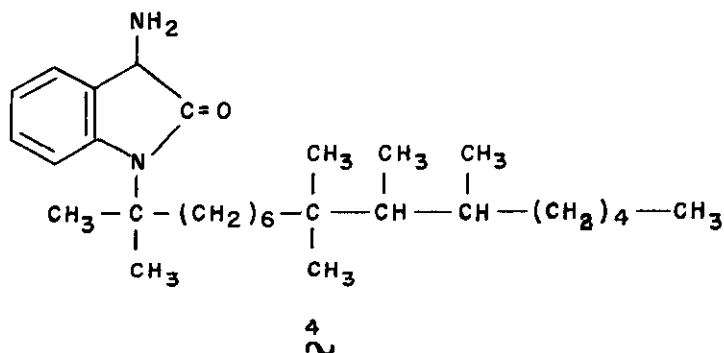
spectrum could best be explained by keeping the amino group on the ring system.

Therefore, structure for the compound could be written as (3):



The major peaks, other than the base peak at m/e 149 were at m/e 163, 167 and 279. These are explained in Charts 1 and 3. The various other peaks in the mass spectrum and the position of methyl groups in the side chain are explained in Charts 2 and 3.

Hence the final structure assigned to the component on the basis of above data was (4):

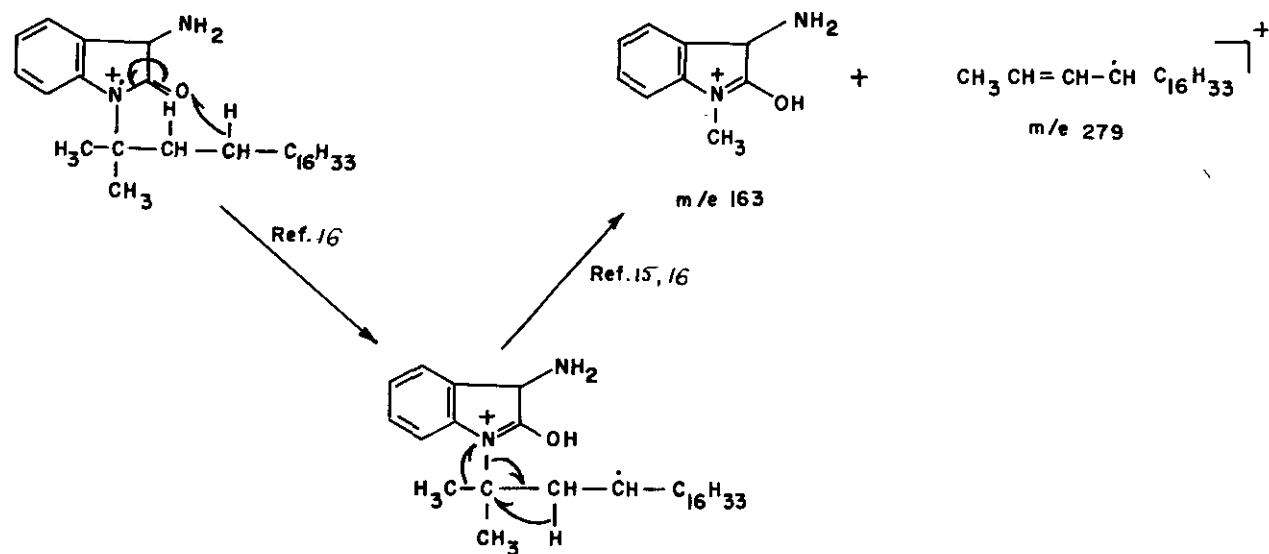
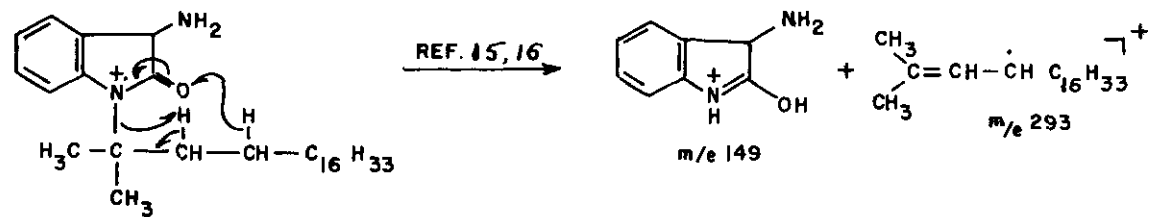


The benzpyridone type structure for the molecule is supported by the work of Snyder⁷ on a California crude oil; 2- and 4-pyridones and quinolones were reported to be present in this oil.

CONCLUSION

Repeated column, inverse-phase column and thin layer chromatography of Darius crude (300-470°C fraction) resulted in the isolation of a compound, the UV, IR, NMR and mass spectral data of which suggested that it was a benzpyridone carrying a long N-alkyl chain.

Chart I



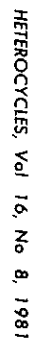
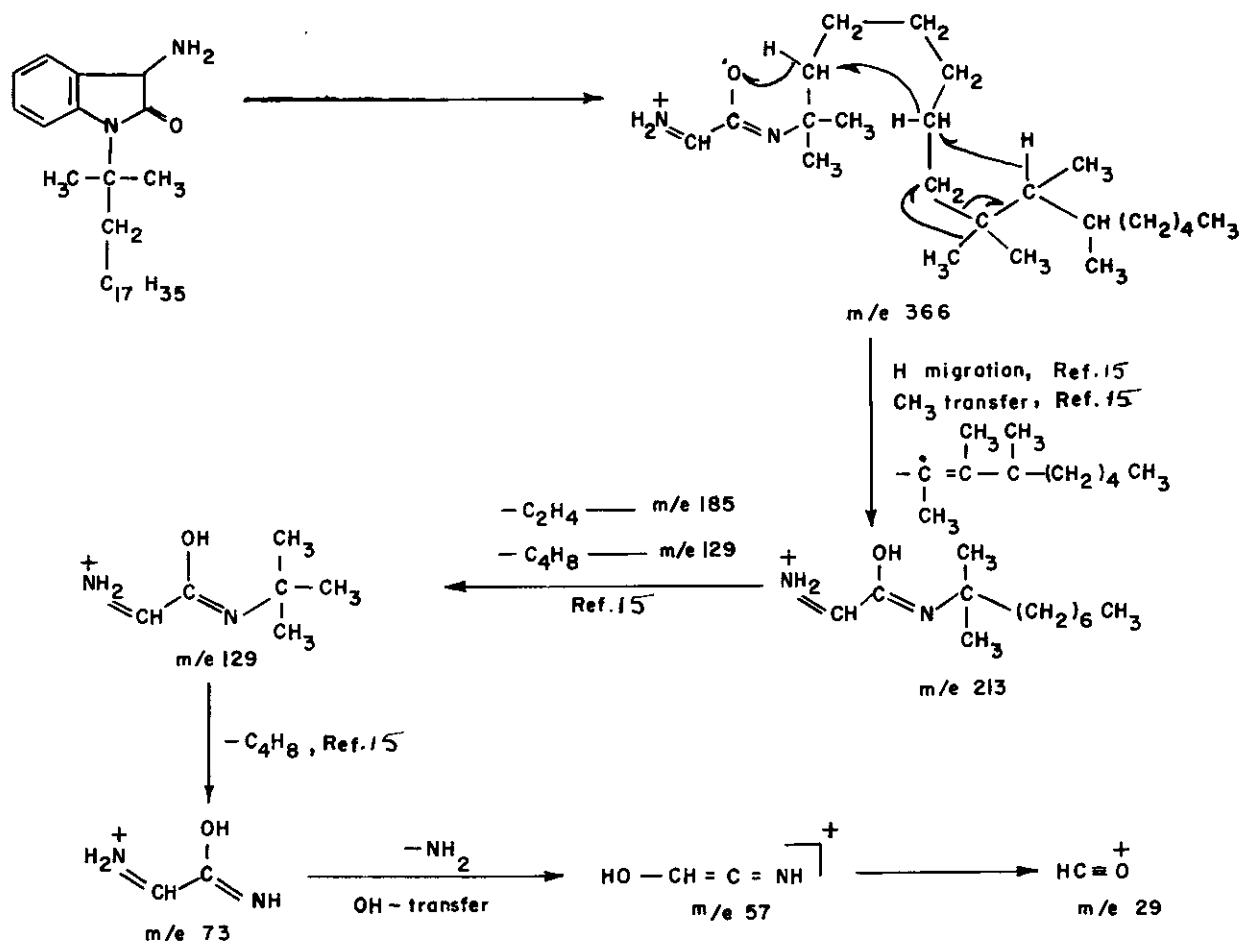


Chart 3



Acknowledgement

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