

# Jeans and Means

## 3. The Story of Indigo

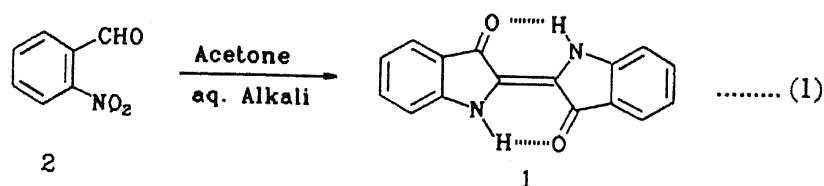
### *Subramania Ranganathan*



After nearly a three-decade long innings as an inspiring teacher and researcher at IIT Kanpur, S Ranganathan is now at RRL, Thiruvananthapuram. He and his chemist wife, Darshan, plan to set up (without government assistance) 'Vidyanatha Education Centre', to promote education, art and culture.

The mechanism of formation of indigo from 2-nitrobenzaldehyde and acetone is discussed in this article. Some new methods of making indigo are also described.

The organic chemist is a creator. It is this fact that contributed a great deal to the early development of organic chemistry. The early realisation that many useful compounds could be made more economically in the laboratory than from natural sources and the pursuit of such prospects in the dye industry were responsible for the development of organic chemical industries. Discoveries became the logical outcome of prolific and intuitive experimentation as exemplified by Perkin's synthesis of mauve in 1856 and Baeyer's synthesis of indigo in 1878. The remarkably simple synthesis of indigo (1) from 2-nitrobenzaldehyde and acetone in the presence of aqueous alkali (eq. 1) must have come as a most pleasant surprise.



Today we can explain the reaction; yet, by any standards it is still fascinating. In this article, we will try to analyse the steps involved in the synthesis of indigo. The mechanistic approach will be further simplified through a short discussion on oxidation numbers of organic compounds.

Even to this day, the mechanism of the alkali-mediated chemical transformation shown in equation 1 is some food for

Indigo [from Greek *indicon*, Indian substance] is perhaps the oldest dye known and has a history dating back to 5000 years. Indigo has attracted merchant ships to India since ancient times. No other naturally occurring material could give cotton the kind of lovely blue as indigo could. The trade suffered badly towards the later part of the last century, since the industrial preparation of indigo virtually wiped out indigo cultivation. Interestingly, we may end up going back to the natural sources for getting indigo, albeit in a different way, through genetically engineered organisms.

The increase in the demand for indigo is a direct result of the fascination for blue jeans, that has

neither gender nor age bias. The origin of jeans as an apparel makes an interesting story. The city of Genoa in Italy specialized in making sail ships. The sails were, naturally, made of rough and tough cotton. An entrepreneur found that old, dirty, torn sails could be dyed with indigo and sold as dress material. Thus jeans were born. People liked jeans, for they were comfortable. Nowadays jeans come in different hues, like stone washed, bleached and machine gunned! It seems that jeans are here to stay. With increasing demand the price of jeans is going up and along with it the price of indigo. This and environmental factors will in the very near future make the preparation of indigo by natural means a preferred option.

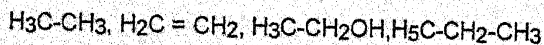
Johann Friedrich Adolf von Baeyer (1835-1917) was awarded the chemistry Nobel prize in 1905 in recognition of his services to the development of organic chemistry and chemical industry through his work on organic dyes and hydroaromatic combinations. Baeyer's name is synonymous with indigo and his impact on science was profound. His life is an inspiration to scientists. His first achievement was the preparation of barbituric acid, commonly known as sleeping pills. By 1880 he became well known for his work on indigo and other synthetic organic compounds, which were patented and marketed successfully. With his student, William Perkin, he formulated the Baeyer strain theory which indicated why rings of five and six carbon atoms are most common. Among the other notable students were Thiele, Schlenk, Wieland, Meyer, Emil Fischer and Otto Fischer.

Baeyer studied chemistry at Heidelberg University with Bunsen, whose emphasis on the importance of physics in chemical training and research is well known. Additionally, he had the good fortune of having Kekule as his teacher. One of the greatest characteristics of Baeyer's research was his ability to use simple equipment. His dictum was that good research can be done in simple, home-made fashion (an aspect our chemists could take note of). One day a student brought a mechanical stirrer to the laboratory. Baeyer spotted the gadget and was immediately apprehensive and suspicious of its merits. He sought the opinion of Mrs Baeyer and her first remark on seeing it was, "what a lovely way of making mayonnaise!" [whipped egg and olive oil, essentially]. Baeyer, it appeared, was speechless; the stirrer stayed and proliferated!

### Analysis of the Oxidation Number of Organic Compounds

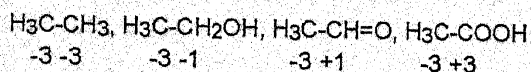
1. For a bond that connects the same atoms [regardless of the nature of ligands attached to it] the oxidation number count is zero. For example, the *contribution* from each carbon below is '0':

Examples:



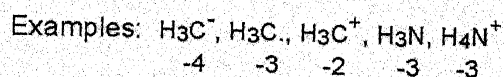
2. The oxidation number contribution of bond A-B will be related to the electronegativities or dipole moments. That is, the positive end contributes +1 and the negative end -1.

Examples:



This example shows how the progressive two-electron-oxidation of ethane to acetic acid, changes the oxidation number of the oxidised carbon by two units at a time.

3. Over and above the computed number, for every positive charge +1 should be added and for every negative charge -1 should be added.

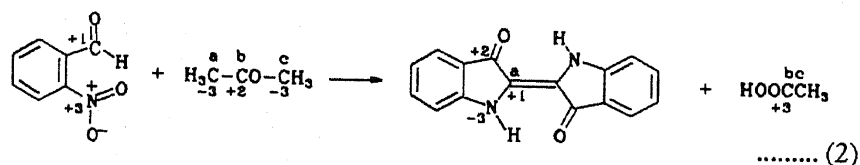


An analysis similar to the one above would show that for the progressive two electron reduction of a nitro compound to an amine, the oxidation number of the nitrogen atom decreases by two units at a time.

thought! We will try to understand the details of this transformation in two stages, through the analysis of the changes in oxidation numbers.

The concept of oxidation numbers has greatly simplified the analysis of transformations in the inorganic area, such as balancing equations. A similar concept, although too simplistic, is equally useful in organic chemistry. The rules for determining the oxidation numbers of atoms in organic molecules are summarised in the box.

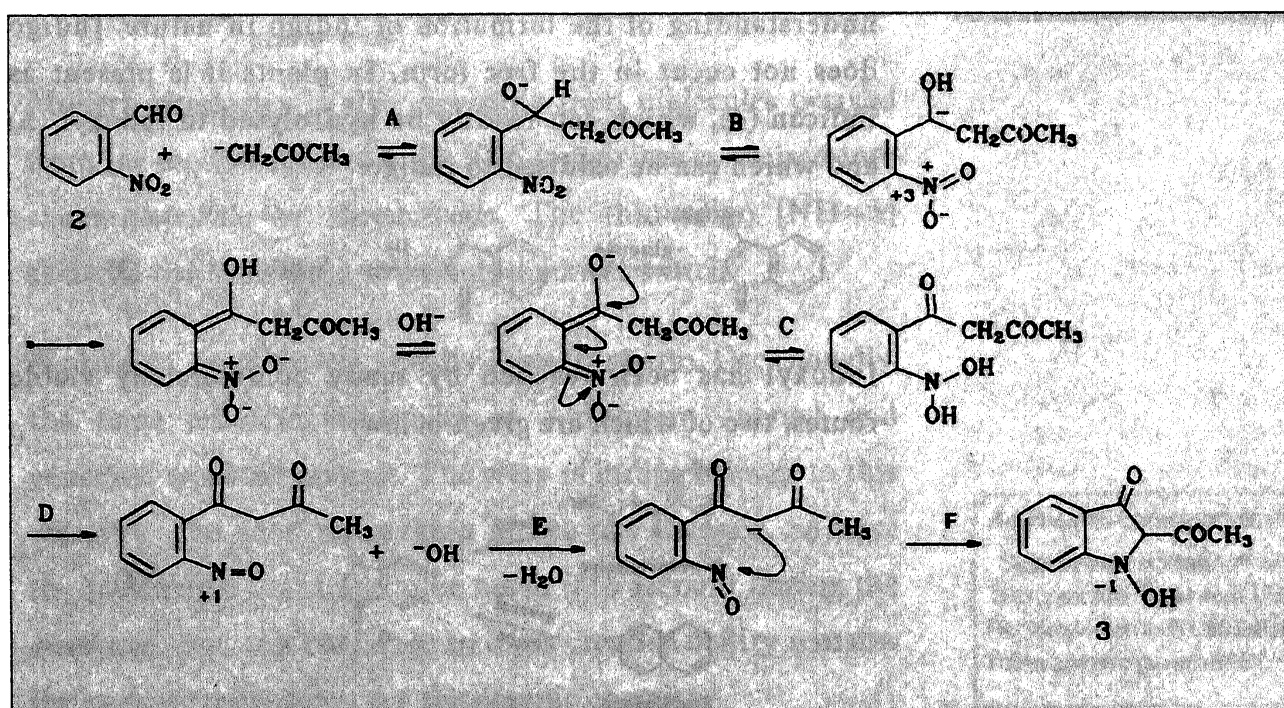
From this perspective, eq. 1 can be rewritten with the oxidation numbers of the important atoms as follows:

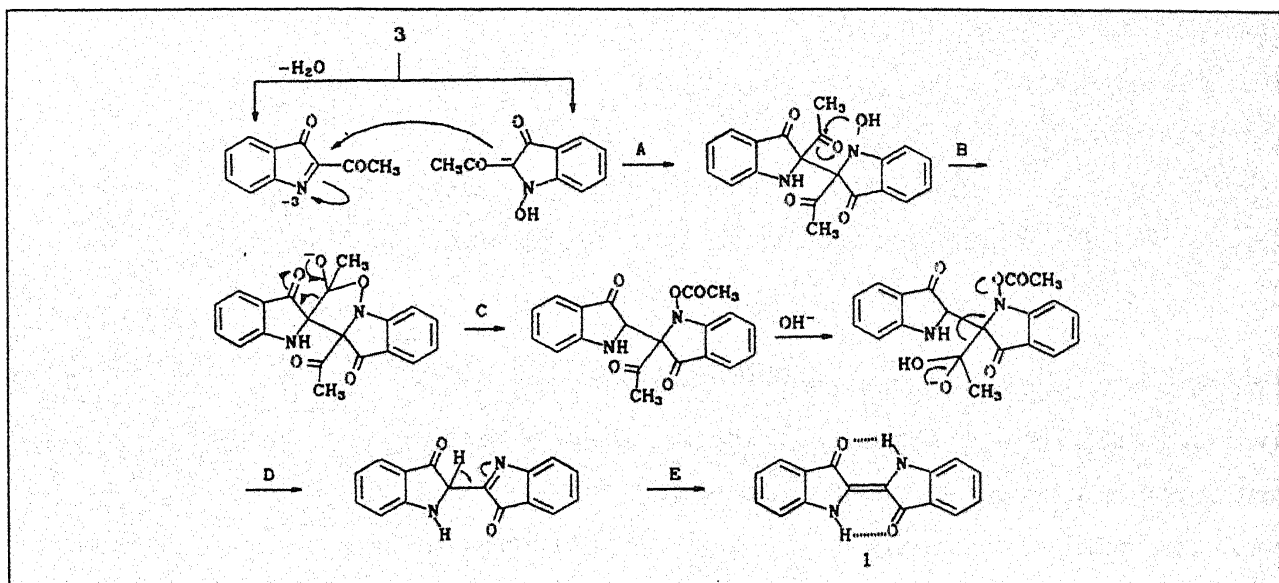


There is a remarkable change in the oxidation number of the nitrogen atom during the reaction. Of the six electrons needed for the  $\text{NO}_2 \rightarrow \text{NHR}^-$  (+3 to -3) change, five have come from acetone and one from the aldehyde group. Here the transfer of electrons has been 'done' in a clever manner through a series of transformations shown in *Schemes 1* and 2.

The presence of alkali is important in deprotonating acidic hydrogens to produce nucleophilic species, which undergo reactions characteristic of them. The acid-base equilibria also promote hydrogen transfers. With these general ideas in mind, we can divide the overall transformation of 2 to 1 into two segments. The first cascade of reactions is triggered by the addition of  $\text{CH}_3\text{COCH}_2^-$  (formed by an acid-base reaction of acetone with  $\text{OH}^-$ ) to the aldehyde group of 2. This ultimately leads to the formation of compound 3 via nucleophilic addition, hydrogen transfer and dehydration steps. The sequence is shown in *Scheme 1*. The changes in the oxidation number of nitrogen at crucial stages are also indicated.

*Scheme 1 A: nucleophilic addition; B: hydrogen shift; C: aromatization and protonation; D: dehydration; E: deprotonation and F: intramolecular nucleophilic addition.*

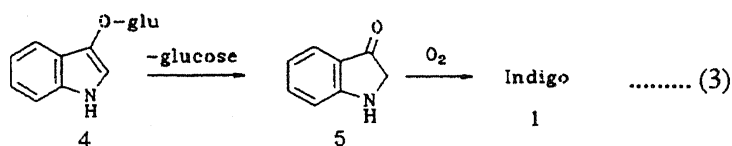




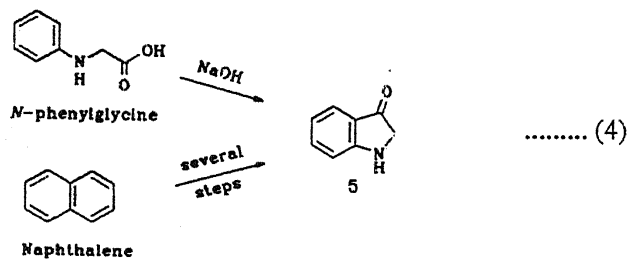
**Scheme 2 A & B: nucleophilic addition; C: retro-aldol reaction; D: fragmentation and E: tautomerisation.**

The second sequence of reactions begins with the coupling of two species, both generated from 3. Through a series of nucleophilic addition, fragmentation and tautomerisation steps (Scheme 2) indigo is ‘magically’ formed!

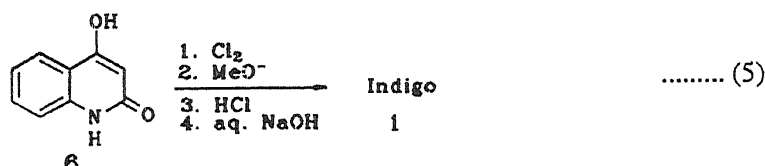
The structure of indigo as 1 was established only in 1883, five years after Baeyer’s synthesis. Later, routes to indigo were discovered rapidly and many of these were commercially exploited. These endeavours were facilitated by the understanding of the formation of indigo in nature. Indigo does not occur in the free form. In plants it is present as indican (4), which can readily be hydrolysed to indoxyl (5) and which can be oxidised to indigo.



Indoxyl has been reached by many commercially viable routes, two of which are given below:

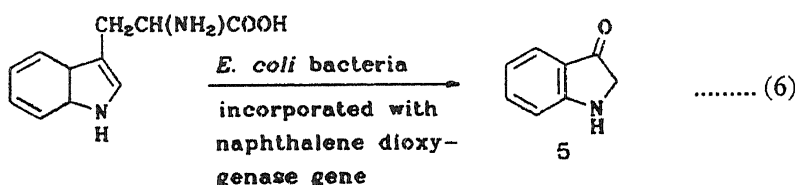


The quantitative transformation of 4-hydroxycarbostyryl (6) to indigo (eq. 5) is a process of recent origin. It demonstrates that the quest for indigo by exotic pathways is by no means over.



It would be challenging to work out how the 6 → 1 change takes place.

Although it may not strike us as elegant, many compounds currently prepared by organic synthesis can be made by genetically manipulated organisms. This trend will not only cut down costs but would also obviate environmental hazards, invariably associated with synthetic procedures. The case of indigo provides an excellent example. This route may prove to be the preferred procedure for large scale preparation of indigo.



Modern chemistry is also emerging from molecules derived from the modification of 1. In 1995 indigo was converted into sheet materials by thermolysis. The thioindigo [NH=S] skeleton has been used as a photochemical switch.

A problem, once solved, usually loses its charm. Occasionally, the same problem resurfaces in a different context and generates renewed interest. The story of indigo belongs to this category. The need for making indigo has changed. So have the parameters that have to be taken into account during the synthesis. But, the challenge to one's creative ability remains the primary motivation for the organic chemist.

### Suggested Reading

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