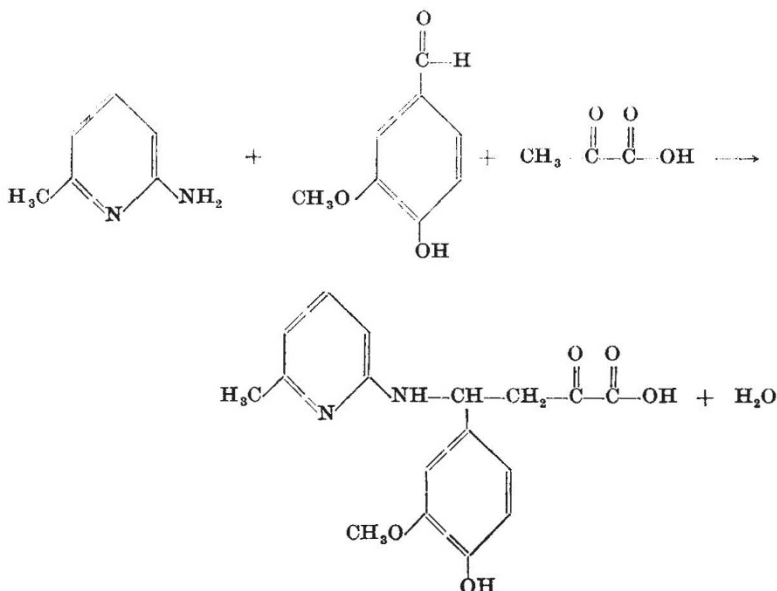


The results of the analysis for γ -(6-methyl-2-pyridylamino)- γ -(3-methoxy-4-hydroxy-phenyl)- α -oxo-butyric acid are as follows. The assigned molecular formula is $C_{17}H_{18}N_2O_5$ and the molecular weight 330. On this basis the theoretical content of the elements by weight is: carbon, 61.81 per cent; hydrogen, 5.45 per cent; nitrogen, 8.48 per cent. The composition found was: carbon, 61.61 per cent; hydrogen, 5.61 per cent; nitrogen, 8.36 per cent.

The ultra-violet absorption in distilled water was: λ_{\max} 350 m μ ($\epsilon = 3,857$); 290 m μ ($\epsilon = 5,911$); 230 m μ ($\epsilon = 10,840$).

The reaction can be represented as



The properties of the compound agree with the proposed structure. It is soluble in acids and bases, showing the presence of both $-\text{NH}$ and $-\text{COOH}$ groups. The product is insoluble in ordinary solvents such as ether, chloroform, alcohol and acetone.

I thank Dr. Zimmerman, of the University of Melbourne, Australia, for carrying out the analyses.

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Spontaneous Decomposition of a Sample of Pure Endrin

It is well known that both isodrin and endrin produce compounds containing a rearranged carbon skeleton when treated with acids, heat or ultra-violet light¹⁻³. Both thermal and acid-catalysed decompositions of endrin yield mainly a ketone which has the same elementary formula as endrin but contains an additional five-membered ring and has lost the olefinic double-bond. This communication reports an instance in which a pure, recrystallized sample of endrin stored in the dark for several years under normal ambient temperature conditions underwent this rearrangement.

The sample, weighing about 40 g, was prepared as colourless crystals in 1961 by column chromatography and recrystallization from methanol/benzene. It was derived from technical grade material supplied by Shell

Research, Ltd. The crystals were readily soluble in solvents such as acetone and benzene; a solution in ethanol absorbed light in the ultra-violet region with a maximum at 222–3 nm and the infra-red spectrum of a solid disk had characteristics which agreed with those of published spectra of endrin. The strong absorption bands arising from $\text{C}=\text{C}$ stretching at 6.25 μ and the oxirane ring at 11.7 μ were especially noticeable.

In 1965 the crystals, although stored in a clean, dry, glass bottle at normal temperature in the dark, had become slightly discoloured and the material was therefore recrystallized from methanol/benzene. Although this was accomplished, much more solvent was needed than had been used for the original crystallization, and it was clear that the solubility properties of the sample had changed. In addition, it was found that the absorption in the ultra-violet region at 222–3 nm, which had previously been used for analytical purposes, was now very low and indicated an endrin content of not more than 5 per cent.

The new substance was purified by extraction with an amount of hot 4 : 1 mixture of methanol and acetone which would have dissolved a similar weight of endrin. The extraction was repeated and the insoluble residue, which amounted to 72 per cent by weight, recrystallized from toluene. Its melting point was in the range 280°–285° C, with decomposition, and it was thus almost certainly the aforementioned ketone, compound XVII of Soloway *et al.*³. The identity was confirmed by infra-red spectroscopy, which showed that the band at 6.25 μ had disappeared while a new absorption band at 5.7 μ ($\text{C}=\text{O}$ stretching) was now present.

All the strong and medium absorption bands were identical, both qualitatively and quantitatively, with those appearing in the spectrum of the ketone given by Phillips, Pollard and Soloway². The substance did not depress the melting point of another sample of the ketone made by treatment of endrin with hydrochloric acid and both compounds behaved identically when examined by thin-layer and gas-liquid chromatography. Further confirmation of the ketonic nature was also provided by the preparation of a 2,4-dinitrophenylhydrazone.

It was interesting to note that the original technical grade of endrin, stored under the same conditions for the same time, had not suffered any appreciable decomposition and provided a new supply of pure endrin in high yield. The decomposition is therefore either inhibited by impurities in the technical grade or is erratic at room temperature—occurring in some samples and not in others.

This tendency to undergo rearrangement is a property of the isodrin series of Diels-Alder compounds which have an *endo-endo* configuration. It has been a complicating factor in gas-liquid chromatographic analysis and in the formulation of insecticides like endrin. The present experience shows that almost complete decomposition of pure endrin can occur even when it is stored in the dark under normal laboratory temperature conditions. The identity of samples of endrin and related compounds which are used as standards for chemical analysis and bioassay should therefore be checked at frequent intervals.

I thank L. C. Thomas, of the Chemical Defence Experimental Establishment, Porton, for providing the infra-red spectra of endrin and the ketone. F. BARLOW

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