

Preparation and Purification of Bisacid A2 (2,2-Diphenylolpropane 4,4-Dioxyacetic Acid). II

R. S. LENK, *Polytechnic of the South Bank, Dept. of Chemistry & Chemical Technology, London, S.E. 1, England*

Synopsis

In an earlier communication¹ the preparation of Bisacid A2 was described. This paper describes the attempts at spotting impurities in the products so obtained by subjecting them to thin-layer chromatography. No traces of impurities could be detected since no separation whatever was observed. Infrared spectra of pure Bisacid A2 were found to be identical with the spectrum of Nanu and Boboescu.² It was also seen that the product obtained by the standard preparation in 70-73% yield with a minimum melting point of 173°C could not be demonstrably improved by esterification and rehydrolysis. Second crops from first mother liquors from the aqueous acetic acid recrystallization of the crude precipitated product of the condensation reaction (as well as ether extracts from these mother liquors) showed that both contained material with phenolic OH groups. These are the impurities in the crude product which must be completely removed during purification if the final material is to be used for the synthesis of unsaturated polyester resins for ultimate use as crosslinked reinforced plastics, as alkyd varnish bases, or as fiber-forming saturated polyesters and polyamides. The need for adhering to the standard synthetic procedure was confirmed, in particular the need for multistage condensation, giving an effective yield of 70-73% of pure material

INTRODUCTION

The detailed preparation and purification of Bisacid A2 was described in an earlier communication (1).

CHROMATOGRAPHIC EXAMINATION FOR IMPURITIES

To confirm the purity of the samples of Bisacid A2 prepared and of the Bisphenol-A which served as the starting material in the synthesis, both were subjected to thin-layer chromatography on activated silica gel plates using a 17:3 (v/v) mixture of benzene and pyridine as solvent in one experiment, and a 95:5 (v/v) mixture of heptane and glacial acetic acid in a second. The positions of the substances were located by a 1% (w/v) solution of bromocresol green in a 9:1 (v/v) mixture of ethanol and water. Four runs were carried out, but in none of them was there any indication of separation of any impurities whatsoever. This confirms that the purification technique using aqueous acetic acid for exhaustive recrystallization of the crude Bisacid A2 obtained in the initial condensation reaction is entirely satisfactory.

INFRARED SPECTRA OF BISACID A2 AND BY PRODUCTS

The infrared spectrum of two samples of Bisacid A2 (mp 174–178°C) were determined. The first sample was a standard preparation (four-stage reaction, followed by two recrystallizations from aqueous acetic acid, dissolution in aqueous ammonia, filtration, reprecipitation with HCl, and a further two recrystallizations from aqueous acetic acid). The second sample was obtained by converting the first to its diethyl ester which was recrystallized three times from ethanol (mp 69–71°C), rehydrolyzed with aqueous caustic soda, reprecipitated with HCl, and exhaustively recrystallized from aqueous acetic acid, resulting finally in a melting range of 177–181°C.

The infrared spectra of these two samples were absolutely identical with each other and also with that obtained by Nanu and Boboescu² earlier. The spectrum is shown in Figure 1.

Figure 2 gives the spectrum of the Bisphenol-A used as the starting material. The most significant difference between this spectrum and that

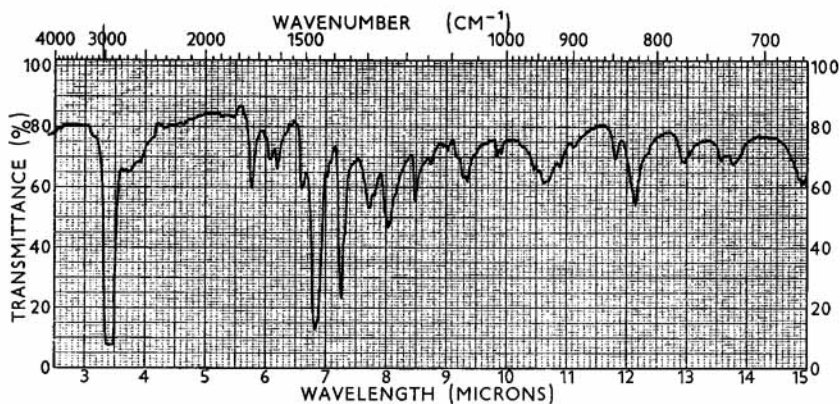


Fig. 1.

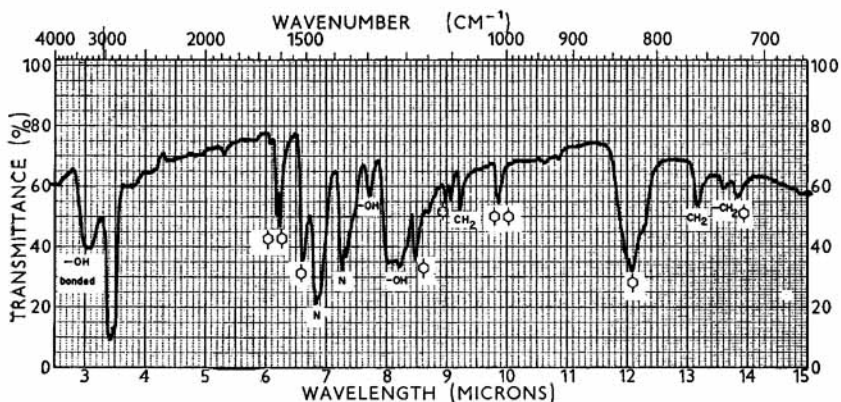


Fig. 2.

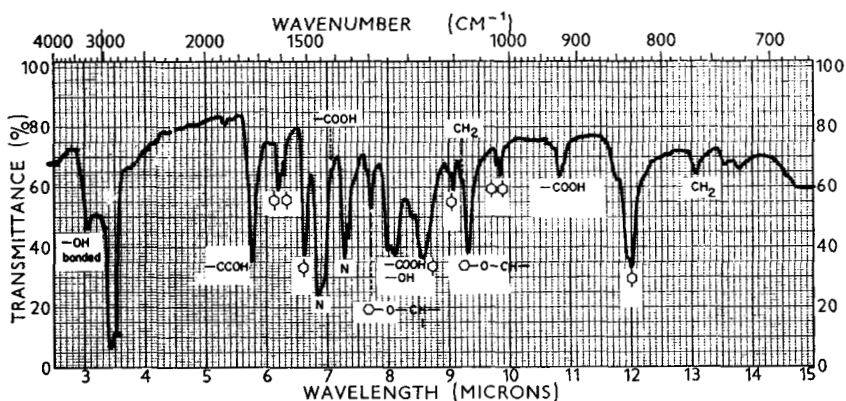


Fig. 3.

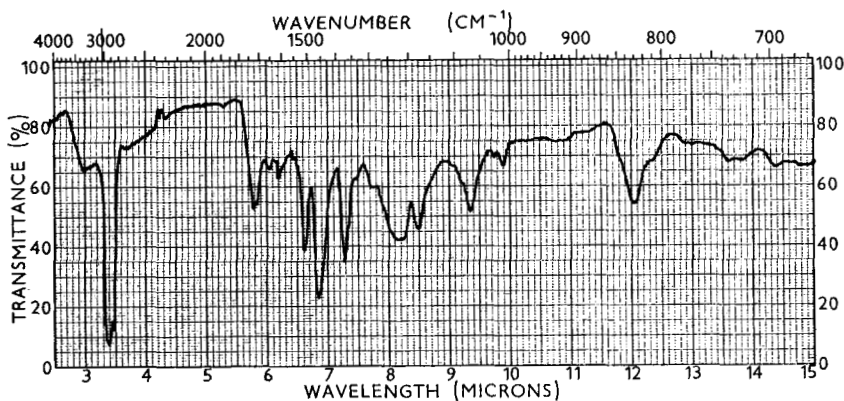


Fig. 4.

for Bisacid A2 is the presence of a large peak at a wavenumber of 3300 cm^{-1} in the former and the total absence of this peak in the latter. This peak is characteristic for phenolic OH.

Figure 3 gives the spectrum of the second-crop precipitate from the mother liquor left after the first recrystallization of the crude reaction product from aqueous acetic acid. This was thrown out after about a fortnight's standing and was separately worked up from aqueous acetic acid. While it was in many respects similar to the spectrum for pure Bisacid A2, it differed from the latter in that it clearly showed the tell-tale peak for phenolic OH at 3300 cm^{-1} , which leads to the conclusion that second-crop material contains diphenylolpropane monoacetic acid.

Figure 4 gives the spectrum of an ether extract from a first mother liquor. Here, too, the distinctive phenolic OH peak is seen at 3300 cm^{-1} .

All the infrared spectra were run in a Nujol mull using sodium chloride discs.

Thus, infrared spectroscopy has supplied convincing evidence that phenolic impurities (especially monoacid) are effectively removed from the crude product by recrystallization from aqueous acetic acid. Owing to the very low solubility of Bisacid A2 in 33% aqueous acetic acid at room temperature and its ready solubility at elevated temperatures, exhaustive recrystallization from this solvent does not affect the yields significantly.

REEXAMINATION OF THE NEED FOR MULTISTAGE CONDENSATION

In the normal preparation of Bisacid A2,¹ the condensation was carried out in four stages with fresh chloroacetic acid at each stage, followed by exhaustive recrystallization with aqueous acetic acid. This resulted in a product with a minimum melting point of 174°C and a yield of between 70% and 73% on Bisphenol-A.

An attempt was made to find a shortcut to the multistage condensation reaction. This involved using $2\frac{1}{3}$ moles of chloroacetic acid per mole of bisphenol-A instead of the four-stage addition of $2 + 1 + \frac{2}{3} + \frac{1}{3}$ moles of chloroacetic acid per mole of Bisphenol-A.

Two batches were run, exhaustively recrystallized, and dried in the usual way, resulting in average yields of about 80% of slightly off-white products with melting ranges of 164–170°C. This proved that, although apparently higher yields were obtainable in this way, the product was unacceptably impure.

The yields from the two batches were combined, redissolved in caustic soda, and subjected to a further three-stage reaction with chloroacetic acid, thus converting the method to that used in the standard preparation described in the earlier communication.¹ After exhaustive recrystallization and drying, the acceptable purity indicated by a melting range of 173–176°C was obtained in 72% yield.

This proved finally that multistage reaction followed by exhaustive recrystallization from aqueous acetic acid is an essential condition for the preparation of Bisacid A2 in a state of adequate purity, and that the yield obtainable in this way cannot be expected to substantially exceed 70–73%.

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References

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