The Preparation and Purification of Diphenylolpropane 4,4'-Dioxyacetic acid (Bisacid A2)

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Synopsis

Earlier work on the synthesis of bisacid A2 is reviewed. The problems associated with the achievement of a pure product in good yield are pointed out. The procedure for obtaining same is described. It is believed that the melting point (or rather melting range) of bisacid A2 prepared from specially pure bisphenol-A and purified as described is higher than that of any bisacid A2 previously reported in the literature.

INTRODUCTION

Bisacid A2* can be made by reacting monochloracetic acid and bis-phenol-A in aqueous alkaline solution under reflux, but the yields are poor unless certain procedures are followed. The motivation for synthesizing the acid in the early postwar period was the intended use of its simple diesters as plasticizers for PVC with which they proved to be compatible. An extensive report on the properties of the simple diesters and their plasticizer performance has been given by Nanu and Boboescu,[1] who also pointed to the potential usefulness of the diacid for the preparation of linear saturated and crosslinkable unsaturated derivatives by polycon-densation. (Nanu and Boboescu call the diacid "dian diacetic acid.") The polycondensation reactions and some of the products, however, had earlier been investigated and described by Lenk in a British patent ap-plication.[2]

In the early postwar period, bisphenol-A was just beginning to be commercially available as an intermediate in the production of epoxy resins. Later it found an additional outlet as the starting material for polycarbonates.

It was soon appreciated that there existed two major problems before bisacid A2 of high purity could be made such that suitable high molecular weight products could be obtained by subsequent polycondensation:

* Nomenclature: "Bisacid AX" is a dioxy alkylic acid with X number of C atoms attached to the nonaromatic end of the ether link, including the carboxyl C. "Bis-ester AXY" is bisacid AX esterified with an alkanol having Y number of C atoms. (Further designation such as n-, iso-, etc., may be necessary.)

1. The provision of ultrapure bisphenol-A, that is to say, of a starting material free from other phenolic impurities, especially monophenols. Isomeric bisphenols (say 2,4' instead of the 4,4') are also highly undesirable impurities, if the resin is intended for the subsequent production of potential fiber-forming derivatives, where molecular symmetry is of the utmost importance. (The by-products of the bisphenol-A reaction have been studied by Neumann and Smith.[3])

2. The fact that there is competition between the main substitution reaction and hydrolysis of monochloracetic acid giving nonreactive glycollic acid. Not only does the hydrolytic side reaction constitute a waste of reagent, but, more importantly, it also produces HCl which in turn displaces the diphenol from its sodium salt and renders it nonreactive. To counteract this, it is necessary to keep on adding alkali which in turn tends to hydrolyze more monochloracetic acid to glycollic acid.

Few (if any) workers have pointed out the need for really pure bisphenol-A, possibly because they were principally interested in ultimately making modified crosslinked polymers such as oil-based alkyd-type surface coatings (as, for instance, Lenk[2] earlier on) where a high molecular weight chain is not important since high molecular weights can ultimately be achieved by catalyzed crosslinkage using paint driers or suitable peroxides or hydroperoxides. In this work, however, care was taken to obtain especially pure bisphenol-A from Kepec G.m.b.H. (W. Germany) which had a melting point of 155–156°C and a maximum phenol content of 0.01%.

Earlier workers thought that one could cope with the hydrolytic side reaction by simply using a suitably large excess of monochloracetic acid and by avoiding heat, as far as possible, in the preparation of the sodium salt. But since the desired reaction is carried out under reflux, it is impossible to avoid extensive hydrolysis, and the conversion reaction is inefficient. Day and Bradley[4] have claimed that the efficiency of the main reaction is improved, not so much by using a large excess of Na monochloracetate, as by stepwise addition of the latter at intervals of several hours. They also include a small amount of KI, but do not give reasons for this, and it is not clear what function the KI fulfills, apart from acting as a somewhat inefficient acid–base indicator. It would appear that the hydrolytic production of HCl should really be counteracted by automatic neutralization to maintain the reactivity of the reagents while avoiding excessive amounts of alkali. In fact, the practice adopted in this work was that of neutralizing the hydrolytically produced HCl before each successive step of the stepwise reaction and by allowing the reaction mixture to cool to room temperature overnight before doing so.

Day and Bradley[4] claim that their method afforded a yield of up to 97% with similar percentage purity. However, it was not stated how "purity" was assessed, nor did they state what method of purification was suitable and what yield could be obtained. No melting point was given and no comment appertaining to the physical appearance of the crude bisacid A2

after final precipitation with mineral acid was made. (The crude bisacid A2 invariably comes down as a honey-like, sticky semisolid which cannot be filtered and must be washed by decantation.) The only purification mentioned (without giving details) was "washing with water."

Rust and Canfield[5] used the same basic reaction but without describing any attempt to improve either the yield or the purity of the product by stepwise reaction or otherwise. They were chiefly interested in making the alkyl ester for use in coatings.

Tanaka and Takahashi[6] carried out the reaction in the presence of ethanol. This is evidently possible under alkaline conditions, but in the writer's experience bisacid A2 esterifies readily (although perhaps not extensively) in the presence of nonaqueous alcohol even in the absence of the usual acidic esterification catalysts, so much so that alcohol is an unsuitable recrystallization solvent for bisacid A2. Tanaka and Takahashi reported a melting point of 169–170°C. In the earlier work of Lenk,[2] a bisacid of melting point 158–168°C had been obtained which could be raised to a fairly sharp 168°C by ether extraction. Nanu and Boboescu[1] were able to reach a melting point of 173°C by rehydrolysis of the bisethyl ester (bisester A22). In the present series of experiments, melting ranges of up to 175–181°C were obtained by particularly lengthy recrystallization sequences including—inter alia—the hydrolysis of the bisester A22. It should be noted that the melting point of bisacid A2 is seldom sharp, even for a product of high purity indicated by a theoretical acid value of 325 or one close to that value.

The isolation and characterization of the main impurity in the crude bisacid A2 has been attempted and successfully accomplished in the present work. It proved to be the monooxyacetic acid of bisphenol-A ("monoacid A2").

EXPERIMENTAL

Synthesis

The reaction was carried out on the multistage principle suggested by Day and Bradley[4] in amounts of up to 3 moles of bisphenol-A, with up to four successive stages of reaction involving molar proportions of up to 6, 3, 2, and 1 mole of sodium monochloracetate, respectively.

The sodium salt of bisphenol-A was made by adding 2 moles of NaOH per mole of bisphenol-A to the latter in the presence of water. Sodium monochloracetate was freshly made immediately prior to use by dissolving 1 mole of NaOH per mole of monochloracetic acid in water and adding solid CO_2 in order to cool and simultaneously convert the caustic soda solution to sodium carbonate. The carbonated caustic solution was then added carefully to a fresh aqueous solution of monochloracetic acid, with further addition of solid CO_2 as necessary to keep the temperature below 40°C to prevent excessive hydrolysis.

The two solutions were now brought together, refluxed for 4 hr, and allowed to cool to room temperature overnight. The mixture was neutralized with NaOH, and the next step portion of Na monochloracetate (freshly made as before) was added. This procedure was repeated up to the 4th step, whereupon the crude bisacid A2 was precipitated with concentrated HCl and washed with water by decantation.

Purification of the Crude Bisacid A2

The honey-like mass obtained after precipitation and washing tended to crystallize a little more on standing, but always still remained rather sticky. The mass was dissolved in glacial acetic acid and refluxed while sufficient water was gradually added to dilute the glacial acetic acid to 40% aqueous. By keeping the solution under reflux, the dilution did not cause throw-out of crystals, or if it *did* cause throw-out through overfast water addition, the crystals readily redissolved on heating. On cooling, white leaflets separated which could be readily filtered and which contained much less sticky oily material than the original crude. The mother liquor was deeply yellow, and the yellow component could be extracted with ethyl acetate or (better) with ether. After washing with water and removal of the solvent from the mother liquor extract, a clear yellow amorphous glass was obtained which was believed to be the monoacid of bisphenol-A and which showed the expected strong absorption for phenolic OH in the infrared spectrum. This acid is referred to as "monoacid A2."

The crystals of bisacid A2 were then similarly recrystallized from 33% aqueous acetic acid, dissolved in aqueous ammonia, and filtered to remove any mechanical impurities. The bisacid A2 was precipitated (concd. HCl), filtered, and recrystallized first from 40% and then from 33% aqueous acetic acid, when the mother liquor was water white, showed no trace of yellowness, and threw out no milky precipitate on dilution. This indicated that the monoacid had been quantitatively removed. The crystal cake was now washed free from acetic acid by repeated resuspension in water, filtration, and draining and was finally dried in vacuo at 60°C.

Using this method, melting ranges covering 4–6°C were obtained for various batches which fell within the limits of 170–181°C, with yields of up to 70% theoretical.

It is thought that the yield is greatly dependent on the method of neutralizing the hydrolytically produced HCl. It would seem that this ought to be done automatically, but until one can effectively standardize on this, variations in yield must be expected.

The "ultrapurification" by rehydrolysis of bisester A22, which is described below, resulted in the recovery of only 33% of bisacid A2 and, although large, glistening, and free-flowing white leaflets of the latter were obtained, the material did not seem to have a melting point which was significantly different from the starting material (starting material, 175–177°C; "ultrapure" material, 174–178°C). However, these melting points are higher than any previously reported in the literature.

The method of "ultrapurification" consisted in the conversion of purified bisacid A2 into bisester A22 by refluxing with a large excess of absolute alcohol in the presence of a small amount of p-toluenesulfonic acid while passing freshly generated gaseous HCl through the solution. The bisester (mp 69–71°C) was twice recrystallized from IMS and hydrolyzed by refluxing with aqueous caustic soda solution until a clear solution was obtained. The bisacid A2 was reprecipitated with concd. HCl and recrystallized first from 40% and then from 33% aqueous acetic acid, exhaustively washed with water, filtered, drained, and dried in vacuo at 60°C.

References

1. I. Nanu and V. Boboescu, *Bul. Stiint. Si Tehnic, Inst. Politeh. Timisoara*, **8** (22), 51 (1963).
2. R. S. Lenk, Brit. Pat. 21,192 (July 15, 1956).
3. F. W. Neumann and W. E. Smith, *J. Org. Chem.*, **31** 4318 (1966).
4. H. M. Day and M. H. Bradley, U.S. Pat. 2,541,003 (Feb. 6, 1951).
5. J. B. Rust and W. B. Canfield, U.S. Pat. 2,672,478 (Mar. 16, 1954).
6. S. Tanaka and R. Takahashi, Japan Pat. 29–1834 (Apr. 7, 1954).