NOTES

Alicyclic Diamines. Polyadipamides of Bis-(4-aminocyclohexyl)-methane

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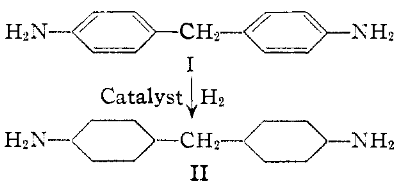
Hydrogenation of bis-(4-aminophenyl)-methane (I) yields bis-(4-aminocyclohexyl)-methane (II).



The bis-(4-aminocyclohexyl)-methane is obtained as mixtures of the three geometric isomers, namely, the *cis–cis*, *cis–trans* and *trans–trans* configurations.[1] Under various hydrogenation conditions[2] mixtures of bis-(4-aminocyclohexyl)-methane are obtained which vary in the proportions of the three isomers present. An estimate of the relative amounts can be obtained by isolation of the individual isomers, methods for which have been described.[1]

Configuration of the diamine isomers plays an important role in determining the properties of the polyamides prepared therefrom. Investigation of representative polyadipamides was undertaken to elucidate this situation.

Discussion

The adipic acid polyamides of the individual pure isomers and of known mixtures of the isomers exhibited considerable differences in melting point. In light transmission the polymers ranged from glass-like clarity to opacity. Polymer properties for a particular isomer mixture have been readily reproduced. The results for various compositions are given in Table I.

Table I

Polyadipamides of Bis-(4-aminocyclohexyl)-methane

Isomer composition of diamine, %			Light transmission	Softening temp., °C.
c–c	*c–t*	*t–t*		
..	97.5	2.5	Transparent	253
..	95.2	4.8	Opaque	261
15.0	77.9	7.1	Transparent	277
30.0	57.9	12.1	Transparent	255
52.4	28.2	19.4	Transparent	244
73.7	..	26.3	Transparent	257
15.0	75.3	9.7	Translucent	260
30.0	55.5	14.5	Translucent	259
52.1	25.6	22.3	Translucent	262
30.1	50.5	19.4	Opaque	>300
15.0	70.5	14.5	Opaque	>300

The polyamide from adipic acid and the *trans–trans* diamine isomer is highly crystalline, opaque and infusible below its decomposition temperature (about 310°). The polyamide from the *cis–trans* isomer is transparent, crystalline and orientable as determined by X-ray diffraction, and softens at about 252°. The polyamide from the *cis–cis* isomer is transparent, amorphous, and not readily orientable. It softens at about 253°.

Adipic acid polyamides were prepared from two-component mixtures of the pure isomers. All the polyamides from mixtures of the *cis–trans* and *cis–cis* isomers were transparent and softened between 244 and 260°. Increased crystallinity and orientability were noted as the proportion of the *cis–trans* isomer was increased. Polyadipamides of mixtures of *cis–cis* and *trans–trans* isomers with up to 26% of the latter were transparent and fusible. Polyamides from mixtures of the *cis–trans* and *trans–trans* isomers with more than 2.5% of the latter were opaque.

In three-component systems quantities of the *trans–trans* isomer between 2.5 and 26%, depending on the proportion of the *cis–trans* and *cis–cis* isomers, also gave transparent, fusible polyamides. Further increasing the concentration of the *trans–trans* isomer by about 8% gave opaque, higher melting polyadipamides. The polyamides with appreciably larger proportions of *trans–trans* isomer have been infusible below 300° and opaque.

In general, isomer mixtures obtained by hydrogenation which were liquid at 25° gave fusible, transparent polyadipamides while solid mixtures of diamine isomers gave opaque polymers. Short catalyst contact time and low temperature are conditions for hydrogenating bis-(4-aminophenyl)-methane that apparently favor conversion into a preponderance of the *cis–cis* and *cis–trans* isomers.[1,2] This has been realized with bis-(4-aminocyclohexyl)-methane prepared batchwise over ruthenium catalysts at about 100°, and in continuous flow hydrogenation over ruthenium catalysts at about 140–150°. The adipic acid polyamides from bis-(4-aminocyclohexyl)-methane prepared under these conditions have been readily fusible and transparent. Hydrogenation at moderately increased temperatures or appreciably longer contact times has resulted in increased proportions of the *trans–trans* isomers as evidenced by the nature of the adipic acid polyamide which was fusible but opaque. Hydrogenation batchwise at 150° or under continuous flow at temperatures above 160° resulted in further increases in the *trans–trans* isomer content, as inferred from the infusibility and opacity of the adipic acid polyamides.

Experimental

Preparation of Adipic Acid Salts of Bis-(4-aminocyclohexyl)-methane.—The preparation of the adipic acid salts of the diamine isomers is exemplified by the procedure employed for the preparation of the *trans–trans* salt. To a solution of 50.37 g. (0.239 mole) of the *trans–trans* isomer in 290 ml. of absolute ethanol was added all at once a warm solution of 34.82 g. (0.238 mole, 0.42 mole per cent. less than the equivalent amount) of recrystallized adipic acid in

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(1) A. E. Barkdoll, H. W. Gray and W. Kirk, Jr., This Journal, **73**, 741 (1951).

(2) A. E. Barkdoll, D. C. England, H. W. Gray, W. Kirk, Jr., and G. M. Whitman, *ibid.*, **75**, 1156 (1953).

175 ml. of absolute ethanol, an additional 20 ml. of absolute ethanol being used for rinsing. The salt precipitated instantly with incipient boiling of the solution. The hot mixture was stirred thoroughly to ensure homogeneity and was stored at 6° for 2 days. The microcrystalline salt was collected by suction filtration, washed with 20 ml. of absolute ethanol and dried under reduced pressure at 60–80° for several days to remove alcohol, which was held very tenaciously.

Somewhat less ethanol was employed for formation of the adipic acid salts of the other two isomers. The *cis-trans* salt precipitated as tiny, oily spheres that crystallized rapidly on scratching. The diamine samples were weighed in a nitrogen-filled dry-box to prevent absorption of carbon dioxide and water during handling. Polonium-plated gold foil was employed to dissipate the static charges acquired by the diamines during handling. The inflection points for the three salts were in the *p*H range of 7.53–7.58, as determined by electrometric titration of 0.5% aqueous solutions.

Preparation of Polyamides.—Polymer preparations were carried out in Pyrex brand glass tubes 28 × 180 mm. o.d. with a wall thickness of 2 mm. to which were sealed necks 11 × 220 mm. o.d. About 10 g. of salts was polymerized in each run. Mixtures of salts of the different isomers were stirred to assure that the resulting polyamide would be homogeneous. The tube containing the salt was evacuated and filled with oxygen-free nitrogen three times at atmospheric pressure, and then evacuated to a pressure of 5 mm. and sealed. The sealed tube was heated for one hour at 210° in a lead-bath. The tube was then cooled and opened and the contents heated under oxygen-free nitrogen at 1 atm. pressure for one-half hour at 306° (benzophenone vapor bath). Heating was continued for 1.5 hours at 285° (diphenylene oxide vapor bath) without allowing the molten polymer to cool appreciably while changing the bath.

Characterization of Polyamides.—Inherent viscosities[3] were predominantly in the range 0.72–1.05 which indicated that high molecular weight was attained. Polymer melting points were determined in air on a copper block.

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(3) Determined with 0.5 g. of polymer in 100 ml. of *m*-cresol at 25°; *cf.* L. H. Cragg, *J. Colloid Sci.*, **1**, 261 (1946).

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Some Reactions of Cinnamoylpyridinium Chloride

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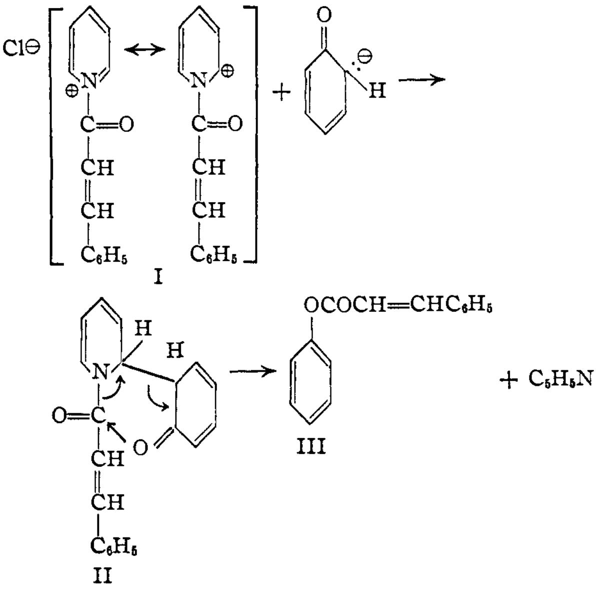
In the course of another investigation we had cause to examine the chemical behavior of cinnamoylpyridinium chloride (I) and, in view of the recent interest[1,2,3,4] in compounds of the same general type as I, we are reporting our results at this time. The reaction of cinnamoyl chloride and pyridine in dry ethereal solution at or slightly below room temperature gave I in essentially quantitative yield as a white solid of rather indefinite melting point. The compound was a powerful acylating agent, reacting with water[1] or dilute solutions of bases[5] to give cinnamic anhydride in 13–71% yield depending on the conditions of the experiment. Acylation of ethyl benzoylacetate with I gave ethyl β-cinnamoyloxycrotonate in 59% yield. The reaction of pyridine, benzoyl chloride and dimethylaniline at room temperature for seven weeks or at 100° for six days has been reported to give 4-(*p*-dimethylaminophenyl)-pyridine in 22–27% yield.[4,6] The latter was obtained in 35% yield (along with traces of cinnamaldehyde) from the reaction of I and dimethylaniline in pyridine at steam-bath temperatures for eight hours.

The most interesting cinnamoylation was that of phenol, for this reaction appeared to take place in two distinct steps. When I was mixed with phenol (in the presence or absence of pyridine) a bright yellow substance formed which slowly and completely disappeared as crystals of colorless phenyl cinnamate deposited (73–83% yield). 2,6-Dimethylphenol behaved in the same fashion, giving 76% of 2,6-dimethylphenyl cinnamate. If the colored substance may be assumed to be a true intermediate, its formation may be rationalized by assuming a mechanism for the reaction similar to that proposed by Doering and McEwen[2] for several reactions of benzoylpyridinium chloride.[7] Thus, I which has an electron deficiency at the α- and γ-positions, reacts with the electron-donating keto form of the phenoxide ion to give the colored complex II,[8] which is converted *via* the quasi six-membered ring to the ester III.



Experimental[9]

Cinnamoylpyridinium Chloride (I).—To a solution of 83.5 g. (0.5 mole) of cinnamoyl chloride (prepared in 95% yield from cinnamic acid and 1.5 moles of thionyl chloride, b.p. 133–134° (15 mm.)) in 200 ml. of dry ether was added slowly with cooling 60 g. (0.76 mole) of pyridine dissolved in 100 ml. of dry ether. The mixture was allowed to stand 30 minutes (protected from moisture) and was filtered, washed with cold ether and dried over potassium hydroxide *in vacuo*. The yield of cinnamoylpyridinium chloride was 113–122 g. (92–98%), m.p. about 122–124°. The compound decomposed when distilled under reduced pressure. The com-

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(1) H. Adkins and Q. E. Thompson, THIS JOURNAL, **71**, 2242 (1949).

(2) W. von E. Doering and W. E. McEwen, *ibid.*, **73**, 2104 (1951).

(3) Q. E. Thompson, *ibid.*, **73**, 5841 (1951).

(4) W. E. McEwen, E. H. Terss and I. W. Elliott, *ibid.*, **74**, 3605 (1952).

(5) E. Wedekind, *Ber.*, **34**, 2070 (1901).

(6) For the original report of this reaction see: E. Koenigs and E. Ruppelt, *Ann.*, **509**, 142 (1934).

(7) See footnote 4 of ref. 2. Apparently Adkins and Thompson[1] have succeeded in isolating benzoylpyridinium chloride (although not in analytically pure form) as well as numerous other aroylpyridinium chlorides.

(8) Intermediate II may be in equilibrium with a similar substance in which the cyclohexadienone unit is in the γ-position (see ref. 2).

(9) Melting points are corrected, boiling points are not. Analyses were by Clark Microanalytical Laboratory, Urbana, Illinois, unless otherwise noted.