ered the rate of evaporation and rate of crystal growth. Although we found no definitely formed crystals which corresponded to Stobbe's description of the "third isomer," we many times encountered mixtures of somewhat similar but wider melting range [131–135° (he gave 133–135°)] which untold times raised false hopes. We have been unsuccessful in every one of our many experiments in obtaining any evidence whatsoever for the existence of a "third isomer." It is therefore clear that of the three products reported by Stobbe[2] (m.p. 133–135°, 148–149° and 164–165°) only the latter two are individual compounds.

The following data in Stobbe's paper[2] are themselves bases for question as to the existence of a third isomer.

(a) For the two higher-melting isomers, melting ranges of 1° were reported, whereas the lowest-melting product (the supposed third isomer) had a wider melting range of 2°.

(b) Melting points obtained from mixtures of this "isomer" with equal amounts of the two higher-melting isomers showed no depressions in either case.

(c) All three products decolorized potassium permanganate solution, with an intermediate rate in the case of the "third isomer."

(d) On dissolution of the isomers in concd. sulfuric or trichloroacetic acid the color from the "third isomer" was intermediate between those from the other two.

(e) The "third isomer" of the three reacted with desoxybenzoin in absolute ethanolic sodium ethoxide at an intermediate rate and gave an intermediate yield of benzameron, $C_6H_5CH[CH(C_6H_5)COC_6H_5]_2$. (We find that the 149° and 165° compounds are not isomerized in any degree whatsoever under the conditions involved.)

All these observations can best be explained on the assumption that the lowest-melting product was a mixture of the other two. (However, it must be mentioned that in the case of bromination Stobbe reported that of the three products, the supposed "third isomer" reacted at a rate other than intermediate).

Still further data were obtained by us which added considerably to the weight of evidence against the existence of Stobbe's "third isomer" and indicated it to be a mixture of the *cis* and *trans* isomers. Stobbe claimed to have obtained a 70% yield of this 133–135° "isomer" and a 5% yield of the 148–149° isomer upon four months exposure to sunlight of a benzene–iodine solution of the 164–165° isomer. In repeating this experiment we used a 10^{-3} molar solution and at the end of one month exposure (which had been shown to be ample to affect photoequilibrium) upon fractionally crystallizing the products we obtained 30% yield of the 149° isomer and approximately 70% of unchanged 165° isomer. These differences in yields were far too great to be accounted for by different experimental conditions.

***p*-Nitrobenzaldesoxybenzoin** (a *cis-p*-nitrobenzalacetophenone) (I), prepared according to Stobbe[2] (m.p. 164–165°), was found upon purification to melt at 169–169.5°.

The stereoisomer (a *trans-p*-nitrobenzalacetophenone) (II) was prepared[2] by sunlight inversion of the isomer (I) and melted at 153–153.5° (Stobbe, m.p. 148–149°[2]).

Sunlight Isomerizations of the 169° Isomer (I).—The first two of the experiments below are repetitions of Stobbe's experiments. The products were isolated by fractional crystallizations from benzene–isoöctane mixtures.

(a) A 1.6% benzene solution containing a trace of iodine was refluxed for 11.5 hours under exposure to diffuse sunlight: yield 13% of II; the rest of the material was nearly pure I. In another experiment with refluxing time 10 hours, the yields were 24% of II and 76% of I. (Stobbe reported smaller yields with 35% yield of the supposed 135° isomer).

(b) In a similar experiment using a 0.16% solution in benzene at room temperature for one month with intermittent additions of iodine to maintain color, the yields were 30% of II and 70% of I (Stobbe reported 70% of the 135° compound).

(c) A 0.6% benzene solution without catalyst was exposed to direct sunlight for two months, with similar results: yields 25% of II and 75% of I.

(d) **Photoequilibrium** was reached within several minutes upon exposure of 10^{-5} molar alcohol solutions of both I and II to direct sunlight, and within 30 seconds under a G.E. sunlamp. A similar solution of I but containing a trace of iodine also came to equilibrium within several minutes in sunlight. Ultraviolet absorption spectra were used to determine these equilibria.

Acid-catalyzed isomerization according to Stobbe's directions of a 1.7% benzene solution of the 169° isomer (I) saturated with dry hydrogen chloride, allowed to stand for one week in darkness at room temperature, gave 2–3% of II, and the rest of the product was I (Stobbe reported 33% of the 133–135° product).

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Some Reactions in the 1,3,5-Triazine Series

BY ALFRED BURGER AND EDWIN D. HORNBAKER[1]

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The purpose of this study was the preparation of 2-chloro-1,3,5-triazine as an intermediate in the synthesis of other monosubstituted triazine derivatives. The catalytic hydrogenolysis of halogen substituted triazine derivatives has been studied for monoaminodichlorotriazines[2] and for diaminochlorotriazines,[3] but the stepwise or complete removal of chlorine atoms from cyanuric chloride has not been reported. Hydrogenation experiments using nickel or palladium catalysts with cyanuric chloride under various conditions, even by the Rosenmund method, have remained inconclusive in our hands, and similar failures have been attributed to a poisoning of the catalyst by the reaction products in another laboratory.[4]

The reduction of cyanuric chloride with lithium aluminum hydride in ether solution took an unexpected course. The only reaction product was 2-dimethylamino-4,6-dichloro-1,3,5-triazine. The path of this reaction may be visualized as a hydrogenolysis of the triazine ring with the formation of dimethylamine which then reacts with as yet unchanged cyanuric chloride.

The only monosubstituted derivatives of 1,3,5-triazine containing functionally reactive groups reported in the literature are 2-phenoxytriazine,[2] 2-aminotriazine[5,6] and four simple alkylaminotriazines.[2] In the hope of utilizing 2-aminotriazine as a synthetic intermediate, we subjected this compound to several typical simple reactions of α-aminoazines but observed only formation of inorganic ammonium salts, or recovery of starting material. This behavior suggests the absence of a primary amino group, and this conclusion is borne out by the ultraviolet absorption spectrum which shows no peak at about 236 mμ as it is found for melamine.[7] Cyanuric chloride shows a similar peak at 238 mμ which is attributed to a typical triazine ring.[7]

We are grateful to Parke, Davis and Co. for support of this work, and to American Cyanamid Co. for the cyanuric chloride used in this study.

Experimental

Reduction of Cyanuric Chloride.—To a stirred solution of 8.0 g. of lithium aluminum hydride in 500 ml. of dry

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(1) Parke, Davis & Co. Fellow.

(2) R. Hirt, H. Nidecker and R. Berchtold, *Helv. Chim. Acta*, **33**, 1365 (1950).

(3) J. R. Geigy A.G., Swiss Patent 252,530 (1949), 261, 811(1949).

(4) C. Grundmann, H. Ulrich and A. Kreutzberger, *Chem. Ber.*, **86**, 181 (1953).

(5) O. Diels, *Ber.*, **32**, 691 (1899).

(6) J. P. English and J. H. Paden, British Patent 566,933 (1942)

(7) I. M. Klotz and T. Askounis, THIS JOURNAL, **69**, 801 (1947)

ether was added 20.0 g. of pure cyanuric chloride in several portions. The solution was stirred for another 15 minutes, excess hydride was decomposed with water, 200 ml. of 10% sulfuric acid was added and the mixture was extracted with ether. The ether extract yielded 1.5 g. of colorless needles which after recrystallization from petroleum ether melted at 124–124.5° (cor.).

Anal. Calcd. for $C_5H_6Cl_2N_4$: C, 31.11; H, 3.13; N, 29.02. Found: C, 31.52; H, 3.10; N, 29.13.

A mixture melting point with an authentic sample of 2-dimethylamino-4,6-dichloro-1,3,5-triazine[8] showed no depression.

Ultraviolet Spectrum.—The ultraviolet absorption spectrum of 2-amino-1,3,5-triazine in a 10^{-5} molar aqueous solution was measured with a Beckman model DU spectrophotometer at 26°. A continuously decreasing absorption was observed from 225 to 240 mμ.

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[8] W. M. Pearlman and C. K. Banks, THIS JOURNAL, **70**, 3726 (1948).

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Determination of the Configuration of 4-Cyclohexylcyclohexanols

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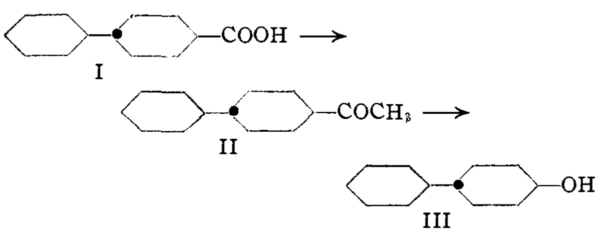
In the course of a study of the hydrogenation of 4-hydroxybiphenyl-4′-carboxylic acid,[1] it became of interest to determine, with certainty, the stereochemistry of the 4-phenyl- and the 4-cyclohexylcyclohexanols. In 1948, Ungnade[2] prepared the pure *cis* and *trans*-isomers of this series and assigned the configurations on the basis of method of preparation and on thermodynamic stability. Recently, Dauben and Hoerger[3] showed that by converting a carboxylic acid to a methyl ketone and cleaving the resulting ketone with perbenzoic acid,[4] an acid could be related, stereospecifically with retention, to an alcohol. Since Fieser, *et al.*,[5] have related *trans*-4-cyclohexylcyclohexylcarboxylic acid (I) to *trans*-hexahydroterephthalic acid, a compound whose stereochemistry has been rigorously established by Mills and Keats,[6] application of the methyl ketone–perbenzoic acid sequence above to *trans*-acid I would determine the stereochemistry of the 4-substituted cyclohexanols in an unequivocal manner.



Such a sequence of reactions was performed and it was found that *trans*-acid I was, indeed, related to the *trans*-alcohol III. Thus, the stereochemical configurations of the 4-phenyl- and 4-cyclohexylcyclohexanols assigned by Ungnade[2] are correct. It is of passing interest to note that in this series, the thermodynamically stable isomer is the one which has both of its substituents in equatorial conformations.[7]

Experimental

***trans*-4-Cyclohexylcyclohexylcarboxylic Acid** (I).—The acid was prepared following the procedure of Fieser, *et al.*,[5] m.p. 160.5–161.9° (lit. 161–162°).

***trans*-4-Cyclohexylcyclohexanol** (III).—A solution of 0.9 g. (4.28 millimoles) of *trans*-acid I in 15 ml. of dry ether was added dropwise with stirring to 18 ml. of a 0.6 *M* solution of methyllithium in ether. Following the addition, the mixture was stirred for 12 hours and then poured onto ice. The ethereal layer was removed, washed neutral with water, dried and the solvent removed through a small column. The residue weighs 0.8 g. (89.7%) and was used directly in the oxidation.

Perbenzoic acid (0.638 g.) in 8.8 ml. of chloroform was added to the crude ketone which had been dissolved in 5 ml. of chloroform. The solution was allowed to stand for 8 days at room temperature in the dark. At the end of this time the reaction was diluted with ether and washed thoroughly with dilute sodium hydroxide. The residue remaining after removal of the solvents was heated for 7 hours with 50 ml. of 1 *N* sodium hydroxide in 30 ml. of methanol and the methanol removed under reduced pressure. The aqueous residue was extracted with ether, the ether distilled and the 4-cyclohexylcyclohexanol recrystallized from hexane, yield 0.28 g. (40%), m.p. 99.6–102.4° (lit.[2] 103–104°). The phenylurethan was prepared and melts 154.9–156.6° (lit.[2] 156–156.8°).

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[1] W. G. Dauben and M. Tanabe, in press.

[2] H. E. Ungnade, *J. Org. Chem.*, **13**, 361 (1948).

[3] W. G. Dauben and E. Hoerger, THIS JOURNAL, **73**, 1504 (1951).

[4] R. B. Turner, *ibid.*, **72**, 878 (1950); T. F. Gallagher and T. H. Kritchevsky, *ibid.*, **72**, 882 (1950).

[5] L. F. Fieser, *et al.*, *ibid.*, **70**, 3186 (1948).

[6] W. H. Mills and G. H. Keats, *J. Chem. Soc.*, 1373 (1935).

[7] D. H. R. Barton, *Experientia*, **6**, 316 (1950).

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The Structure of the Solid Product from the Condensation of Methyl γ-Bromocrotonate with Sodium Methoxide[1]

BY ANDRE S. DREIDING AND RICHARD J. PRATT

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Owen and Sultanbawa[2] reported the isolation of a small amount of a solid from the reaction of methyl γ-bromocrotonate with dry sodium methoxide in benzene. The product was characterized by its analysis (empirical formula of $C_5H_6O_2$), melting point (168–169°) and ultraviolet absorption spectrum ($\lambda_{\max}^{\text{alc}}$ 303 mμ, $E_{1\text{cm}}^{1\%}$ 2600). The authors considered that it was possibly methyl cyclopropenecarboxylate.

A re-examination of the reaction confirmed the observations of Owen and Sultanbawa, the solid product being formed in 1.3% yield. However, its high melting point and its spectrum, which appeared uncharacteristic of either of the double bond isomers of methyl cyclopropenecarboxylate, suggested a reconsideration of its structure.

α-Haloesters are known to be attacked by bases with the formation of enolates.[3] The vinylogous reaction with methyl γ-bromocrotonate (I) is the abstraction of a proton from the γ-position with the

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[1] Supported in part by grants to the Detroit Institute of Cancer Research from the American Cancer Society, Inc., the Michigan Cancer Foundation and The Kresge Foundation.

[2] L. N. Owen and M. U. S. Sultanbawa, *J. Chem. Soc.*, 3098 (1949).

[3] M. S. Newman and B. J. Magerlein, "The Glycidic Ester Condensation" in R. Adams, "Organic Reactions," Vol. 5, John Wiley and Sons, Inc., New York, N. Y., p. 413.