were used as a source of scandium, approximately 40 g. having been recovered to date by a modification of the procedure of Fischer and Bock.[8] The ionium was then recycled to the dibutoxytetraethylene glycol step.

The losses of ionium incurred in the re-extraction and precipitation steps are less than 0.02 and 0.04%, respectively. The loss at the dissolution step is zero.

Consequently, the over-all loss in ionium, making use of simple recycle procedures, is limited essentially to the loss incurred in the initial extraction from the Mallinckrodt waste. The resultant yield is, therefore, 95% or more, depending upon the efficiency of the initial extraction.

In practice, the ionium was not recovered from the aqueous wastes resulting from the fluoride precipitation step by simple recycle of these wastes to the next feed. Instead, these aqueous wastes, which were found to have an average Pa^{231} content of 0.3 mg. per liter were set aside for recovery of Pa^{231}.[9] Following recovery of the Pa^{231}, the ionium was recovered by recycle of the aqueous waste to the initial extraction step.

Acknowledgment.—The authors wish to thank W. M. Manning and S. Lawroski of the Argonne National Laboratory for making the combined facilities of the Chemistry and Chemical Engineering Divisions available and the Mallinckrodt Chemical Works, St. Louis, Missouri, and the St. Louis Area Office of the United States Atomic Energy Commission for supplying the feed material.

[8] W. Fischer and R. Bock, *Z. anorg. allgem. Chem.*, **249**, 146 (1942).

[9] R. Elson, G. W. Mason, D. F. Peppard, P. A. Sellers and M. H. Studier, This Journal, **73**, 4974 (1951).

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NOTES

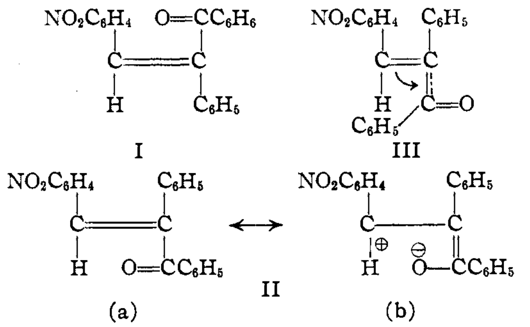
The Non-existence of the "Third Isomer" of *p*-Nitrobenzaldesoxybenzoin

By W. Bruce Black[1] and Robert E. Lutz

Received May 16, 1953

This work stemmed from studies in progress on stereoisomeric (*cis–trans*) pairs of chalcones (benzalacetophenones) substituted in the α- or β-positions, studies dealing with differences in the ultraviolet absorption spectra and their correlation with differences in chemical reactivities of the conjugated systems involved.

Stobbe[2] in an extensive series of researches has claimed the existence of three isomers in each of two α-phenylchalcone series (*cf.* I, II). He assumes two of these in each series to be *cis–trans* isomers, but he has not explained the nature of the supposed "third isomer" in any instance. Only *cis* and *trans* forms can be accounted for in terms of classical formulations. We thought at first that conjugation and resonance between the styryl system and the carbonyl group in one stereoisomer [presumably the *trans*-chalcone form (II)] might conceivably impart sufficient double bond character to the bond between these two systems so that *cis–trans* isomerism based on planarity of this area of the molecule might prevail, with the carbonyl oxygen pointing inward toward the β-position (II) or outward from it (III).[3] It was later shown[4] that significant resonance between the styryl and carbonyl systems existed only in the *trans*-α-phenylchalcone system,[4] as might have been predicted. Thus the "third isomer" could conceivably be represented (by III) as an example of the kind of isomerism spoken of by Pauling[5] as possible when the double bond character between two conjugated double bonds becomes sufficiently large to maintain planarity of the system. Under the stimulus of this idea (unsound though it was here) careful and extensive attempts were made, unsuccessfully, to reproduce Stobbe's experiments in the *p*-nitrobenzaldesoxybenzoin series. However, the results of these attempts led us to conclude that in this series the "third isomer" does not exist as a compound and that Stobbe's product was in reality a mixture of the normal *cis* and *trans* isomers (I and II).



Experimental

Each of Stobbe's isomerization reactions on the high-melting isomer where he obtained high yields of the "third isomer," was repeated and the products were fractionally recrystallized with exceeding care (*e.g.*, more than 40 recorded fractionations were made on a single reaction product). In no case was a sample obtained that could not be resolved into one and the other of the same pair of isomers. The best recrystallization solvent was a benzene–isoöctane mixture. Stobbe had used benzene–petroleum ether mixtures, but we found that substitution of isoöctane for petroleum ether diminished creeping of the solvent and advantageously low-

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[1] Holder of Philip Francis du Pont Research Fellowship, 1952–1953.

[2] H. Stobbe and F. Wilson, *Ann.*, **374**, 237 (1910).

[3] *Cf.* a consideration of the conformation of the bromochalcones, R. E. Lutz, D. F. Hinkley and R. H. Jordan, This Journal, **73**, 4647 (1951).

[4] W. B. Black and R. E. Lutz, *ibid.*, paper in press.

[5] L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1948, p. 218.

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

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RECEIVED MAY 11, 1953

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).