Notes A department for short papers of immediate interest.

Cyclopropanes XXII.[1] Determination of Geometrical Isomers by Spectrophotometric Methods

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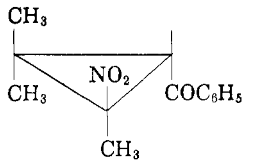
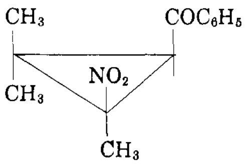
It has been demonstrated that *cis* and *trans* isomers of certain aroyl ethylene oxides[3] and ethylenimines[4] can be identified by spectrophotometric methods. In the ultraviolet absorption spectra, the maximum arising from the aroyl group of the *trans* isomer occurs, in every case, at a lower frequency (higher wave length) than does the corresponding maximum of the *cis* isomer. Also the extinction coefficient, $\epsilon_{max.}$, of the *trans* compound is always greater than that of the *cis* isomer. In the infrared absorption spectra, in most cases, the carbonyl stretching frequency of the *trans* compound occurs at lower values than that of the *cis* isomer.

Cromwell has discussed these observations in terms of increased hyperconjugation through the three-membered ring with *trans* substituents and has suggested that *cis* and *trans* aroyl cyclopropanes could be distinguished by similar spectrophotometric differences.[5] He suggested that any differences in the absorption spectra of stereoisomeric cyclopropanes would be apparent only in the ultraviolet spectra, and not in the infrared region. No clear-cut examples of the separation of *cis-trans* isomers of simple aroyl cyclopropanes have been reported, but a number of aroyl nitrocyclopropanes have been described in earlier papers of this series, and geometrical isomers have been separated in two cases where this proposed "*trans* hyperconjugation" might occur.

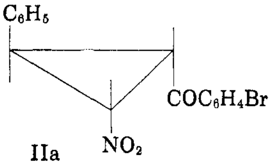
The two possible isomers of 1-benzoyl-2-nitro-2,3,3-trimethylcyclopropane (I) have been prepared.[6] The infrared absorption spectrum of each isomer (in Nujol) showed a band at 1670 cm.$^{-1}$.



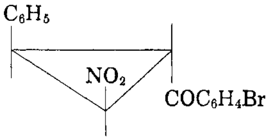
Ia., m.p., 55° (*trans*)



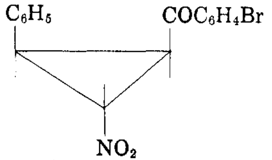
Ib., m.p., 101° (*cis*)



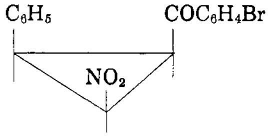
IIa



IIb



IIc



IId

The ultraviolet spectrum of the isomer melting at 55° showed a maximum at 249 mμ ($\epsilon_{max.}$ 14.9 × 10^{-3}); that of the isomer melting at 101° showed a maximum at 248 mμ ($\epsilon_{max.}$ 13.5 × 10^{-3}). In analogy with the spectrophotometric differences shown by ethylene oxides and ethylenimines, the lower melting isomer must be the *trans* form, Ia. The following observations also support this designation: the 55° isomer is isolated in 98 to 1 excess over the 101° isomer when these cyclopropanes are prepared by dehydrobromination of the corresponding bromonitro ketone, and the 55° isomer is stable toward methanolic ammonia whereas the 101° isomer is converted to the 55° compound by the same reagent.

Kohler[7] reported three of the four possible geometrical isomers of 1-(*p*-bromobenzoyl)-2-nitro-3-phenylcyclopropane (II). Smith and Holly[8] have re-investigated these isomers and reported melting points of 120°, 135°, and 169°.[9]

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(1) Paper XXI, Smith and Kohlhase, *J. Org. Chem.*, **21**, 816 (1956).

(2) Du Pont Postdoctoral Fellow 1954–1955.

(3) Wasserman and Aubrey, *J. Am. Chem. Soc.*, **77**, 590 (1955); Cromwell and Setterquist, *J. Am. Chem. Soc.*, **76**, 5752 (1954).

(4) Prostenik, Salzman, and Carter, *J. Am. Chem. Soc.*, **77**, 1856 (1955); Cromwell, Barker, Wankel, Vanderhorst, Olson, and Anglin, *J. Am. Chem. Soc.*, **73**, 1044 (1951).

(5) Cromwell and Hudson, *J. Am. Chem. Soc.*, **75**, 872 (1953); Cromwell and Graff, *J. Org. Chem.*, **17**, 414 (1952).

(6) Smith, Kohlhase, and Brotherton, *J. Am. Chem. Soc.*, **78**, 2532 (1956).

(7) Kohler and Williams, *J. Am. Chem. Soc.*, **41**, 1649 (1919).

(8) Smith and Holly, *J. Am. Chem. Soc.*, **78**, 1472, 1475 (1956).

(9) Since publication of the work of Smith and Holly, it has been discovered that the "isomer" of II melting at 120° is actually a mixture of the other two isomers. This fact, however, does not invalidate the arguments presented here, or in the paper by Smith and Holly,[10] as to the configurations of the isomers of II melting at 135° and 169°. We are greatly indebted to Prof. Weldon G. Brown and his student, Mr. John Neumer, for calling to our attention, in a private communication, that their evidence obtained in a study of these compounds indicated strongly that the "isomer" melting at 120° was not a pure compound.

(10) Smith and Holly, *J. Am. Chem. Soc.*, **78**, 1480 (1956).

The structure IId which has three substituents on one side of the planar cyclopropane ring would be a comparatively unstable one, and in the following discussion it will be assumed that the isomer with this structure has not been isolated. The carbonyl stretching frequencies in the infrared spectra (in Nujol) of the two isomers melting at 135° and 169° are located, respectively, at 1674 and 1670 cm.$^{-1}$. Table I shows that the maximum in the ultraviolet absorption spectrum of the isomer melting at 169° occurs at the higher wave length and has the larger extinction coefficient. This suggests that it should be the "*trans*" compound.

TABLE I[a]

ULTRAVIOLET ABSORPTION MAXIMA OF THE ISOMERS OF II

Melting Point	Solvent	Concentration	λ Max., Mμ	$\epsilon \times 10^{-3}$
135°	95% ethanol	2.1×10^{-5}	261.0	18.80
	Abs. ethanol	4.213×10^{-5}	262.7	20.30
169°	95% ethanol	2.19×10^{-5}	264.0	21.70
	Abs. ethanol	4.258×10^{-5}	263.5	22.10

[a] All spectra were obtained on a Beckman Model D Spectrophotometer.

In the case of this cyclopropane, "*trans*" means that the phenyl (electron donor in this case) and *p*-bromobenzoyl (electron acceptor) groups are on opposite sides of the plane of the cyclopropane ring. However, this is true in both structures, IIa and IIb. The nitro group is also an electron acceptor and will conjugate with a *trans* phenyl group as in IIa in competition with the aroyl group. Structure IIb with the nitro group in a noncompetitive position *cis* to the phenyl group is probably the compound melting at 169°. In this case the isomer melting at 135° can be either IIa or IIc. The other possibility, considered to be less likely, is that structure IIa represents the isomer melting at 169° and the 135° compound is IIc.

The former conclusion, *i.e.*, the 169° compound is best represented as IIb and the 135° isomer is either IIa or IIc, is supported by other chemical and physical evidence reported by Smith and Holly.[10]

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3-Isoxazolidone

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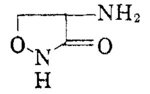
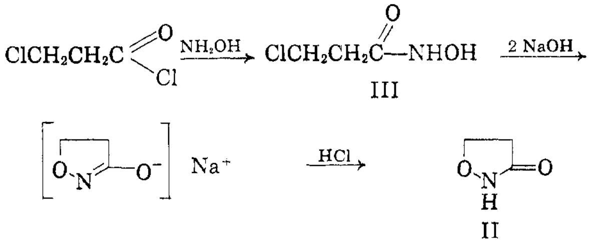
Cycloserine has been shown to be D-4-amino-3-isoxazolidone (I)[1,2] and a synthesis has been reported.[3] The synthesis of I involved the cyclization of an α-substituted β-halopropionohydroxamic acid. In order to determine the conditions necessary for this reaction, the preparation of a simple analog, 3-isoxazolidone (II),[4] was first undertaken.



I

β-Chloropropionohydroxamic acid (III) was prepared by the reaction of β-chloropropionyl chloride with aqueous hydroxylamine at −10°. The resulting acid (III) gave a red-violet color with ferric chloride.[5] Treatment of III with two equivalents of aqueous sodium hydroxide at 50° gave a solution of *ca.* *p*H 9. An aliquot of this solution after acidification failed to give a color with ferric chloride, showing that the hydroxamic acid was no longer present. Neutralization of the solution with one equivalent of acid yielded 3-isoxazolidone (II). The compound is a crystalline solid which, after reaction with hydroxylamine, gives a red-violet color with ferric chloride. This indicates that 3-isoxazolidone reacts with hydroxylamine in a manner similar to that of a lactone[5] to give a hydroxamic acid (probably 3-aminoxypropionohydroxamic acid).



EXPERIMENTAL[6]

β-Chloropropionohydroxamic acid. Hydroxylamine hydrochloride (27.5 g.) was dissolved in 167 ml. of 2.5*N* sodium hydroxide and the solution was cooled to −10°. To this solution, β-chloropropionyl chloride (25.0 g.) was added dropwise with stirring. The temperature was maintained at −5° to −10° during the addition and for 30 min. longer. The resulting solution was extracted with four portions of butanol and the combined extracts were dried over anhydrous magnesium sulfate and concentrated *in vacuo.* The residue solidified on cooling. The solid was extracted with several portions of refluxing ether, and the extracts were combined and concentrated to a small volume. The crystalline precipitate that separated was redissolved in ether and

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[1] Kuehl, Wolf, Trenner, Peck, Howe, Hunnewell, Downing, Newstead, Buhs, Putter, Ormond, Lyons, Chaiet, and Folkers, *J. Am. Chem. Soc.*, **77**, 2344 (1955).

[2] Hiddy, Hodge, Young, Harned, Brewer, Phillips, Runge, Stavely, Pohland, Boaz, and Sullivan, *J. Am. Chem. Soc.*, **77**, 2345 (1955).

[3] Stammer, Wilson, Holly, and Folkers, *J. Am. Chem. Soc.*, **77**, 2346 (1955).

[4] After this work had been completed the cyclization of ethyl 3-aminoxypropionate with alkali to 3-isoxazolidone (isolated as the potassium and silver salts) was reported (ref. 2).

[5] Feigl, *Spot Tests II*, Elsevier Publishing Co., Houston, Tex., 1954, pp. 170–171.

[6] Analyses by R. N. Boos and associates; infrared spectrum by R. W. Walker. Melting points were determined on a Kofler micro hot stage.