mg.-atoms) of sodium and 10 ml. of anhydrous methanol. This mixture was evaporated to dryness *in vacuo* at 40°. A solution of the residual white solid in 10 ml. of pure dioxane was added to a solution of 7-chloro-*v*-triazolo[4,5-*d*]pyrimidine prepared by the procedure described above (*cf.* XVII) from 434 mg. (3 mmoles) of 4,5-diamino-6-chloropyrimidine, 350 mg. of freshly distilled isoamyl nitrite, and 20 ml. of purified dry dioxane. Reaction conditions were identical with those used to prepare XVII. The cooled reaction mixture was diluted with 100 ml. of water, and the aqueous solution was extracted with three 100-ml. portions of ether. Acidification of the aqueous layer to pH 5 precipitated a white crystalline solid that was separated by filtration, washed with water, and dried *in vacuo* at 56°; wt., 536 mg.; m.p., 214° dec.

Acknowledgment.—The authors express their appreciation to Mr. W. E. Fitzgibbon and associates of the Organic Preparations Section for preparing large quantities of some of the required compounds; to Misses Margaret Kennerly and Mary Broadaway for paper chromatographic determinations; and to Dr. W. J. Barrett, Dr. W. C. Coburn, Jr., Dr. P. D. Sternglanz, and associates of the Analytical Section for spectra determinations and most of the microanalyses. Some of the microanalyses were performed by the Galbraith Microanalytical Laboratories, Knoxville, Tennessee.

Stereospecificity of the Addition of Bromine to *cis*- and *trans*-Stilbene[1]

ROBERT E. BUCKLES, JANE M. BADER, AND ROLAND J. THURMAIER

Department of Chemistry, University of Iowa, Iowa City, Iowa

Received August 23, 1962

The reaction of bromine with *cis*- or *trans*-stilbene in relatively nonpolar solvents (dielectric constant 2–3) was found to involve 90–100% stereospecific, *trans* addition. As solvents of higher and higher dielectric constant were used the addition became progressively less stereospecific giving more and more *meso*-α,α'-dibromobibenzyl from *cis*-stilbene in place of the *dl* isomer. With solvents of dielectric constant around 35 or higher, the reaction was essentially nonstereospecific with both stilbenes giving 80–100% *meso*-dibromide. With a bromide (or tribromide) salt present much of the stereospecificity was restored in these relatively polar solvents; that is, *cis*-stilbene gave more *dl*-dibromide.

Almost since its first synthesis[2] the addition of bromine to *cis*-stilbene under the usual mild conditions favoring the polar mechanism rather than the free radical mechanism[3] has been found to be essentially stereospecific and *trans*. Although the original report[2] on *cis*-stilbene gave the product of bromine addition in ether solution in sunlight as *meso*-α,α'-dibromobibenzyl, the reaction was reported[4] a few years later to give an 83% yield of *dl*-α,α'-dibromobibenzyl in cold carbon disulfide in the dark. Since these original reports, varying amounts of *dl*- and *meso*-dibromides have been reported as products of the reaction, but always with the *dl*-isomer predominating for the polar mechanism.[5] Free radical addition, on the other hand has led[5b] to *meso*-dibromide as the major product just as has the isomerization[5c] of the *dl*-dibromide or the bromination of bibenzyl.[6] With *trans*-stilbene all additions of bromine have been reported[5b,c,6a,7] to give the *meso*-dibromide as the major product, but in some experiments[7ac,] isolable yields of the order of 10% have been reported for the *dl*-isomer. With pyridinium tribromide [pyridinium dibromobromate (1)] as a brominating agent in acetic acid more clean-cut, stereospecific additions have been reported[8]; that is, there was neither isolable *dl*-dibromide from *trans*-stilbene nor *meso*-dibromide from pure *cis*-stilbene. Such results appear to be analogous to the stereospecific additions of chlorine to *cis*- and *trans*-stilbene with tetrabutylammonium iodotetrachloride [tetrabutylammonium tetrachloroiodate (III)] as a source of chlorine.[9]

The present investigation is concerned with the stereospecificity of the addition of bromine to *cis*- and *trans*-stilbenes under conditions favorable to the polar mechanism. Additions were carried out in various solvents either with or without a bromide salt present. The water-insoluble, solid product mixtures were isolated with no attempt being made to separate solid impurities such as *trans*-stilbene or other addition products from the dibromides. The amounts of *meso*- and *dl*-dibromides in a mixture were estimated by two methods: infrared analysis of the dibromide mixture and debromination by sodium iodide followed by spectrometric analysis of the stilbene mixture. In each case the analysis was, at best, a semiquantitative estimate of the composition of the dibromide mixture.

---

(1) This research was supported by a grant from the National Science Foundation.

(2) R. Otto and F. Stoffel, *Ber.*, **30**, 1799 (1897).

(3) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt Co., New York, N. Y., 1959, pp. 520–527, 736–739.

(4) J. Wislicenus and M. Jahrmarkt, *Chem. Zentr.*, **I**, 464 (1901).

(5) (a) F. Straus, *Ann.*, **342**, 190 (1905). (b) R. E. Buckles, *J. Am. Chem. Soc.*, **71**, 1157 (1949). (c) R. E. Buckles, W. E. Steinmetz, and N. C. Wheeler, *ibid.*, **72**, 2496 (1950); (d) D. Y. Curtin and E. E. Harris, *ibid.*, **73**, 4519 (1951); (e) R. E. Buckles and N. G. Wheeler, *Org. Syn.*, **33**, 88 (1954).

(6) (a) R. E. Buckles, E. A. Hausman, and N. G. Wheeler, *J. Am. Chem. Soc.*, **72**, 2494 (1950); (b) F. D. Greene, W. A. Remers, and J. W. Wilson, *ibid.*, **79**, 1416 (1957).

(7) (a) J. Wislicenus and F. Seeler, *Ber.*, **28**, 2693 (1895); (b) A. Breuer and T. Zincke, *Ann.* **198**, 154 (1879); (c) P. Pfeiffer, *Ber.*, **45**, 1810 (1912).

(8) L. F. Fieser, *J. Chem. Educ.*, **31**, 291 (1954).

(9) R. E. Buckles and D. F. Knaack, *J. Org. Chem.*, **25**, 20 (1960).

TABLE I

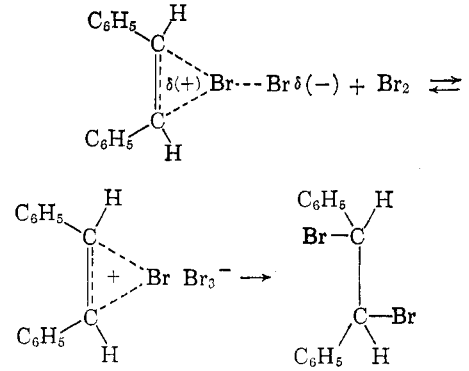
APPROXIMATE FRACTION OF *meso*-α,α'-DIBROMOBIBENZYL FROM THE ADDITION OF BROMINE TO *cis*-STILBENE

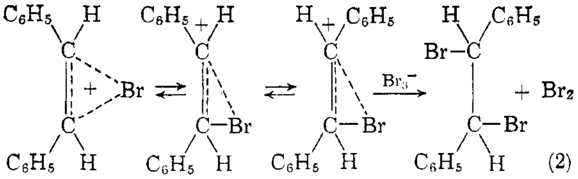
Solvent	D^a	No bromide salt	Bromide salt present
Heptane	1.9	0	...
Cyclohexane	2.0	0	...
CCl_4	2.2	0	...
Benzene	2.3	0.1	...
CS_2	2.6	0.1	...
C_6H_5Cl	5.7	0.4	...
Acetic acid	6.2	0.5^b	...
CH_2Cl_2	9.1	0.5	0
$(CH_2Cl)_2$	10.7	0.4	0
t-BuOH	10.9	$0.3^{b,c}$	...
BuCN	17.4	0.4	...
C_6H_5CN	25.2	0.6^b	...
$C_6H_5NO_2$	34.8	0.9	0.5
CH_3NO_2	35.9	0.9	...
CH_3CN	37.5	0.7	0
H_2O^d	78.5	...	0
H_2O^e	78.5	0.8	0.4

[a] Values of the dielectric constant, *D*, are taken from A. A. Maryott and E. R. Smith, "Table of Dielectric Constants of Pure Liquids," National Bureau of Standards Circular 514, 1951. [b] Experiments with *trans*-stilbene in this solvent gave *meso*-dibromide in each case, but unidentified impurity other than *dl*-dibromide or *trans*-stilbene was consistently present. The same type of impurity was presumably a contaminant in the products from *cis*-stilbene, but its presence was less apparent. [c] Experiments with *cis*-stilbene in *t*-butyl alcohol gave erratic results with the fraction of *meso* dibromide varying from 0.1 to 0.4. [d] The water contained cetyltrimethylammonium bromide and sodium bromide. [e] The water contained sodium dodecyl sulfate.

In Table I are summarized the approximate compositions of the dibromide mixtures obtained from the addition of bromine to *cis*-stilbene in sixteen different solvents. In these same solvents *trans*-stilbene reacted with bromine to give essentially all *meso*-dibromide whether a bromide salt was present or not. In a number of experiments especially when a bromide salt was present the addition of bromine was incomplete and considerable *trans*-stilbene could be detected in the reaction product. Several of these experiments had to be run several times in order to get satisfactory bromine additions. In general, however, unless specifically noted in Table I, the crude dibromides were isolated in essentially 100% yield and the estimates of their compositions indicated only very small amounts of by-products.

The fact that the polar addition of bromine to *cis*-stilbene is most stereospecific in the least polar solvents is rather surprising. Such results can be interpreted in terms of the charge distribution of the polar bromonium-type intermediates shown in equation 1. Such intermediates would be most stable in relatively nonpolar solvents if the charges were as widely distributed over the molecule or ions as possible. Attack by bromine or tribromide ion on either of these bromonium-type intermediates would lead to the *dl*-dibromide as expected from *trans*-addition. As the solvent which is used is more and more polar, the positive ion (or the ion pair) would become more and more easily solvated when the plus charge was predominantly associated with only one benzyl system as shown in equation 2. Such an intermediate would lose its stereochemical identity as fast as rotation about the central bond became relatively rapid compared with the second step of equation 1. As a manifestation of the *cis* effect[10] *cis*-stilbene would then give rise to the more stable *meso*-dibromide. Increased concentration of tribromide (or bromide) salt evidently enhances the rate of the second step of equation 1 relative to that of the rotation of equation 2 so that stereospecificity would be at least partially restored.


(1)


(2)

Product isolation experiments on the addition of bromine to *cis*-stilbene at ice bath temperature in the dark were disappointing. For some reason such experiments gave consistently higher yields of *meso*-dibromide than the amount detected in dibromide products isolated from the smaller scale reactions. Such variation in isolated products has often characterized the reports in the literature as described above in the introductory paragraph.

The compounds most likely to be present in the products isolated as solids from the bromine additions are the *dl*- and *meso*-dibromides and *trans*-stilbene. The predominant infrared bands which were useful for the identification of these compounds are listed in Table II. Because of the low solubility of *meso*-dibromide, quantitative determinations of infrared spectra were not satisfactory. Semiquantitative estimates of the amounts dibromides were possible, however, if no by-products were present. The most intense band for the compounds listed is the one around 692 cm.$^{-1}$—probably associated with the out-of-plane deformation of phenyl hydrogen atoms. This band had approximately the same intensity on a molar basis for

(10) D. Y. Curtin and D. B. Kellom, *J. Am. Chem. Soc.*, **75**, 6011 (1953).

TABLE II

PREDOMINANT INFRARED FREQUENCIES (CM.$^{-1}$) IN CARBON DISULFIDE SOLTUIONS

meso-$(C_6H_5CHBr)_2$	*dl*-$(C_6H_5CHBr)_2$	*trans*-$(C_6H_5CH)_2$
...	...	527
...	535	539
554	...	...
...	630	...
609	614	...
628	636	...
...	670	...
692	695	692
762	772	763
...	...	962

each of the two dibromides. Thus, this peak absorbance served as an approximate isoabsorptive point[11] or internal measure of the concentration of the dibromide mixture in the solution. For the *dl*-dibromide the bands at 535, 772, and especially 630 cm.$^{-1}$ were used for identification while for the *meso* isomer the bands at 762, 628, 609, and especially 554 cm.$^{-1}$ were used. When *trans*-stilbene was present, the bands at 527, 539, and 962 cm.$^{-1}$ were most helpful with an intensity increase in the characteristic band of *meso*-dibromide at 762 cm.$^{-1}$ also being observed.

TABLE III

DEHALOGENATION OF STILBENE DIHALIDES BY SODIUM IODIDE IN 95% ETHANOL

Halogens		Isomer	Time heated, hr.	Reaction, %	*trans* in product, %
Br	Br	*meso*[a]	22	88 ± 6[b]	100 ± 10[b]
Br	Br	*meso*	1.44×10^{3}[c]	96	100
Br	Br	*dl*[d]	22	45 ± 10[b]	31 ± 5[b]
Br	Br	*dl*	1.44×10^{3}[c]	<3	...
I	Cl	*erythro*	22	46	100
I	Cl	*erythro*	168	80	100
Br	Cl	*erythro*	22	12	94
Br	Cl	*erythro*	168	74	100
Br	Cl	*threo*	22	8	40
Br	Cl	*threo*	168	19	45
Cl	Cl	*meso*[e]	22	1	20
Cl	Cl	*meso*[e]	168	1	30
Cl	Cl	*dl*[e]	22	1	45
Cl	Cl	*dl*[e]	168	4	87

[a] These results were obtained from twenty-eight experiments involving known dibromide mixtures. [b] The precision represents the 95% confidence limits. [c] These experiments were carried out at room temperature. [d] These results were obtained from seventeen experiments with pure *dl*-dibromide. [e] The dichlorides were so unreactive that the results have little meaning.

The partially stereospecific debromination of mixtures of *meso*- and *dl*-α,α′-dibromobibenzyl by iodide ion served to give mixtures of *cis*- and *trans*-stilbenes which could be analyzed by the absorbance at two different wave lengths.[11] Under the conditions used (2.0×10^{-5} *M* dibromide heated under reflux for 22 hr. with 1.7×10^{-2} *M* sodium iodide in 95% ethanol) it was found, as shown in Table III, that the *meso*-dibromide consistently reacted almost completely to give all *trans*-stilbene while *dl*-dibromide reacted more slowly as expected[12] to give about 30% *trans*-stilbene. An estimate of the amount of *meso*-dibromide in the mixture was arrived at by the correction of the amount of *trans*-stilbene present after debromination for the 30% known to accompany the *cis*-stilbene from the *dl*-dibromide. The remaining amount of *trans*-stilbene was then a measure of 88% of the *meso*-dibromide in the mixture of dibromides.

The dehalogenations of the stilbene dihalides by sodium iodide are summarized in Table III. *cis*-Stilbene was not isomerized to the *trans* isomer under the conditions of the dehalogenation reactions. The stereospecific *trans* dehalogenation mechanism[13] must be modified by some rotation about the central bond to a more favorable conformation (a manifestation of the *cis* effect[10]) in the case of the *dl*-dibromide or the *threo*-bromochloride. An S_N2 reaction by iodide ion preceding the dehalogenation appears to be less likely in these cases. Such a mechanism is observed[13] with 1,2-dibromides in which the substitution is faster than the elimination. The stilbene dichlorides may undergo a slow substitution by iodide ion (but faster than direct elimination) followed by relatively rapid dehalogenation of the iodochloride, but the reactions with the dichlorides were too slow for any conclusive results to be obtained.

More extensive rotation about the central bond was observed during dehalogenation of the *dl*-dibromide by zinc or copper in 95% ethanol as shown in Table IV. From 80 to 90% *trans*-stilbene was formed in these cases. Such results are consistent with those reported[8,14] for similar dehalogenations. The nonstereospecific dehalogenation of the *dl*-dibromide by zinc in ether–acetic

---

[11] J. D. Fitzpatrick and M. Orchin, *J. Org. Chem.*, **22**, 1177 (1957); Moshe Ish-Shalom, J. D. Fitzpatrick, and M. Orchin, *J. Chem. Educ.* **34**, 496 (1957).

[12] W. G. Young, D. Pressman, and C. D. Coryell, *J. Am. Chem. Soc.*, **61**, 1640 (1939).

[13] J. Hine, "Physical Organic Chemistry," 2nd ed., McGraw Hill Book Co., New York, N. Y., 1962, pp. 208–210.

[14] W. M. Schubert, B. S. Rabinowitch, N. R. Larson, and V. A. Sims, *J. Am. Chem. Soc.*, **74**, 4590 (1952).

TABLE IV
DEBROMINATION OF STILBENE DIBROMIDES BY ZINC OR COPPER

Isomer	Metal	Time heated, hr.	Reaction, %	*trans* in product, %
meso	Zn	0.5	80	100
meso	Zn	1.0	90	100
meso	Zn	15	97	100
meso	Cu	0.5	21	100
meso	Cu	15	94	100
dl	Zn	0.5	43	90
dl	Zn	1.0	99	87
dl	Zn	15	93	88
dl	Cu	0.5	16[a]	100[a]
dl	Cu	15	105	82

[a] The filtered reaction mixture was cloudy so that estimates of absorbances were quite unreliable because of scattering.

acid has been interpreted[8] as involving isomerization of *cis*-stilbene to *trans*-stilbene. On the other hand it has been reported[14] that rotation about the incipient double bond must take place during the debromination by zinc in ethanol or by magnesium in tetrahydrofuran. Under the reaction conditions *cis*-stilbene was not isomerized. This interpretation of the debrominations by zinc of copper in 95% ethanol must also be inferred from the present investigation. Neither *cis*-stilbene nor *dl*-α,α'-dibromobibenzyl was isomerized extensively enough to account for observed nonstereospecificity under the conditions of debromination.

Experimental

Stilbenes.—The *cis*-stilbene, b.p. 135–136° (10 mm.), prepared by the modified procedure[6e,15] involving the decarboxylation of α-phenylcinnamic acid, was usually used without further purification. Chromatographic separation on alumina followed by elution with hexane did not seem to improve its purity as determined by its absorption spectrum[16] n the ultraviolet region.

Commercial *trans*-stilbene was crystallized from hexane or ethanol until material of m.p. 124–125° was obtained. Its ultraviolet spectrum checked well with that observed during an earlier study.[16]

Stilbene Dihalides.—Stilbene dihalides used were available from earlier investigations: *meso*-α,α'-dibromobibenzyl,[5b] m.p. 237–239° (dec.); *dl*-α,α'-dibromobibenzyl,[5c] m.p. 110–111°; *meso*-α,α'-dichlorobibenzyl,[9] m.p. 191–192°; *dl*-α,α'-dichlorobibenzyl,[9] m.p. 91–92°; *erythro*-α-bromo-α'-chlorobibenzyl,[15,17] m.p. 222–224° (dec.); *threo*-α-bromo-α'-chlorobibenzyl,[15,17] m.p. 99–101°; α-chloro-α'-iodobibenzyl (presumably *erythro*),[18] m.p. 133–134° (dec.).

Bromide Additions.—A 0.10-g. sample (5.6×10^{-4} mole) of either *cis*- or *trans*-stilbene and 2.5 ml. (1.6×10^{-3} mole) of a stock solution of bromine (1.0 g. of bromine per 10 ml. of solution) were mixed with 15 ml. of solvent. The reaction mixtures were allowed to stand at room temperature in the dark for at least 3 days. The bromine color of the reaction mixtures was removed by excess aqueous sodium sulfite. Water-insoluble solvents were removed by steam distillation. The aqueous residue contained the solid dibromide product which was separated by filtration on a sintered glass filter and washed with water. When a water-soluble solvent was used, the reaction mixture was mixed with enough water to precipitate all of the dibromide, which was isolated by filtration. Yields of crude dibromides of the order of 0.20 g. (100%) were consistently obtained. The compositions of these crude mixtures are summarized in Table I.

In the experiments with a bromide salt present the same amounts of reagents and solvent were used, but 0.81 g. (2.5×10^{-3} mole) tetrabutylammonium bromide[19] was also added to the reaction mixture. In the case of ethylene chloride as a solvent, experiments with 0.20 g. (6.2×10^{-4} mole) of tetrabutylammonium bromide were also carried out. In other experiments in ethylene chloride 0.48 g. (1.0×10^{-3} mole) of tetrabutylammonium tribromide[19] was used instead of bromine. In each of these cases with *trans*-stilbene reaction times of at least three weeks were necessary. The amount of bromide present in each case did not affect the composition of the dibromide mixture. From *trans*-stilbene *meso*-dibromide was obtained when the addition was complete. From *cis*-stilbene *dl*-dibromide was the product.

Bromine additions in water were carried out with 0.10 g. (5.6×10^{-4} mole) of stilbene in 250 ml. of water containing 0.25 g. (1.6×10^{-3} mole) of bromine. In some of the experiments 0.9 g. of sodium dodecylsulfate was used as a surface-active agent; in others, 0.9 g. of cetyltrimethylammonium bromide. In all of the experiments, when bromide ion was present, 3.5 g. of sodium bromide dihydrate was dissolved in the water. No reaction took place with *trans*-stilbene in water unless it was first dissolved in 2 ml. of benzene. The products of these reactions were isolated by filtration followed by extensive washing in order to remove the detergent.

In larger scale experiments 4.0 g. (0.022 mole) of *cis*-stilbene in 90 ml. of solvent was mixed slowly with 5.0 g. (0.031 mole) of bromine in 50 ml. of solvent in the dark at 0–3°. The solution was evaporated in the dark. The residue was mixed with 30 ml. of hot absolute ethanol. Cooling yielded *meso*-dibromide. From ethylene chloride was obtained 4.0 g. (53%); from carbon tetrachloride 2.3 g. (38%); from carbon disulfide, 1.8 g. (24%).

Bromination of the solvent was not a serious side reaction under the conditions used for the bromine addition reactions. The stock solutions of bromine appeared to be stable for several weeks in the dark with no appreciable loss of color nor evolution of hydrogen bromide being apparent.

Dehalogenation by Sodium Iodide.—A 4.0×10^{-3}-g. sample (1.18×10^{-5} mole) of the dibromide mixture was weighed and mixed with 10 ml. of 0.10 M sodium iodide in 95% ethanol and 50 ml. of 95% ethanol in a flask of low actinic, red borosilicate glass. This solution was boiled under refluxed for 22 hr. It was then cooled and the volume was made up to 100 ml. in a volumetric flask. A little powdered sodium sulfite was mixed with the solution in order to remove the color caused by triiodide ion. The ultraviolet absorption spectrum of the solution was measured in order to determine[11] the composition of the stilbene mixture. Known mixtures and pure samples of *meso*- and *dl*-α,α'-dibromobibenzyl were subjected to this debromination method and the measured compositions of the stilbene mixtures were correlated with those of the dibromide mixtures. The results are summarized in equations 3 and 4 where: A is the total concentration of stilbene in the solution; B is the concentration of *cis* stilbene in the solution; C is the concentration of *trans*-stilbene arising from *meso*-dibromide; D is the original concentration of dibromide mixture based on the final volume; M is the calculated fraction of *meso* isomer in the original mixture based on the amount which was dehalogenated to *trans*-stilbene; and N is the actual fraction of *meso* isomer in the mixture. The precision sets the 95% confidence limits of the numbers.

---

(15) R. E. Buckles, J. L. Forrester, R. L. Burham, and T. W. McGee, *J. Org. Chem.*, **25**, 24 (1960).

(16) R. E. Buckles, *J. Am. Chem. Soc.*, **77**, 1040 (1955).

(17) R. E. Buckles and J. W. Long, *ibid.*, **73**, 998 (1951).

(18) R. E. Buckles and D. F. Knaack, unpublished work.

(19) R. E. Buckles and L. Harris, *J. Am. Chem. Soc.*, **79**, 886 (1957).

$$\left(A - \frac{B}{0.69 \pm 0.05}\right)\frac{1}{D} = \frac{C}{D} = M \qquad (3)$$

$$N = (0.88 \pm 0.06)M + (0.03 \pm 0.04) \qquad (4)$$

Dehalogenations with sodium iodide were carried out on other stilbene dihalides which were available. The directions for debrominations were followed with heating for various lengths of time. The results are summarized in Table III.

Solutions in 95% ethanol made up from 10 ml. of 1.09×10^{-3} M *cis*-stilbene, 10 ml. of 5.39×10^{-4} M iodine, and 50 ml. of 0.10 M sodium iodide were boiled for 22 hr. After dilution to 100 ml. and removal of triiodide ion by sodium sulfite the absorption spectrum showed a maximum of 2% isomerization to *trans*-stilbene.

Dehalogenation by Zinc or Copper.—A 4.0×10^{-3}-g. sample (1.18×10^{-5} mole) was weighed and dissolved in 50 ml. of 95% ethanol in a flask of low actinic red borosilicate glass. Excess (0.01 g.) powdered zinc or copper bronze was added and the mixture was boiled under reflux. The solution was filtered and the filtrate was diluted to 100 ml. total volume. The spectrometric analyses of the reaction mixtures are summarized in Table IV.

Solutions of 10 ml. of 1.09×10^{-3} M *cis*-stilbene, 0.005 g. of copper or zinc metal, and 0.005 g. of copper(II) bromide or zinc bromide with 40 ml. of 95% ethanol were boiled under reflux for 22 hr. The solutions were diluted to 100 ml. Analysis showed 5% isomerization with zinc bromide and 10% isomerization with copper(II) bromide.

A 0.20-g. sample of *dl*-dibromide in 50 ml. of 95% ethanol containing 0.20 g. of zinc bromide was boiled for 0.5 hr. With copper(II) bromide a similar reaction mixture was boiled 22 hr. The dibromide which was isolated by dilution with water in each case was essentially pure *dl*-dibromide based on infrared analysis. With 0.20 g. each of copper(II) bromide and copper metal the product was a mixture of *dl*-dibromide and *trans*-stilbene. No *meso*-dibromide could be detected by infrared analysis. Similar experiments carried out at room temperature with mixtures of bromine and excess copper bronze for 14 days gave products which were *meso*-dibromide contaminated in several experiments with *trans* stilbene. No *dl*-dibromide could be detected by infrared analysis.

Absorption Spectra.—Ultraviolet spectra were measured in 1.00-cm. silica cells on a Cary Model 11 recording spectrophotometer. Analyses of stilbene mixtures were based on the following molar absorptivities: at 295 mμ, *trans* 2.70×10^4, *cis* 0.78×10^4; at 307 mμ, *trans* 2.61×10^4, *cis* 0.47×10^4; at 320 mμ, *trans* 1.63×10^4, *cis* 0.17×10^4.

Infrared spectra were measured in carbon disulfide solutions in 1.0-mm. potassium bromide cells. Mineral oil mulls were also used. Measurements were made on the following Perkin–Elmer spectrometers: Model 21 with a sodium chloride prism, NaCl Model 137B Infracord, and KBr Model 137 Infracord. The predominant, useful absorption bands are summarized in Table II.

Other Methods of Analysis of Stilbene Dibromides.—Since *meso*-dibromide is quite insoluble a gravimetric analysis was possible, but in such a determination the amount of *dl*-dibromide could not be checked quantitatively. Melting points of mixtures of *meso*- and *dl*-dibromides were of little value. The *meso* isomer was essentially insoluble in the liquid *dl* isomer so that there was little effect on the m.p. with relatively large amounts of *dl* present. Solutions of *meso*- and *dl*-dibromides in carbon tetrachloride showed only very small differences (0.0003 at 10^{-3} M) in refractive index. Such differences could be accentuated by the use of a Zeiss Laboratory Interferometer with an all-glass, 10-cm. cell. The liquid in the constant temperature bath of the instrument had to have approximately the same index of refraction as the solvent used in the cell so that the interference fringes would be properly aligned. The best bath liquid tried for carbon tetrachloride (n^{15}D 1.46305) as a solvent was a mixture (n^{15}D 1.46301) of 40% alkane fraction, b.p. 135–144°, and 60% mixed xylenes. Although this was a possible method of analysis for dilute solutions of the dibromides, the use of the interferometer was not pursued further in the present investigation.

A New Method for the Synthesis of Amino Acids. Synthesis of Amino Acids and Their Derivatives through 2,4-Disubstituted 2-Imidazolin-5-ones[1]

AKHLAQ R. KIDWAI AND GANAPATHIPLACKAL M. DEVASIA

Department of Chemistry, Aligarh Muslim University, Aligarh, India

Received April 27, 1962

Unsaturated 2,4-disubstituted 2-imidazolin-5-ones were prepared in good yields by the condensation of aldehydes with a mixture of glycine ester and an imidic acid ester as well as with a mixture of their hydrochlorides. They were hydrogenated to saturated 2-imidazolin-5-ones which were hydrolyzed to acylamino acid amides, acylamino acids, and amino acids under different conditions.

One of the best methods of preparing α-amino acids (especially aromatic) is the reduction and hydrolysis of unsaturated 2,4-disubstituted 5-oxazolones (azlactones) (IV, —O— instead of —NH—).[2] Unsaturated 2,4-disubstituted 2-imidazolin-5-ones (IV) which are the nitrogen analogs of the oxazolones have not been used so far in the synthesis of amino acids. The present work describes (a) two improved methods of synthesis of the unsaturated 2-imidazolin-5-ones (IV); (b) their hydrogenation to the saturated 2-imidazolin-5-ones (V); and (c) hydrolysis of the latter into acyl amino acid amides (VI), acyl amino acids (VII), and amino acids (VIII).

(a) Synthesis of Unsaturated 2,4-Disubstituted 2-Imidazolin-5-ones (IV).—The known methods of preparing the unsaturated 2,4-disubstituted 2-imidazolin-5 ones (IV) are not of much practical importance.[3,4]

---

[1] From the Ph.D. thesis of G. M. Devasia, 1961. This work was supported by the Scientific Research Committee, U.P., and the Aligarh Muslim University.

[2] H. E. Carter, "Organic Reactions" Vol. III, John Wiley & Sons, Inc., New York, N. Y., 1947, pp. 198–239.

[3] K. Hofmann, "The Chemistry of Heterocyclic Compounds," Vol. VI, Interscience Publishers, Inc., New York, N. Y., 1953, pp. 93–97.

[4] H. Lehr, S. Karlan, and M. W. Goldberg, *J. Am. Chem. Soc.* **75**, 3640 (1959).