a stoichiometric yield of glycine and ammonia. N-Formylglycine was inactive and thus not considered as an intermediate in the conversion of formiminoglycine to glycine.

TABLE I

FUNCTION OF TETRAHYDROFOLIC ACID IN FORMIMINOGLYCINE DEGRADATION

Thunberg tube, 4.5 ml.; 100 μM. phosphate buffer, *p*H 7.5; 3 μM. $Na_2S_2O_4$; extract (4 mg. bacterial nitrogen); 1 mg. THFA where indicated (prepared according to Broquist, THIS JOURNAL, **73**, 3535 (1951) half life in absence of O_2 about 2 weeks); after evacuation, 40 μM. substrate tipped from side arm; incubated 60′ at 35°.

Substrate and enzyme	Substrate used, μM.	Products formed Glycine	NH_3 μM.
Formiminoglycine, 40 μM.			
Extract, crude	40	21	56
Extract, Dowex	0	0	0
Extract, Dowex + THFA, 1 mg.	38	36	42
N-Formylglycine, 40 μM.			
Extract, crude	0	0	..
Extract, Dowex + THFA, 1 mg.	0	0	..

These observations suggested to us that formiminotetrahydrofolic acid might occur as an intermediate as

$$\text{Formiminoglycine} + \text{THFA} \rightleftharpoons \text{glycine} + \text{formimino-THFA} \quad (2)$$

$$\text{Formimino-THFA} \xrightarrow{H_2O} \text{THFA} + \text{ammonia} + \text{formate} \quad (3)$$

To test this postulate, 40 μM. glycine-2-C^{14} and 40 μM. unlabeled formiminoglycine were incubated with "Dowexed" extract, alone and with added tetrahydro-folic acid. Aliquots were chromatographed as described above and the chromatographs scanned for radioactivity with an actigraph (Nuclear instrument, Model C-100) previously calibrated with glycine-2-C^{14} of known activity. As shown in Table II, the radioactivity of glycine-2-C^{14} was equilibrated rapidly with formiminoglycine in a tetrahydrofolic acid and enzyme dependent reaction. Formylglycine does not exchange with glycine-2-C^{14} nor form formiminoglycine. Hydrolysis of the formiminoglycine formed yielded C^{14} in the glycine only. The reaction sequence beyond "formimino-tetrahydrofolic acid," of which one route leads to ammonia plus formate (reaction 3), is slower than the exchange. Preliminary data indicate that the formimino carbon from formiminoglycine (C_8 of purine) may become available for hydroxymethylation,[9] thus implying a variety of reactions and enzymatic steps beyond the postulated "formimino-tetrahydrofolic acid" intermediate. The activity of tetrahydrofolic acid with these unfractionated extracts does not impinge upon the coenzyme form of this factor.[10]

TABLE II

FORMIMINO TRANSFER TO GLYCINE-2-C^{14}; TETRAHYDROFOLIC ACID DEPENDENCE

Protocol as Table I; substrates, 40 μM. glycine-2-C^{14} (SA 3150 dis./sec./μM.); 40 μM. formiminoglycine; 1 mg. THFA where added.

Incubation, min.	C^{14}, dis./sec./μM. Glycine	Formimino-glycine
0	3150	0
2	2210	905
5	1650	1230
15	1530	1310
15, w/o extract	3150	0
15, w/o THFA	3150	0

The accumulation of formiminoglutamic acid from histidine in folic acid deficient rats,[11,12] and in preparations of mammalian liver[13] and of microorganisms,[14] suggests a similar sequence for this substrate and thus that formimino transfer may constitute a biologically important reaction type.

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THE STEREOCHEMISTRY OF BASE-CATALYZED ADDITIONS OF THIOLS TO ACETYLENES

Sir:

Although a high degree of stereospecificity has been realized for the addition of hydrogen, halogens and hydrogen halides to acetylenes, similar studies on *nucleophilic* additions have not been published.[1] We have now observed that base-catalyzed additions of thiols to the acetylenic compounds, phenylacetylene, 2-butyne, chloroacetylene and *p*-tolylmercaptoacetylene, proceed in a *trans* fashion.

Refluxing an alcoholic solution of phenylacetylene with sodium *p*-toluenethiolate for 15 hours resulted in a 79% yield of *cis*-ω-styryl *p*-tolyl sulfide (none of the *trans* isomer was isolated), which was readily oxidized by hydrogen peroxide to its sulfone, m.p. 76–77°, λ_{max} 266 mμ, ϵ_{max} 14 × 10^3; *trans* form,[2] m.p. 121°, λ_{max} 276 mμ, ϵ_{max} 25.9 × 10^3. *trans*-ω-Styryl *p*-tolyl sulfone also has been prepared by the Friedel–Crafts reaction of *trans*-ω-styrenesulfonyl chloride[3] with toluene.[4]

Similar results were obtained with sodium methanethiolate and phenylacetylene, the product being methyl *cis*-ω-styryl sulfide, yield 73%, b.p. 101.5° (5 mm.). (*Anal.* Calcd. for $C_9H_{10}S$: C, 71.95; H, 6.71. Found: C, 71.28; H, 6.88.) Its sulfone, m.p. 66–67°, λ_{max} 261 mμ, ϵ_{max} 19.9 × 10^3, was different from the *trans* isomer[4], m.p. 78–79°, λ_{max} 264 mμ, ϵ_{max} 23.7 × 10^3. The 78–79°

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m.p. isomer showed the characteristic *trans* absorption band at 10.35 μ. Both of these compounds were reduced to methyl β-phenylethyl sulfone.

With 2-butyne, an alcohol solution of sodium *p*-toluenethiolate reacted to give a 65% yield of 2-*p*-tolylmercapto-*trans*-2-butene, b.p. 83–86° (2 mm.), $n^{20}D$ 1.5634. (*Anal.* Calcd. for $C_{11}H_{14}S$: C, 74.10; H, 7.91. Found: C, 73.82; H, 7.87). This product has a strong infrared absorption band at 7.70 μ; *trans*-2-butene and 2-chloro-*trans*-2-butene have a similar band at 7.80 μ which is absent in their *cis* isomers.

Chloroacetylene was treated with an alcoholic solution of an equimolar amount of sodium *p*-toluenethiolate to give [in addition to a 52.2% conversion (77.4% yield) to *cis*-bis-(*p*-tolylmercapto)-ethene[5]] *cis*-1-chloro-2-(*p*-tolylmercapto)-ethene (13.7% conversion, 20.3% yield), b.p. 99–102° (2.2 mm.), $n^{20}D$ 1.5901, and having a strong characteristic absorption at 7.78 μ. This band is absent in the spectrum of the *trans* isomer as prepared by adding *p*-toluenesulfenyl chloride to acetylene[6]; neither of these isomers showed infrared absorption bands associated with the group, $>C{=}CH_2$. (*Anal.* Calcd. for the *cis* sulfone, m.p. 39–40°, $C_9H_9SO_2Cl$: C, 49.84; H, 4.19; Cl, 16.36. Found: C, 50.17; H, 4.80; Cl, 16.00). The rule of *trans* elimination[7] [*cis*-1-chloro-2-(*p*-tolylmercapto)-ethene undergoes the sodium ethoxide-promoted reaction with thiolate reagent to form the *cis*-bis(arylmercapto)-ethene much more readily than the *trans* isomer does] also supports these assignments of configuration.

p-Tolylmercaptoacetylene, b.p. 73.0–77.0° (2.5 mm.), $n^{20}D$ 1.5721. (*Anal.* Calcd. for mercuric deriv., $(C_9H_7S)_2Hg$: C, 43.65; H, 2.85; S, 12.96; Hg, 40.52. Found: C, 43.50; H, 2.87; S, 12.84; Hg, 40.47), characteristic infrared absorption bands at 3.08 and 4.90 μ, on treatment with an alcoholic solution of an equimolar amount of sodium *p*-toluenethiolate gave *cis*-bis-(*p*-tolylmercapto)-ethene[5,8] (77% conversion) without any of its *trans* isomer being isolated.

These nucleophilic additions may be proceeding by a stepwise mechanism, with formation of the intermediate carbanion, $\overset{\cdot\cdot}{\square}C{=}C\begin{matrix}R'\\R''\end{matrix}$. This configuration of the carbanion would be expected on the basis that in the transition state the negative charge (electron pair) and the negatively charged thiolate group would tend to be as far apart as possible. Considering the stereochemistry of the isoelectronic oximes, such a carbanion would be expected to be geometrically stable. However, the mechanism of addition may also involve a synchronous process. Evidence is now being sought to clarify this point.

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