

spectra in acidic and neutral solutions showed great similarity to those of 3-hydroxykynurenine (III),⁵ while the bathochromic shifts in the three peaks upon passing from neutral to alkaline solution were closely parallel to those observed for *m*-hydroxyacetophenone⁶ (see Table I).

Table I. Ultraviolet Spectra (EtOH)^a

	I		3-Hydroxykynurenine		<i>m</i> -Hydroxyacetophenone	
	λ_{\max}	ϵ	λ_{\max}	ϵ	λ_{\max}	ϵ
1 N HCl	365	(350)	370	(740)	308	(2,300)
	320	(1,520)	315	(2,650)		
	254	(4,040)	252	(8,750)		
	218	(6,200)	<i>b</i>			
Neutral	378	(3,070)	370	(4,250)	251	(9,100)
	273	(5,100)	269	(9,840)	215	(17,600)
	235	(13,800)	<i>b</i>			
1 N NaOH	414	(2,660)			349	(2,400)
	292	(5,150)	<i>b</i>		266	(5,000)
	253	(13,600)			234	(22,800)
Δ , neutral	+36				+41	
	-19				+15	
	+18				+19	

^a λ_{\max} , $m\mu$ (ϵ). ^b Not measured.

The high-resolution mass spectrum of I revealed its composition as $C_{10}H_9NO_4$ (M^+ at m/e 207.05411; calcd. 207.05315), and showed prominent peaks for loss of CO_2 (m/e 163.06360 = $C_9H_9NO_2$, calcd. 163.06332); $COOH$ (m/e 162); $COO(H) + CO(+H)$ (m/e 133.05265, 134.06037, and 135.06809 = C_8H_7-9NO , calcd. 133.05276, 134.06059, and 135.06841; ions a, b, and c); $COOH + C_2H_2$ (m/e 136.03966 = $C_7H_8NO_2$, calcd. 136.03985; ion d); and $CO_2 + CO + CH_3$ (m/e 120.04473 = C_7H_8NO , calcd. 120.04494; ion e).⁷

Air oxidation of I in basic solution gave xanthurenic acid (IIa), identical with synthetic material⁸ by paper chromatography in two widely differing systems. Furthermore, oxidation of the dimethyl derivative of the pigment (see above) with chloranil in refluxing benzene gave methyl 4-hydroxy-8-methoxyquinaldate (IIb), shown identical with synthetic material⁸ by melting point and mixture melting point (undepressed), infrared spectrum (superimposable), thin-layer chromatography, and fluorescence (brilliant yellow-white).

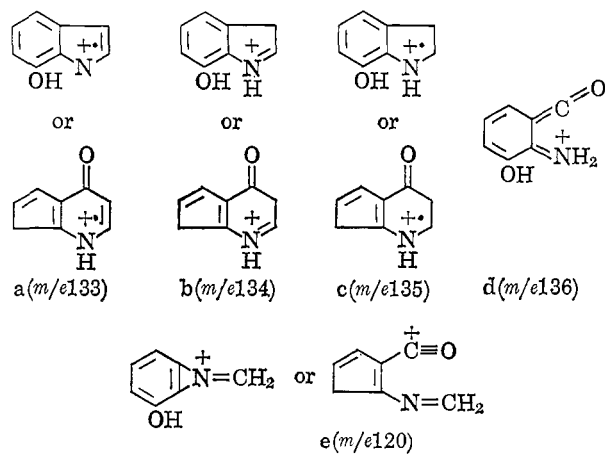
The absolute configuration of the natural pigment was inferred as L through the large positive molecular rota-

(5) C. E. Dalgliesh, *Biochem. J.*, **52**, 3 (1953). While I, by infrared, is clearly zwitterionic in the crystalline state, the basic nitrogen appears to remain unprotonated in neutral ethanolic solution.

(6) L. Doub and J. M. Vandenbelt, *J. Am. Chem. Soc.*, **71**, 2414 (1949).

(7) The author is especially indebted to Dr. Dieter Becher of Stanford University for the high-resolution mass spectral work on I, which aided materially in the resolution of its structure. Appropriate metastable peaks were observed for most fragmentations. For a discussion of the expulsion of CO from phenols (leading to the alternative structures for a, b, c, and e), see H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day, San Francisco, Calif., 1964, pp. 167, 168.

(8) Synthesized by a minor variant of the published method (A. Furst and C. J. Olsen, *J. Org. Chem.*, **16**, 412 (1951)), in which the initial condensation was effected at 0° spontaneously and in quantitative yield with *o*-anisidine and dimethyl acetylenedicarboxylate (K. S. Brown, Jr., unpublished investigations). The author thanks Professor F. Feigl and Dr. A. Roseira for generous donations of *o*-anisidine, and Dow Quimica do Brasil S. A. for a sample of Dowtherm A.



tion change (+130° in MeOH) observed upon passing from the neutral to the protonated form.⁹

Besides being a new butterfly pigment, compound I probably represents a new metabolite of tryptophan. Further work is presently under way to study its biogenesis¹⁰ and to investigate its possibly wider role in insect metabolism.^{3, 10}

(9) This property, characteristic in aqueous solutions for α -amino acids possessing the L-configuration, should not be expected to change qualitatively in methanolic solution. See J. S. Fruton and S. Simmonds, "General Biochemistry," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1953, p. 97.

(10) Compound I could theoretically be produced either by stereospecific cyclization of $\beta(o$ -amino-*m*-hydroxybenzoyl)acrylate (see A. Butenandt, U. Scheidt, and E. Biekert, *Ann.*, **586**, 229 (1954), in which I is suggested as a nonisolable intermediate in the base-catalyzed *in vitro* cyclization of 3-hydroxykynurenine to xanthurenic acid) or by stereospecific reduction of xanthurenic acid in the insect (see footnote 3). The presently accepted pathway for the biosynthesis of xanthurenic acid (spontaneous cyclization of the α -ketocarboxylate resulting from transamination of 3-hydroxykynurenine) would probably favor the latter pathway.

(11) The author gratefully acknowledges financial assistance from the Rockefeller Foundation in support of a joint research project between Stanford University and the Universidade do Brasil, on Brazilian natural products. Some initial experiments leading to this work were performed by Dr. Ed Paschoal Carrazoni of the Universidade do Recife. Special thanks are due to Dr. Olaf Mielke of the Museu Nacional, Rio de Janeiro, for his assistance in location, collection, and identification of the insects studied. The author is indebted to Prof. Carl Djerassi of Stanford University for his inspiration, guidance, and assistance during the course of this work.

Keith S. Brown, Jr.¹¹

Centro de Pesquisas de Produtos Naturais
Faculdade Nacional de Farmacia
Rio de Janeiro ZC-82, Brazil

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Additions of Iodine Azide to Olefins.

Stereospecific Introduction of Azide Functions¹

Sir:

The chemistry of organic and inorganic azides attracted renewed attention recently when it was shown that these compounds are useful in the generation of nitrene intermediates and in the synthesis of a variety of heterocyclic compounds.² In connection

(1) (a) Stereochemistry of Organic Nitrogen Compounds. VI. For paper V see A. Hassner and W. A. Wentworth, *Chem. Commun.* (London), 44 (1965). (b) Support of this work by Grant 2004A1,4 from the Petroleum Research Fund, American Chemical Society, and by Grant CA4474 of the National Institutes of Health is gratefully acknowledged.

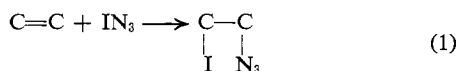
(2) See, for instance (a) D. H. R. Barton and A. N. Starratt, *J. Chem. Soc.*, 2444 (1965); (b) F. D. Marsh and M. E. Hermes, *J. Am. Chem. Soc.*, **86**, 4506 (1964); (c) R. Huisgen, *Angew. Chem. Intern. Ed. Engl.*, **2**, 565 (1963); (d) L. H. Zalkow, A. C. Oehlschlager, G. A. Cabat, and R. L. Hale, *Chem. Ind.* (London), 1556 (1964); (e) W. Lwowski and T. W. Mattingly, Jr., *J. Am. Chem. Soc.*, **87**, 1947 (1965).

Table I

Olefin	Adduct ^a	Yield, %
Cyclohexene	<i>trans</i> -1-Azido-2-iodocyclohexane	82
Styrene	α -Azido- β -iodoethylbenzene	70
<i>cis</i> -Stilbene	<i>threo</i> -1-Azido-2-iodo-1,2-diphenylethane	63 (89-90) ^b
<i>trans</i> -Stilbene	<i>erythro</i> -1-Azido-2-iodo-1,2-diphenylethane	80 (133-134 ^c)
<i>cis</i> -2-Butene	<i>threo</i> -2-Azido-3-iodobutane	67
<i>trans</i> -2-Butene	<i>erythro</i> -2-Azido-3-iodobutane	64
2-Cholestene	2 β -Azido-3 α -iodocholestane	20 (101-102 ^c)

^a Satisfactory analyses were obtained for all new compounds. All spectral data (infrared n.m.r., mass) are consistent with the assigned structure. ^b The numbers in parentheses indicate melting points. All other compounds were obtained as liquids.

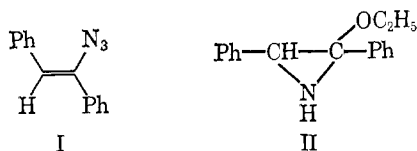
with our efforts toward stereospecific introduction of nitrogen functions into organic compounds,³ we wish to report the addition of iodine azide to olefins leading to β -iodo alkyl azides (eq. 1) in good yield (see Table I).



Iodine azide was described by Hantzsch⁴ as an unstable solid prepared from silver azide and iodine. We were able to generate this pseudohalogen more conveniently from iodine monochloride and sodium azide in dimethylformamide or acetonitrile solution and add it *in situ* to several olefins.⁵ That this addition occurs stereospecifically *trans* is shown by exclusive formation of the *threo*- and *erythro*-2-azido-3-iodobutane, respectively, from *cis*- and *trans*-2-butene. Similar stereospecificity was observed for *cis*- and *trans*-stilbene. Furthermore the product of addition to 2-cholestene is the *trans*-diaxial 2 β -azido-3 α -iodocholestane.⁶ Addition of iodine azide to styrene followed by subsequent dehydrohalogenation yielded the known α -azido styrene⁷ thereby establishing the position of the azide function. These data are accommodated by assuming an iodonium ion intermediate which is opened *trans*-diaxially in the steroid example and at the benzylic carbon in the styrene case⁸ by the azide ion.

trans-1-Azido-2-iodocyclohexane on dehydrohalogenation with base yields only 3-azidocyclohexene, suggesting the low acidity of a hydrogen α to an azide function.

Reaction of *threo*-1-azido-2-iodo-1,2-diphenylethane with alcoholic base yields α -azido-*trans*-stilbene (I), m.p. 43-45°. Light irradiation of I might be expected to lead to 2-phenylindole *via* a nitrene intermediate in



(3) A. Hassner and C. Heathcock, *J. Org. Chem.*, **30**, 1748 (1965).

(4) A. Hantzsch, *Ber.*, **33**, 524 (1900).

(5) The same products are obtained if olefin is added to a clear orange solution obtained by filtration of the sodium azide-iodine monochloride reaction mixture. This infers that one is dealing with an iodine azide species in solution. A mixture of bromine and sodium azide leads merely to the formation of dibromide from the olefin.

(6) For conformation assignments in steroids based on n.m.r. spectra see A. Hassner and C. Heathcock, *J. Org. Chem.*, **29**, 1350 (1964).

(7) G. Smolinsky, *ibid.*, **27**, 3557 (1962).

(8) A. Hassner and C. Heathcock, *Tetrahedron Letters*, 1125 (1964).

analogy with the suggestion by Wenkert and Barnett⁹ for the pyrolysis of 2-phenylcyclohexanone oxime to tetrahydrocarbazole. However, the only product, isolated in 40% yield from the photolysis of I in cyclohexane, was 2,3,5,6-tetraphenylpyrazine. This product may have arisen from the initially formed 2,3-diphenylazirine. On the other hand, treatment of *erythro*-1-azido-2-iodo-1,2-diphenylethane with ethanolic base yielded only 2,3-diphenyl-2-ethoxyaziridine (II), m.p. 83-85°, and no unsaturated azide. The structure of II was obvious from its n.m.r. and mass spectrum and from its conversion under acid conditions to 2,3,5,6-tetraphenylpyrazine.¹⁰

Reduction of the azido function in β -iodo azides can be accomplished by means of diborane. Thus α -azido- β -iodoethylbenzene was converted to α -amino- β -iodoethylbenzene in 75% yield, isolated as its hydrochloride.

(9) E. Wenkert and B. F. Barnett, *J. Am. Chem. Soc.*, **82**, 4671 (1960).

(10) α -Amino ketones are known to dimerize readily and ultimately to lead to pyrazines.

Alfred Hassner, Louis A. Levy

Department of Chemistry, University of Colorado
Boulder, Colorado

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An Electron Impact Study of the Bond Dissociation Energies of Some Trimethyltin Compounds

Sir:

In common with many areas of organometallic chemistry, bond dissociation energies in organotin compounds are virtually unknown. However, a considerable body of thermochemical data is available for alkyltin molecules,¹⁻⁷ which combined with electron impact dissociation data permits calculation of bond dissociation energies in these compounds. We wish to report here results of such an electron impact study of the formation of the trimethylstannium ion from substituted trimethylstannanes.

Appearance potentials of the $(\text{CH}_3)_3\text{Sn}^+$ ion were determined by the retarding potential difference method⁸ on a modified Bendix Model 14-101 time-of-flight mass spectrometer. The energy spread of the electrons was approximately 0.1 e.v. and xenon was used to calibrate the electron energy scale. The results are shown in Table I. The indicated uncertainties in the appearance potentials are average deviations for replicate experiments performed over a period of several months.

The appearance potentials in Table I were measured for m/e 165 which corresponds to the Sn^{120} isotope and which is the most abundant mass peak in all the spectra. The agreement of our appearance potential

(1) E. R. Lippincott and M. C. Tobin, *J. Am. Chem. Soc.*, **75**, 4141 (1953).

(2) W. J. Jones, D. P. Evans, T. Gulwell, and D. C. Griffith, *J. Chem. Soc.*, 39 (1935).

(3) W. F. Lautsch, *Chem. Tech.* (Berlin), **10**, 419 (1958).

(4) A. A. Balandin, E. I. Klabunovskii, M. P. Kozina, and O. D. Ul'yanova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, **12** (1957).

(5) C. R. Dillard, E. H. McNeill, D. E. Simmons, and J. B. Yeldell, *J. Am. Chem. Soc.*, **80**, 3607 (1958).

(6) I. B. Rabinovich, V. I. Telnai, P. N. Nikolhev, and G. A. Razuvaev, *Dokl. Akad. Nauk SSSR*, **138**, 852 (1961).

(7) J. V. Davies, A. E. Pope, and H. A. Skinner, *Trans. Faraday Soc.*, **59**, 2237 (1963).

(8) R. E. Fox, W. M. Hickam, and T. Kjeldaa, *Rev. Sci. Instr.*, **26**, 1101 (1955).