J. CHEM. SOC., CHEM. COMMUN., 1982

Synthesis and cis-to-trans Isomerization of N,N'-Diacyl Derivatives of Indigotin Jun-ichiro Setsune,^a Hirofumi Wakemoto,^a Kimihiro Matsukawa,^a Sho-ichi Ishihara,^b Ryo-ichi Yamamoto,^b and Teijiro Kitao^{*a} ^a Department of Applied Chemistry, University of Osaka Prefecture, Sakai, Osaka 591, Japan ^b Material Research Laboratory, Matsushita Electric Industrial Co., Ltd., Moriguchi, Osaka 570, Japan

The oxidative rearrangement of O,O'-diacyl derivatives of leucoindigo with dichlorodicyanobenzoquinone in dimethyl sulphoxide affords N,N'-diacyl derivatives of indigotin in high yield; it has been found that the heat of *cis*-to-*trans* isomerization in acetonitrile for N,N'-bis(phenylacetyl)indigotin is 29.9 kcal mol⁻¹ (60 cal g⁻¹).†

N,N'-Disubstituted derivatives of indigotin are of interest in solar systems because solar energy may be stored as chemical energy in the *cis*-isomer. One advantage of this system is the absorption spectrum, which matches the photochemically active part of the solar spectrum very well. The disadvantages of this system are the low quantum yield of the photochemical *trans*-to-*cis* isomerization, low solubility, and the low stability of the energy-rich *cis*-form, which rapidly back-isomerizes to the stable *trans*-form at higher temperatures.¹ The photochemically storable energy does not exceed half of that which can be stored in hot water between 20 and 70 °C (*i.e.* 50 cal g^{-1}).¹

We now report a new preparation of *trans-N*,N'-diacyl derivatives of indigotin, and a kinetic study of the *cis*-to-*trans* isomerization of N,N'-diacyl derivatives of indigotin in the dark.

*trans-N,N'-*Diacyl derivatives of indigotin are typically prepared by the method of Blanc and Ross,² in which indigo and the appropriate acid chloride are refluxed together in pyridine or 2,6-lutidine (yield *ca.* 40%); however, the hitherto unknown derivatives *trans-N,N'*-bis(ethoxycarbonylacetyl)-indigotin (**2d**) and *trans-N,N'*-bis(phenylacetyl)indigotin (**2e**) are not obtained.

Compound (2d) has been prepared by O,O'-diacylation of leucoindigo with ethoxycarbonylacetyl chloride, and subsequent oxidative rearrangement of O,O'-bis(ethoxycarbonylacetyl)leucoindigo (1d) with 2,3-dichloro-5,6-dicyano-1,4benzoquinone (DDQ) in dimethyl sulphoxide (DMSO) (83% yield) (Scheme 1). Compound (1d) may also be prepared from indigo with ethoxycarbonylacetyl chloride in the presence of

 $\dagger 1 \text{ cal} = 4.184 \text{ J}.$



Scheme 1. i, RCOCl; ii, Zn, NaOAc, EtOAc, 50 °C, 5 h; iii, DDQ, DMSO, room temp.

zinc and sodium acetate in ethyl acetate (47% yield). *trans*-N,N'-Diacetylindigotin (2a) (92% yield) and (2e) (70% yield) have also been prepared by this method. If the oxidative rearrangement is carried out with a mixture of O,O'-diacetyl-leucoindigo (1a) and O,O'-bis(phenylacetyl)leucoindigo (1e), no cross-product, *trans*-N-acetyl-N'-phenylacetylindigotin, may be isolated from the reaction mixture.

The *trans-N*,*N'*-diacyl derivatives of indigotin were dissolved in a solvent such as benzene, acetonitrile, or cyclohexane, the concentration being *ca*. 10^{-4} mol 1^{-1} , and the solution was then irradiated with filtered light (>500 nm) for an appropriate period. This afforded a solution of the corres-

Table 1. Absorption characteristics of N,N'-diacylindigotin $(2\mathbf{a}-\mathbf{e})^{\mathbf{a}}$

(2)	R	λ_{m}	x/nm	$\epsilon (\lambda_{\max})^{\mathrm{b}}$	$\epsilon'(\lambda_{\max})^c$
a	Me	$\begin{cases} cis \\ trans \end{cases}$	438 565	4460 510	600 7020
b	Et	{ cis { trans	440 573	4340 550	810 7310
c	Pri	{ cis { trans	477 581	3810 550	600 6950
d	-CH ₂ CO ₂ H	$Et \begin{cases} cis \\ trans \end{cases}$	424 556	3970 780	980 6420
e	-CH ₂ Ph	$\begin{cases} cis \\ trans \end{cases}$	441 575	4080 400	530 6780

^a In benzene. ^b After irradiation. ^c Isomerisation to *trans*-isomer.

Table 2. Kinetic data and heat of *cis*-to-*trans* isomerization for N,N'-diacylindigotin (2a—f) in benzene and acetonitrile.

				$-\Delta H^{a}$	
(2)	Solvent	k^{e} s ⁻¹	t ^e /min	kcal mol ⁻¹	cal g ⁻¹
a	∫ Benzene	$6.4 imes10^{-5}$	186	7.3 (8.1) ^d	21 (23) ^d
	Acetonitrile	$4.6 imes 10^{-5}$	249		
b	Benzene	$1.8 imes 10^{-5}$	642	6.6	18
с	Benzene	$2.8 imes10^{-5}$	413	9.8	24
d	Benzene	2.4×10^{-5}	471	9.3	20
e	∫ Benzene	$1.1 imes 10^{-4}$	110	12.2	26
	Acetonitrile	$9.1 imes10^{-6}$	1264	29.9	60
fb	Benzene			(3.2) ^e	(6.8)e

^a Heat of isomerization was measured by a twin isoperibol calorimeter (Tokyo Riko Co., Type TIC-211) and is equal to the difference within an accuracy of 15%. ^b N,N'-Dibenzoylindigotin. ^c At 17 °C. ^d Ref. 1. ^e Ref. 3.

ponding *cis*-rich mixture, which was then kept in the dark. The change in absorption of the solution with time showed the isomerization of the *cis*-isomer to the *trans*-isomer (Table 1). From the change in the *cis*-isomer percentage and the amount of heat evolved when diethylamine, toluene-*p*-sulphonic acid, or hydrochloric acid was added as an isomerisation catalyst, the heats of isomerization were also calculated (Table 2).

It is generally accepted that the size and the structure of substituents on the nitrogen atoms of the indigotin molecule sterically affect the *cis*-to-*trans* isomerization in this compound. The half-life and the heat of isomerization of the hindered acylindigotin are both far greater than those of N,N'-diacetyl-indigotin (Table 2). Compound (2e) has a high stability (*cis*-form half-life at 17 °C is 1264 min) and large heat of *cis*-to-*trans*-isomerization [29.9 kcal mol⁻¹ (60 cal g⁻¹)] in aceto-nitrile.

In conclusion, the oxidative rearrangement of O,O'-diacyl derivatives of leucoindigo provides a convenient synthesis for new interesting derivatives of N,N'-diacylindigotin which are not directly accessible by known methods.

Received, 18th May 1982; Com. 563

References

- 1 H. D. Scharf, J. Fleischhauer, H. Leismann, I. Ressler, W. Schleker, and R. Weitz, *Angew. Chem.*, *Int. Ed. Engl.*, 1979, 18, 652.
- 2 J. Blanc and D. Ross, J. Phys. Chem., 1968, 72, 2817.
- 3 Battelle Development Corporation, U.S.P., 4,004,572 (1977).