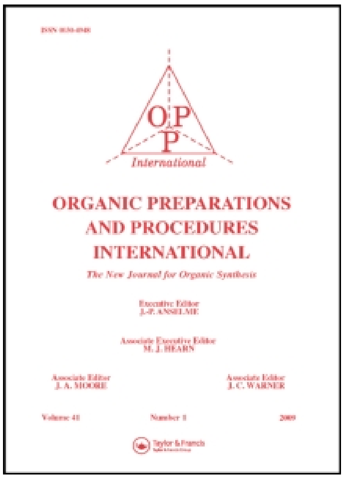


Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

SYNTHESIS AND PHOTOSTABILITY OF SOME N-ALKYL-N,N'-DIARYLFORMAMIDINES

Joseph A. Virgilio[a]; Emanuel Heilweil[a]
[a] Research Department, Givaudan Corporation, Clifton, New Jersey

To cite this Article Virgilio, Joseph A. and Heilweil, Emanuel(1978) 'SYNTHESIS AND PHOTOSTABILITY OF SOME N-ALKYL-N,N'-DIARYLFORMAMIDINES', Organic Preparations and Procedures International, 10: 2, 97 — 100

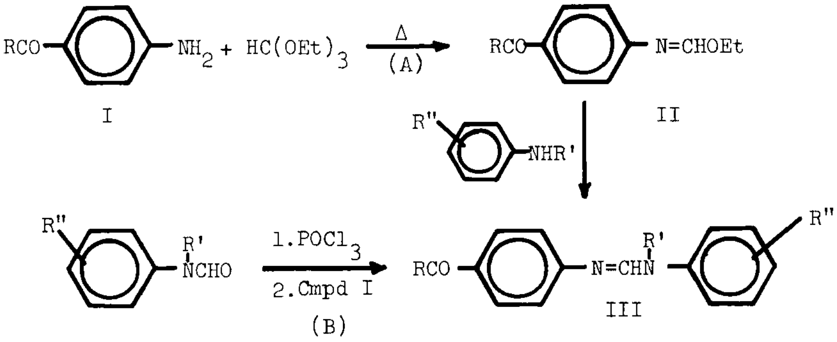
To link to this Article: DOI: 10.1080/00304947809355018

URL: http://dx.doi.org/10.1080/00304947809355018

SYNTHESIS AND PHOTOSTABILITY OF SOME N-ALKYL-N,N'-DIARYLFORMAMIDINES

Submitted by Joseph A. Virgilio* and Emanuel Heilweil
(10/31/77)
Givaudan Corporation
Research Department
125 Delawanna Avenue
Clifton, New Jersey 07014

In recent years there has been great interest in trisubstituted formamidines due to the range of their biological activity.[1-6] Formamidines of general structure III having outstanding UV absorbing and photostability properties, may be synthesized by routes A or B.



These formamidines III were ideal UV absorbers in that they were thermally stable compounds which had a broad intense spectrum between 290 and 400 nm and were stable to UV radiation in this region. They protect plastics, dyes and juvenile hormones against UV degradation by sunlight.

EXPERIMENTAL

Method A

Ethyl(4-ethoxycarbonylphenyl)formimidate (II, R = EtO).- Ethyl 4-aminobenzoate (82.6 g, 0.50 mole) and triethyl orthoformate (148.2 g, 1.0 mole) were heated at 145° until 56 ml of ethanol had been collected by distillation. The excess triethyl orthoformate was removed by vacuum distillation. The residue was distilled to yield 91.5 g (83%) of product, bp. 142°/1.0 mm;

mp. 41-42°.

Anal. Calcd for $C_{12}H_{15}NO_3$: C, 65.14; H, 6.83; N, 6.33.

Found: C, 65.01; H, 6.77; N, 6.54.

TABLE 1. Physical Data for III

						Elemental Analysis % Calculated (% Found)		
	R	R'	R"	Yield[a]	bp °C(mm)	C	H	N
IIIa	EtO	Me	H	56[b]	188(0.1)	72.33	6.41	9.92
						(72.22)	(6.34)	(9.89)
IIIb	EtO	Me	4-MeO	80	200(0.01)	69.21	6.47	8.96
						(69.38)	(6.29)	(9.24)
IIIc	EtO	Me	4-EtO_2C	50	89-91[c]	67.78	6.26	7.90
						(67.71)	(6.34)	(7.80)
IIId	EtO	Me	4-Me_2N	93	230(0.1)	70.13	7.13	12.91
						(69.95)	(7.08)	(13.12)
IIIe	EtO	Me	3,4-Cl_2	65	78-80[d]	58.14	4.68	7.97
						(58.10)	(4.50)	(8.12)
IIIf	EtO	Me	2-MeO	70	200(0.05)	69.21	6.47	8.96
						(69.47)	(6.49)	(9.01)
IIIg	EtO	Me	4-*n*-BuO_2C	61	89-90[c]			7.32
								(7.23)
IIIh	*n*-BuO	Me	H	68	204(0.08)	73.52	7.15	9.02
						(73.70)	(7.15)	(8.95)
IIIi	EtO	*n*-Bu	H	45	190(.1)	74.04	7.46	8.63
						(73.96)	(7.20)	(8.78)
IIIj	EtO	*n*-octyl	H	42	235(.1)	75.74	8.49	7.36
						(75.47)	(8.51)	(7.33)
IIIk	EtO	Et	H	85[e]	225(1.0)	72.94	6.80	9.45
						(73.05)	(6.75)	(9.41)
IIIl	NH_2	Me	H	25[e]	139-142[c]	71.14	5.96	16.58
						(71.22)	(5.90)	(16.18)

---

a) Method A unless otherwise noted. b) 95% yield by Method B. c) mp (°C), recrystallized from benzene/hexane. d) mp. (°C), recrystallized from hexane. e) Method B.

Ethyl(4-n-butoxycarbonylphenyl)formimidate (II, R = n-BuO).- The same procedure as above with n-butyl 4-aminobenzoate (97 g, 0.5 mole) yielded 85.9 g (69%) of pure product, bp. 136°/0.1 mm.

Anal. Calcd for $C_{14}H_{19}NO_3$: C, 67.46; H, 7.66; N, 5.62.
Found: C, 67.51; H, 7.73; N, 5.92.

Equimolar quantities of the formimidate II and the appropriate n-alkyl aniline were mixed and heated at 190°. Ethanol was removed from the reaction mixture through a short distillation column. When the ethanol had ceased distilling, the viscous oils were distilled in vacuo (see Table 1 for physical properties).

Method B

Phosphorus oxychloride (0.5 mole) was added dropwise to a solution of N-alkylformanilide (0.5 mole) in 400 ml of ethylene dichloride. The mixture was heated at 40° for 15 min. The appropriate aminophenylcarboxylate (0.5 mole) was added in portions and the solution was refluxed 2 hrs. The solution was poured into 300 ml of 30% sodium hydroxide and 800 g of ice. The ethylene dichloride was separated, dried ($MgSO_4$), filtered and concentrated. The viscous oils were distilled in vacuo and the solids recrystallized (see Table 1).

Photostability Testing.- Since one of the most important characteristics of a UV absorber is its stability to solar exposure (radiation of 290 nm and above), a method had to be selected to rapidly evaluate this property. The test method of choice was the irradiation of a solution (isopropanol) of the UV absorber in a pyrex flask under an Hanovia lamp 679 A (450 watts). The pyrex flask filters out UV radiation of 290 nm and below. Samples were withdrawn from the flask at various intervals and their spectra taken to determine if any degradation had occurred. In a typical run, eight different solutions were irradiated including one or two commercial absorbers as controls. Stability was measured by the number of hours which were required for the solution to lose 25% of its UV absorbing property. The results are presented in Table 2. To insure that results of the accelerated test method were reliably predicting use conditions, replicate solutions were exposed outdoors to solar radiation and to radiation from 4 GE fluorescent lamps (black light). Results of the balck light, solar exposure and accelerated (Hanovia lamp) tests rated the UV absorbers in the same order of photostability.

TABLE 2. UV Properties of III

Compound	λ^c	ε	Photostability (hrs)
IIIa	313	26,200	>32
IIIb	312	26,300	>32
IIIc	323	32,800	>32
IIId	324	22,100	12-16
IIIe	312	29,500	>32
IIIf	312	27,500	>32
IIIg	323	36,800	>32
IIIh	312	27,100	>32
IIIi	312	26,700	>32
IIIj	314	28,300	>32
IIIk	313	27,700	>32
IIIl	316	22,700	16-32
Tinuvin P[a]	337	13,800	>32
Cyasorb UV 9[b]	325	8,500	16-32

---

a) 2-(2-Hydroxy-5-methylphenylbenzotriazole (Tinuvin P,® Ciba-Geigy)

b) 2-Hydroxy-4-methoxybenzophenone (Cyasorb UV 9,® American Cyanamid)

c) In isopropanol

REFERENCES

1. R. M. Hollingworth, Environmental Health Perspective, 14, 57 (1976).
2. E. G. Gemrich II, G. Kaugars and V. L. Rizzo, J. Agric. Chem., 24, 593 (1976).
3. N. Steiger, U.S. Pat. 3,153, 303 (1964);CA, 61, 14584 (1964).
4. R. F. Homer, U.S. Pat. 3,119,831 (1964);CA, 60, 11955 (1964).
5. H. J. Gerjonick, U.S. Pat. 3,189,648 (1965); CA, 63, 9959 (1965).
6. P. Benko *et al.*, Acta Pharm. Hung., 38, 219 (1968); CA, 69, 57703k. (1968).