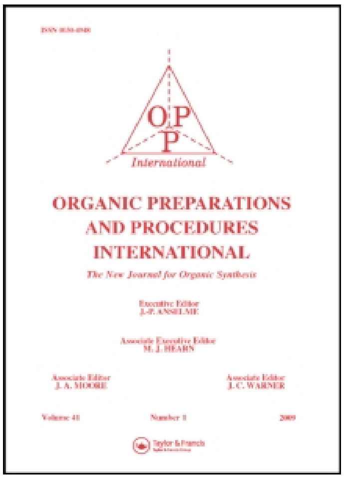

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REACTIONS OF N-AMINOPHTHALIMIDE WITH ELECTROPHILES. PREPARATION AND PROPERTIES OF SOME NEW TRIACYLHYDRAZINES

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Hydrazine hydrate (100%, 5.0 ml) was added dropwise and the mixture was refluxed for 2 hrs. The catalyst was removed by filtration and the crude product (1.69 g) was precipitated by addition of water. Recrystallization from toluene afforded 1.53 g (84%) of 2-aminocarbazole as colorless prisms, mp. 239-241° (sealed capillary), lit.[4] mp. 238-239° (dec.).

IR (KBr): 730, 770, 820, 850 (C-H def.); 1320, 1620, 3320, 3400 (NH_2) cm^{-1}. MS, m/e: 183 (15.1), 182 (M^+, 100.0), 181 (28.3), 154 (13.7), 127 (7.4).

Anal. Calcd for $C_{12}H_{10}N_2$: C, 79.09; H, 5.53
Found: C, 79.17; H, 5.63

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REACTIONS OF N-AMINOPHTHALIMIDE WITH ELECTROPHILES. PREPARATION AND PROPERTIES OF SOME NEW TRIACYLHYDRAZINES

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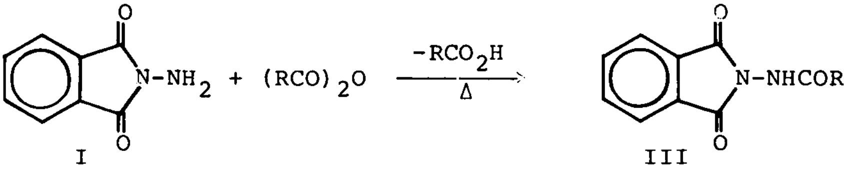
In accord with the earlier results of Drew and Hatt,[1] N-aminophthalimide (I) undergoes rearrangement with refluxing dilute hydrochloric acid to yield phthalhydrazide (II). Chattaway and Tesh[2] have reported related skeletal rearrangements under basic conditions or upon heating in glycerol at 210°. We further found that I was inert toward esters under conditions which normally allow for the acylation of simple hydrazines.[3,4] Thus prolonged reaction of I with excess methyl formate did not lead to the introduction of the formyl group, nor did a variety of other esters cause acylation under a range of conditions.[5] Utilization of the acid chlorides to accomplish acylation[6] was not satisfactory in our experience, leading to mixtures which were difficult to purify.



a) R = Me b) R = Et c) R = Pr d) R = *i*-Pr e) R = *n*-Bu

In the event, warming I with neat acid anhydrides led smoothly to triacylhydrazines IIIa-e, which could be obtained in pure form directly from the reaction. The Table summarizes our results. In all examples, yields recorded were 90% or greater. The infrared spectra of the compounds clearly dis-

TABLE. Triacylhydrazines

Compound	mp (°C)	Calcd (Found) C	H	N
IIIa	230-232[a]	--	--	--
IIIb	200-202	60.55(60.34)	4.62(4.53)	12.84(12.69)
IIIc	130	62.06(62.12)	5.21(4.87)	12.06(11.91)
IIId	168	62.06(62.02)	5.21(5.15)	12.06(11.98)
IIIe	109-110	63.41(63.07)	5.73(5.68)	11.38(11.36)

a) lit.[3] mp. 228-230°

played bands characteristic of the acylaminophthalimide structure at 3290-3280 (s), 1800-1790 (m), 1745-1740 (s) and 1670-1660 (s) cm^{-1}. The NMR spectra further supported the structural assignments, displaying the expected signals near 2 parts per million downfield from TMS for the α-hydrogens of the alkyl moieties. Under the conditions noted for a representative experiment, we found no evidence for skeletal rearrangement to the phthalhydrazide framework.

EXPERIMENTAL

Melting points were taken in open capillary tubes using a Mel-Temp apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 727 spectrophotometer as Nujol mulls. Nuclear magnetic resonance spectra were obtained on a Perkin-Elmer R-32 90 Mc spectrometer in dimethyl sulfoxide-d6 using internal tetramethylsilane as the standard. N-Aminophthalimide was conveniently prepared using the known method (ref. 1) or was purchased from Fluka A.-G. Acid anhydrides were used as received from Aldrich Chemical Company or Fluka.

Rearrangement of N-Aminophthalimide to Phthalhydrazide.- N-Aminophthalimide (1.0 g) was refluxed with 6 N hydrochloric acid for 5 hrs. Filtration of the solid material obtained from the cooled reaction mixture (1.0 g), followed by washing with cold water and drying, provide a sample identical (IR) to authentic II.

Preparation of Triacylhydrazines. Representative Procedure.- N-Aminophthalimide (1.0 g, 6.2 mmoles) was mixed with isobutyric anhydride (5 ml, 31 mmoles) in a round bottom flask and warmed to 120° over a heating mantle, forming a homogeneous yellow solution which turned colorless as heating was continued for 5 minutes. After this time, the hot reaction mixture was decanted into a watchglass and allowed to stand for 1 hr, forming colorless prismatic needles. The excess anhydride was drawn off and the residue washed with a small amount of cold ether to give N-isobutyraminophthalimide (IIId).

NMR: δ 7.9 (singlet, 4H), 3.3 (broad singlet, 1H), 2.5 (septet, 1H, J = 6 cps) and 1.1 (doublet, 6H, J = 6 cps).

Prolonged reaction times were avoided as they led to lower yields of less pure products.

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ONE-POT PROCESS FOR BENZOCAINE FROM p-NITROBENZOIC ACID

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The procedures[1] reported to date for the preparation of benzocaine have been modified and a simplified process from p-nitrobenzoic acid is described.