Acyl Alkyl Diimides. III. Influence of Structure on Decomposition

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Eleven compounds of general structure $\mathrm{RCON{=}NC(CN)R_2'}$, where $\mathrm{R = C_6H_5, CH_3, C_6H_5CH_2}$ and $\mathrm{R_2' = (CH_3)_2, (CH_2)_4, (CH_2)_5, (CH_2)_6}$, have been found to decompose in a first-order manner in dilute toluene solution in the temperature range 60–100°. The *N*-acetyl compounds decompose *ca.* four times faster than the corresponding *N*-benzoyl cases. Variation in $\mathrm{R_2'}$ causes changes in rate parallel to those observed by Overberger for the analogous bis-α-cyanoalkyl diimides but of smaller magnitude. The products are those expected from homolytic cleavage, and intermediate *N*-acylketenimines have been trapped by added water in two cases.

Il a été démontré que les onzes composés de structure générale $\mathrm{RCON{=}NC(CN)R_2'}$, où $\mathrm{R = C_6H_5, CH_3, C_6H_5CH_2}$ et $\mathrm{R_2' = (CH_3)_2, (CH_2)_4, (CH_2)_5, (CH_2)_6}$, se décomposent selon un mode du premier ordre en solution diluée dans le toluène et ceci dans l'intervalle de température suivant 60–100°. Les composés *N*-acétylés se décomposent *ca.* quatre fois plus rapidement que les produits correspondants *N*-benzoylés. Les changements dans $\mathrm{R_2'}$ entraînent des variations dans le taux identiques a celles observées par Overberger pour les diimides bis-α-cyanoalcoyle analogues mais avec une amplitude moins prononcée. Les produits sont ceux prévus à partir d'un clivage homolytique et les intermédiaires *N*-acylcetènenimines ont été isolés par addition d'eau dans les deux cas. [Traduit par le journal]

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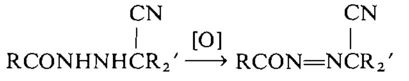
In previous papers we have reported on the synthesis and spectra of a number of acyl alkyl diimides (1) and on the kinetics of the thermal decomposition of one example (2). Our continuing interest in this heretofore relatively neglected class of diimides has prompted us to undertake a more extensive investigation of their properties. In this paper we report the results of a study in which the effect of alteration of both acyl and alkyl substituents on decomposition rates has been investigated. We have also performed a product study on two cases, and have measured the cage effect exhibited by one example.

Accordingly, the benzoyl, acetyl, and phenylacetyl α-cyanoalkyl diimides **2***a*–*k* were obtained by lead tetraacetate oxidation of the *N*′-α-cyanoalkyl acid hydrazides **1***a*–*k*, the latter being synthesized by a general route previously described (1). An alternate route to these hydrazides was also explored, *viz.*: by transfer of the elements of hydrogen cyanide from acetone cyanohydrin to an acylhydrazone of a ketone. This method gave the desired α-cyanoalkyl acid hydrazides in yields of 25–80%. However, the first-mentioned route generally resulted in higher yields of purer products and was the method of choice.



$$\mathrm{RCONHNH}\overset{\mathrm{CN}}{\overset{|}{\mathrm{C}}}\mathrm{R_2'} \xrightarrow{[\mathrm{O}]} \mathrm{RCON{=}N}\overset{\mathrm{CN}}{\overset{|}{\mathrm{C}}}\mathrm{R_2'}$$

1 **2**

a $\mathrm{R = CH_3; R_2' = (CH_2)_5}$
b $\mathrm{R = CH_3; R_2' = (CH_2)_4}$
c $\mathrm{R = CH_3; R_2' = (CH_2)_6}$
d $\mathrm{R = CH_3; R' = CH_3}$
e $\mathrm{R = C_6H_5CH_2; R_2' = (CH_2)_5}$
f $\mathrm{R = C_6H_5; R_2' = (CH_2)_6}$
g $\mathrm{R = C_6H_5; R_2' = (CH_2)_4}$
h $\mathrm{R = C_6H_5; R' = CH_3}$
i $\mathrm{R = }p\text{-}\mathrm{MeOC_6H_4; R_2' = (CH_2)_5}$
j $\mathrm{R = }p\text{-}\mathrm{ClC_6H_4; R_2' = (CH_2)_5}$
k $\mathrm{R = }p\text{-}\mathrm{MeC_6H_4; R_2' = (CH_2)_5}$

The kinetic studies were performed in dilute toluene solution by monitoring the disappearance of the n–π* bands at *ca.* 400 nm (due to product absorption, this method was not applicable in the phenylacetyl case, compound **2***e*; disappearance of **2***e* in chlorobenzene was followed by integration of the $\mathrm{C_6H_5CH_2}$— methylene signal in its n.m.r. spectrum). The results are collected in Table 1, and except where noted, are derived from two runs at each temperature. High concentration runs in the benzoyl series (compounds **2***h* and *j*) indicate little, if any, induced decomposition; such substrate concentration increases in the acetyl series (compounds **2***a* and *d*) actually led to slight decreases in rate, a phenomenon not normally associated with the onset of induced decomposition, and may be due to changes in the nature of the medium

TABLE 1. Rates* and activation energies for the thermal decomposition of $RCON{=}NC(CN)R_2'$ in toluene

Concentration (mol/l ($\times 10^2$))	Temperature (°C)	k ($\times 10^5$ s^{-1})	E_A†	$\Delta S^{\ddagger}$†
		2a, $R = CH_3$, $R_2' = (CH_2)_5$		
4.94	82.0	5.21±0.19‡	27.4±0.9	−3.3±2.4
4.92	85.9	8.62±0.39‡		
1.81	89.7	11.00±0.40‡		
3.66	89.8	12.60±0.40‡		
22.00	89.8	10.70±0.60‡		
40.30	89.8	7.13±0.64‡		
4.87	92.8	17.00±0.60‡		
3.66	97.0	25.30±1.20‡		
4.94	100.6	37.40±1.00‡		
		2b, $R = CH_3$ $R_2' = (CH_2)_4$		
3.90	65.6	1.82±0.09	28.7±0.71	2.2±2.1
3.99	70.7	3.33±0.08		
4.00	76.8	7.29±0.3		
3.99	82.8	14.7 ±0.3		
3.95	91.5	36.5 ±4.0‡		
		2c, $R = CH_3$, $R_2' = (CH_2)_6$		
3.45	59.4	4.44±0.09	26.74±0.27	−0.4±0.8
3.45	66.1	9.82±0.33		
3.56	73.1	21.7 ±1.5		
3.79	79.6	45.1 ±2.2		
		2d, $R = CH_3$, $R' = CH_3$		
4.32	60.8	2.46±0.17	26.32±1.9	−3.1±5.5
4.32	68.6	5.45±0.21		
4.32	75.2	13.5 ±0.5		
3.64	75.2	12.9 ±0.5‡		
18.20	75.2	12.5‡		
36.40	75.2	9.8‡		
4.32	82.0	24.9 ±1.6		
		2e, $R = C_6H_5CH_2$, $R' = (CH_2)_5$		
49.0	74.3	3.08±0.13‡	31.96±1.7	10.5±4.8
49.0	79.3	6.63±0.53‡		
45.0	82.9	9.76±0.53‡		
45.0	87.2	16.2 ±1.7‡		
45.0	91.2	27.7 ±2.5‡		
		2f, $R = C_6H_5$, $R_2' = (CH_2)_6$		
1.87	74.6	6.43±0.23	29.30±1.09	4.3±3.7
1.84	78.6	10.59±0.45		
1.89	82.8	17.81±0.73		
1.85	89.2	35.19±1.57		
		2g, $R = C_6H_5$, $R_2' = (CH_2)_4$		
1.95	76.7	1.62±0.08	31.47±0.85	7.5±3.1
1.89	82.0	3.17±0.16		
1.94	92.6	11.64±0.58		
1.92	98.4	22.52±0.97		
		2h, $R = C_6H_5$, $R' = CH_3$		
1.81	69.2	1.31±0.06	30.53±0.76	6.1±3.3
2.25	73.2	2.28±0.10‡		
22.45	73.2	2.34±0.16‡		
2.22	83.2	7.96±0.36		
1.77	90.0	17.44±0.48		

TABLE 1 (*Concluded*)

2i, R = p-$CH_3OC_6H_4$, R′ = $(CH_2)_5$				
1.33	80.8	0.71±0.04	34.08±1.05	11.8±2.3
1.32	87.9	1.71±0.08		
1.33	94.0	3.94±0.21		
1.32	101.2	9.73±0.38		
2j, R = p-ClC_6H_4, R′ = $(CH_2)_5$				
1.78	79.1	0.86±0.04	31.68±0.93	5.8±2.2
1.78	86.4	2.01±0.06		
1.77	92.8	4.52±0.15‡		
17.70	92.8	5.05±0.47‡		
1.78	99.7	10.44±0.34		
2k, R = p-$CH_3C_6H_4$, R′ = $(CH_2)_5$				
2.00	81.4	1.06±0.04	32.00±0.99	6.6±2.3
2.00	87.3	2.20±0.05		
2.00	95.5	6.01±0.20		
2.00	101.9	12.55±0.68		

*Rate constants calculated by least-squares method.
†Errors in E_a and $\Delta S^{\ddagger}$ are estimated.
‡From one run.

TABLE 2. Calculated rate constants for the thermal decomposition of $RCON{=}NC(CN)R_2'$ at 80° in toluene

R_2'	R = CH_3 k ($\times 10^5$ s^{-1})	k_{rel}*	R = C_6H_5 k ($\times 10^5$ s^{-1})	k_{rel}*	$k_{CH_3CO}/k_{C_6H_5CO}$	R = $C_6H_5CH_2$ k ($\times 10^5$)	$(R_2'C(CN)N{=})_2$† k_{rel}*
$(CH_3)_2$	20.76	4.8	5.32	6.1	3.9		24.3
$(CH_2)_4$	10.17	2.4	2.47	2.8	4.1		11.5
$(CH_2)_5$	4.33	1.0	0.88‡	1.0	4.9	6.69	1.0
$(CH_2)_6$	45.53	10.5	12.48	14.2	3.7		193.7

*Relative to the cyclohexyl case.
†References 6 and 7.
‡Reference 2.

(now *ca.* 0.4 *M* in diimide). Here it should be noted that diimide **2***e* gave good first-order kinetics over 2–3 half-lives although the concentration was necessarily high (*ca.* 0.5 *M*).

Table 2 gives the calculated rate constants at 80.0° for the unsubstituted diimides studied here, and for *N*-benzoyl *N*′-α-cyanocyclohexyl diimide, **2***l*, reported on previously. It can be seen (column 6) that the *N*-acetyl diimides decompose approximately four times faster than the *N*-benzoyl analogs having the same alkyl group, perhaps suggestive of some degree of *N*-acyl cleavage in the transition state. The very slight rate enhancement of the phenylacetyl case, **2***e*, over its acetyl relative, compound **2***a*, can be taken to indicate that loss of carbon monoxide is not concerted with formation of nitrogen. This contrasts with the case of *t*-butyl phenylperacetate in which formation of carbon dioxide is considered to be simultaneous with cleavage of the perester O—O bond (3). In addition, it can be seen that the effects of *p*-substituents on the rate of decomposition of benzoyl diimides having a common alkyl group (Table 3, compounds **2***i*–*l*), is small and that there appears to be no significant contribution from a polar transition state such as 3.[1,2]

TABLE 3. Calculated rate constants for the thermal decomposition of p-X-$C_6H_4CON{=}NC(CN)(CH_2)_5$ at 80° in toluene

Compound 2	X	k ($\times 10^5$ s^{-1})	k_{rel}
l	H	0.88	1.00
i	Me	0.88	1.00
j	Cl	0.94	1.07
k	MeO	0.61	0.69

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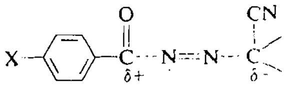
[1] Polar transition states in the formation of benzoyl radicals have previously been invoked (ref. 4 and refs. therein).

[2] It has been suggested from e.s.r. studies (5) that benzoyl radicals are not stabilized by *p*-Cl or *p*-MeO substituents.



3

As inferred previously, the effect of alkyl group variation on rates is quite similar in both the benzoyl and acetyl series (Table 2) and the relative ordering (cyclohexyl < cyclopentyl < isopropyl < cycloheptyl) is the same as that observed by Overberger (refs. 6 and 7, Table 2, column 8) for the corresponding bis-α-cyanoalkyl diimides, and would seem to establish *N*-alkyl bond cleavage. It should be noted that the rate range observed here (10–14) is much less than for the dialkyl compounds (*ca.* 200) of Overberger, and more closely resembles the range of 5 observed for the related *t*-butylcycloalkyl peresters (8, 9). Whether acyl C—N bond cleavage is also occurring is less clear. This bond is expected to be the stronger, being an sp^2–sp^2 bond rather than sp^2–sp^3, and because of conjugation effects. However, the similarity between the activation energies for our compounds and those of Overberger's may support a two bond cleavage, the faster rate of the acetyl compounds reflecting greater acyl C—N bond cleavage, or a more stable acyl radical.

We have also examined the products from the thermal decomposition of compounds **2***d* and *h*. Decomposition of a degassed 0.1 *M* solution of **2***d* in toluene containing added water,[3] at 80° for 8.5 half-lives gave (average of two runs): α-acetylisobutyronitrile (1.3%), tetramethylsuccinonitrile (4%), isobutyramide (7%), *N*-acetylisobutyramide (12%), isobutyronitrile (22%), acetic acid (25%), acetone (14%) and α-methylacrylonitrile (3%), accounting for 67% of the isobutyronitrile radicals but a more disappointing 38% of the acetyl radicals, together with a number of other products which were not identified but which may arise by attack of radicals on the solvent.[4] Decomposition of **2***h* (0.075 *M* in degassed toluene containing water at 90° for 8.5 half-lives) gave (average of two runs): α-benzoylisobutyronitrile (3%), *N*-benzoylisobutyramide (70%),[5] benzaldehyde (2%), tetramethylsuccinonitrile (4%), benzene (2%),[6] and a trace of bibenzyl, accounting for 77% of the benzoyl radicals and 81% of the isobutyronitrile radicals. Neither isobutyronitrile nor α-methylacrylonitrile were detected.

The most notable feature of the product distributions from **2***d* and *h* is the marked preference for combination of the acyl radicals with the isobutyronitrile radicals on nitrogen, rather than on the more sterically hindered carbon, in agreement with the preference previously observed for the recombination of α-cyanoalkyl radicals themselves (12). The *N*-acylketenimines so formed in the cases reported are then presumed to react with water to give the *N*-acylamides observed as the predominant products. Parenthetically, it might be mentioned that *N*-acylketenimines appear to be a hitherto unreported class of ketenimine (13), and, in the absence of water, thermal decomposition of α-cyanoalkyl acyl diimides is a potential route to their isolation.

To return to the products studies, the significant amounts of isobutyronitrile and acetic acid from the diimide **2***d* can most reasonably be explained by nucleophilic attack of water on the carbonyl group of the diimide (14), whilst the isobutyramide probably arises by hydrolysis of *N*-acetylisobutyramide. The acetone formed may arise by reaction of the isobutyronitrile radicals with residual oxygen, although the solutions were considered to be thoroughly degassed.

In contrast to the thermal results, irradiation (λ > 350 nm) of an 8×10^{-2} *M* solution of **2***h* in toluene containing water, followed by g.l.c. analysis, gave benzaldehyde (6%), tetramethylsuccinonitrile (9%), α-benzoylisobutyronitrile (14%), *N*-benzoylisobutyramide (3%), benzene (1%), and a number of other unidentified products. Isobutyronitrile and α-methylacrylonitrile were not analyzed for. The low yield of *N*-acylamide under these photochemical conditions may be due to the lower solubility of water in toluene at room temperature, or photochemical decomposition of the *N*-acylketenimine when formed, or a combination of these factors.

The cage effect in the decomposition of **2***h*

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[3] The rate of decomposition of **2***l* was unaltered on addition of a small amount of water.

[4] No bibenzyl was detected.

[5] In a subsequent set of runs the amounts of α-benzoylisobutyronitrile and *N*-benzoylisobutyramide were determined to be 9 and 58%, respectively.

[6] The decarbonylation of benzoyl radicals generated from dibenzoyl diimide has been observed previously (10) and more recently studied quantitatively in the system:

$$C_6H_5CHO + I_2 \rightarrow C_6H_5CIO + HI \quad (11)$$

in toluene at 90° was measured by the iodine consumption method (15), and found to be 53 ± 3%. Simultaneously, the yield of ketone was measured in the presence of iodine and was observed to fall to 33% of its value in the absence of this scavenger. A similar discrepancy in cage effect determinations by iodine scavenging and product analysis has previously been reported (16).

In conclusion, the work described in this paper establishes that the *N*-benzoyl and *N*-acetyl α-cyanoalkyl diimides examined decompose by first-order kinetics to give radical intermediates. The major mode of recombination leads to *N*-acylketenimines which rapidly react with water present to give *N*-acylamides. *N*-Acetyldiimides decompose more rapidly than the *N*-benzoyl analogs, and variation of the alkyl group affects the rates in a similar, but attenuated, manner to that observed by Overberger, for his bis-α-cyanoalkyldiimides.

Experimental

Instruments used and related information are as reported previously (1, 2). Details of the kinetic method have also been given before (2).

A number of the *N*′-α-cyanoalkyl acid hydrazides and derived diimides have been prepared before; the following are new compounds:

1*b*: yield 50%; m.p. 103–104°; n.m.r.: δ 8.08 (br s, 1H), 4.85 (br s, 1H), 2.02 (s, 3H), 1.55–1.95 p.p.m. (br, 8H).

Anal. Calcd. for $C_8H_{13}N_3O$: C, 57.47; H, 7.84; N, 25.13. Found: C, 57.43; H, 7.82; N, 25.08.

2*b*: yellow oil, yield 92%; λ_{max} (C_6H_{12}) 395 nm (ε 36); n.m.r.: δ 2.30 (s, 3H), 1.8–2.6 p.p.m. (br, 8H).

1*c*: yield 16%; m.p. 94.5°; n.m.r.: δ 8.35 (br s, 1H), 5.02 (br s, 1H), 2.02 (s, 3H), 1.4–2.2 p.p.m. (br, 12H).

Anal. Calcd. for $C_{10}H_{17}N_3O$: C, 61.51; H, 8.78; N, 21.52. Found: C, 61.74; H, 8.82; N, 21.86.

2*c*: yellow oil, yield 91%; λ_{max} (C_6H_{12}) 397 nm (ε 35); n.m.r.: δ 2.35 (s, 3H), 1.8–2.1 p.p.m. (br, 12H).

1*e*: yield 70%; m.p. 98–99°; n.m.r.: δ 7.20 (br d, *J* = 5 Hz, 1H), 7.25 (s, 5H), 5.0 (br d, *J* = 5 Hz, 1H), 3.53 (s, 2H), 0.8–2.0 p.p.m. (br, 10H).

Anal. Calcd. for $C_{15}H_{19}N_3O$: C, 70.01; H, 7.44; N, 16.33. Found: C, 69.69; H, 7.29; N, 16.13.

2*e*: yield 86%; m.p. 43°; n.m.r.: δ 7.27 (s, 5H), 3.93 (s, 2H), 1.90 p.p.m. (br, 10H).

Anal. Calcd. for $C_{15}H_{17}N_3O$: C, 70.56; H, 6.71; N, 16.46. Found: C, 70.52; H, 6.73; N, 16.32.

1*f*: yield 87%; m.p. 123–125°; n.m.r.: δ 7.2–8.17 (m, 6H), 5.2 (d, *J* = 5 Hz, 1 H), 1.2–2.2 p.p.m. (m, 12H).

Anal. Calcd. for $C_{15}H_{19}N_3O$: C, 70.01; H, 7.44; N, 16.33. Found: C, 70.12; H, 7.19; N, 16.39.

2*f*: yield 80%; m.p. 55.5–57°; λ_{max} (C_6H_{12}) 244 (ε 8600), 290 (sh, ε 1400), 321 (sh, ε 275), 408 nm (ε 50); n.m.r.: δ 7.4–8.0 (m, 5H), 1.46–2.4 p.p.m. (m, 12H).

1*g*: yield 50%; m.p. 124.5–126°, n.m.r.: δ 8.1–8.20 (d, *J* = 7 Hz, 1H), 7.23–7.90 (m, 5H), 5.24 (d, *J* = 7 Hz, 1H), 1.57–2.30 p.p.m. (br, 8H).

Anal. Calcd. for $C_{13}H_{15}N_3O$: C, 68.10; H, 6.59; N, 18.33. Found: C, 67.93; H, 6.68; N, 18.39.

2*g*: orange oil, yield 79%; λ_{max} (C_6H_{12}) 244 (ε 8600), 289 (sh, ε 1700), 323 (sh, ε 244), 408 nm (ε 46); n.m.r.: δ 7.47–8.0 (m, 5H), 1.67–2.67 p.p.m. (m, 8H).

1*i*: yield 80%; m.p. 144–146.5°, n.m.r.: δ 8.38 (s, 1H), 7.78 (d, *J* = 8.5 Hz, 2H), 6.87 (d, *J* = 8.5 Hz, 2H), 5.33 (br s, 1H), 3.81 (s, 3H), 1.1–2.37 p.p.m. (m, 10H).

Anal. Calcd. for $C_{15}H_{19}N_3O_2$: C, 65.91; H, 7.01; N, 15.37. Found: C, 66.15, H, 7.27; N, 15.26.

2*i*: yield 89%; m.p. 108.5–109°, λ_{max} (CH_3CN) 286 (ε 10 850), 406 nm (sh, ε 56), n.m.r.: δ 7.98 (d, *J* = 9 Hz, 2H), 7.02 (d, *J* = 9 Hz, 2H), 3.91 (s, 3H), 1.3–2.37 p.p.m. (m, 10H).

1*k*: yield 65%; m.p. 137–139°, n.m.r.: δ 8.36 (s, 1H), 7.70 (d, *J* = 8 Hz, 2H), 7.18 (d, *J* = 8 Hz, 2H), 5.27 (br s, 1H) 2.35 (s, 3H), 0.93–2.27 p.p.m. (m, 10H).

Anal. Calcd. for $C_{15}H_{19}N_3O$: C, 70.01; H, 7.44; N, 16.33. Found: C, 70.16; H, 7.19; N, 16.23.

2*k*: yield 79%; m.p. 80.5–81°; λ_{max} (C_6H_{12}) 255 (ε 10 500), 290 (sh, ε 3000), 321 (sh, ε 510), 409 nm (ε 47); n.m.r.: δ 7.83 (d, *J* = 8 Hz, 2H), 7.28 (d, *J* = 8 Hz, 2H), 2.43 (s, 3H), 1.53–2.36 p.p.m. (m, 10H).

1*j*: yield 87%; m.p. 160–162°, i.r. (Nujol): 3290 (w), 3225 (s), 1640 cm^{-1} (s); n.m.r.: not obtainable due to insolubility.

2*j*: yield 86%; m.p. 81.5–82.5, λ_{max} (C_6H_{12}) 259 (ε 13 000), 415 nm (ε 57), n.m.r.: δ 7.80 (d, *J* = 8 Hz, 2H), 7.50 (d, *J* = 8 Hz, 2H), 1.0–2.3 p.p.m. (br, 10H).

Anal. Calcd. for $C_{14}H_{14}ClN_3O$: C, 60.98; H, 5.12; N, 15.24. Found: C, 61.00; H, 5.13; N, 15.08.

Reaction of acylhydrazones with acetone cyanohydrin: a mixture of the hydrazone (4 mmol), acetone cyanohydrin (3 ml), methanol (7 ml), and either 10% aqueous sodium carbonate solution (0.5 ml) or triethylamine (0.25 ml) was refluxed overnight. The solvent was removed and the desired hydrazide obtained by crystallization (in some cases colored impurities were removed with charcoal).

A typical oxidation of an α-cyanoalkyl acid hydrazide was as follows: a solution of lead tetraacetate (0.92 g, 2.1 mmol) in dichloromethane (15 ml) was added to a solution of the hydrazide (2.0 mmol) in dichloromethane cooled to −20°. The solution was stirred at −20° for 1 h, then decanted from the insoluble lead salts, washed with ice-cold water (2 × 50 ml), cold saturated aqueous sodium bicarbonate solution (2 × 50 ml), ice-cold water (2 × 50 ml), dried, and the solvent was then removed at *ca.* 10°. The benzoyl and phenylacetyl diimides (with the exception of compounds **2***g* and **2***h*) were solids and were recrystallized from pentane. The remaining diimides were orange or yellow oils and were used as obtained; they were pure by n.m.r. and i.r.

α-Benzoyl isobutyronitrile was obtained by methylation of benzoylacetonitrile (17) with methyl iodide. The crude product (b.p. 73–78°/0.25 mm (lit. (18) b.p. 139°/10 mm)) was purified by preparative g.l.c. (Varian Aerograph Model 700) on a 20 ft × 1/4 in. SE-30 column. The pure material was a colorless liquid, λ_{max} (EtOH) 248 (ε 11 000), 282 nm (sh, ε 1100); ν_{max} 1694 cm^{-1}; n.m.r.: δ 1.71 (s, 6H), 7.4–8.4 p.p.m. (m, 5H).

α-Acetyl isobutyronitrile was prepared by methylation of α-acetylpropionitrile (19) with methyl iodide, b.p.

163–166° (lit. (20) b.p. 162–165°), λ_{max} (EtOH): 233 (ε 195), 281 nm (ε 26); ν_{max} 1725 cm^{-1}; n.m.r.: δ 2.43 (s, 3H), 1.53 p.p.m. (s, 6H). *N*-Benzoylisobutyramide, m.p. 155–156° (lit. (21) m.p. 154°) and *N*-acetylisobutyramide, m.p. 68–70° (lit. (22) m.p. 73–74°) were obtained by treatment of benzamide and acetamide, respectively, with isobutyryl chloride. Tetramethylsuccinonitrile was obtained from azoisobutyronitrile (23).

Product identifications were performed on a Varian Model 1740 Gas Chromatograph using the following 5 ft × 1/8 in. columns: 5% DEGSE on acid-washed 80/100 mesh Chromosorb W; 3% SE-30 on 100/120 mesh VarAport 30; 5% Carbowax 20 M on DMCS-treated 80/100 mesh Chromosorb W, and a 10 ft × 1/8 in. 80/100 mesh Chromosorb 103 column. For quantitative analyses, the detector was calibrated using solutions of known concentration of the products. Peak areas were measured with a planimeter.

For measurement of the cage effect, 2 ml aliquots of toluene, 0.037 *M* in **2***h* and 0.074 *M* in iodine were degassed and sealed in tubes, then heated for 8 h at 90°. The iodine concentration before and after was monitored at 498 nm. The cage effect is then given by [(moles diimide at $t = 0$) − (moles I_2 consumed)]/[moles diimide at $t = 0$]. The results given are the average of three determinations.

Photochemical studies were performed on degassed solutions of **2***h* in Pyrex tubes using a Hanovia #901C1 Xenon lamp, and passing the light through a Corning cso 52 filter.

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