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THE PHOTOLYSIS OF DIPHENYLCARBAMOYL AZIDE

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Abstract—In contrast to the thermal decomposition which produces 1-phenylindazolone in 90% yield, the photolysis of diphenylcarbamoyl azide in alcohols (and other solvents) gives 1-phenylbenzimidazolone, diphenylamine and the corresponding carbazates (except in t-amyl alcohol where no carbazate is formed). In no case could 1-phenylindazolone be isolated. The formation of 1-phenylbenzimidazolone is shown to proceed *via* the singlet diphenylcarbamoyl nitrene while the generation of diphenylamine is believed to occur by radical abstraction of the triplet nitrene. The carbazates arise by the Curtius rearrangement of the H bonded azide.

INTRODUCTION

IN THE last ten years, azides have been investigated extensively, both from the mechanistic and synthetic standpoints.[2,3] As a result, several hitherto obscure aspects have been clarified. Some of these studies, those of Lwowski in particular, have attempted to answer some questions about the intriguing behavior of the so-called "rigid" (non-rearranging) azides.[3,4] However, despite the advances made in our knowledge of alkoxycarbonyl and sulfonyl azides,[5] carbamoyl azides, another group of "rigid" azides* have not been examined systematically since Stolle's pioneering work.[6]

In 1964, Lwowski and his students demonstrated that rigid azides could be induced to undergo the Curtius rearrangement by photolysis in methanol.[7] More recently, other investigations of the decomposition of substituted carbamoyl azides have been described.[8–12] We now report the results of the photolysis of diphenylcarbamoyl azide (VI).

RESULTS AND DISCUSSION

The *thermolysis* of certain carbamoyl azides [8a, 9a, 10] can be interpreted in terms of a concerted mechanism in which *no* nitrene intermediates are involved. On the other hand, the candidacy of nitrenes must be considered with greater scrutiny in the *photolysis* of carbamoyl azides. Indeed, while the participation of nitrenes in the

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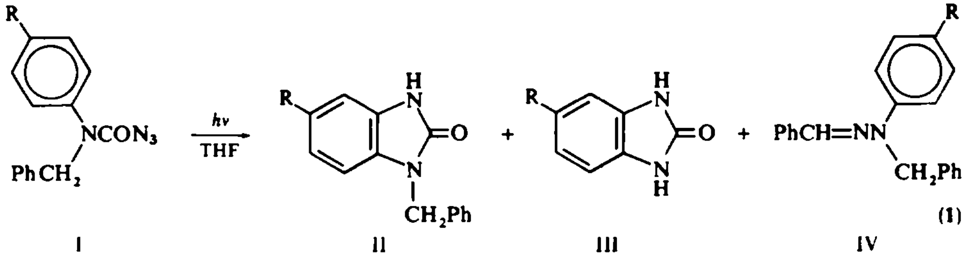
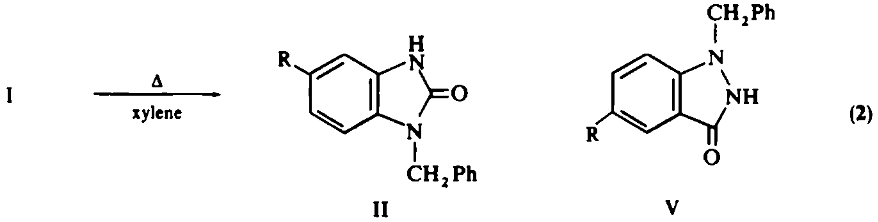
* Actually, as was shown very early by Stolle and his students only the dialkylcarbamoyl azides could be called "non-rearranging". Even in these cases, some traces of the corresponding hydrazines seem to have been detected;[7c] see also Ref 8*b*.

thermally induced Curtius rearrangement[*] seems improbable in view of recent findings,[13] acyl nitrenes[†] have been shown to be intermediates in the photolysis of acetyl[15] and pivaloyl azides.[16,17]

More germane to our results is the report of the *sole* formation of benzimidazolones II and III from the photolysis of *p*-tolyl and *p*-anisyl benzylcarbamoyl azides (I):[9b] in contrast, not only were indazolones (V) isolated in the thermal decomposition but Va was in fact the *major* product in the *p*-tolyl case (Eq. (2)).[9a]



	II	III	IV
(a) R = CH_3	32·0%	8·0%	3·3%
(b) R = CH_3O	30·0%	14·3%	4·1%



	II	V
(a): R = CH_3	9·5%	63·1%
(b): R = CH_3O	35·6%	15·2%

As was previously mentioned, the formation of both II and V in the thermal decomposition of I most likely occurs by a concerted "SN2 displacement" on the azide (Scheme I) either by the ring to give the benzimidazolones (path *a*) *or* by the "amide" nitrogen (path *b*) to give the N-aminoisocyanate (I); cyclization of the latter on the aromatic ring would then lead to the indazolones (V). Evidently, in the thermolysis (Eq. (2)) the less "nucleophilic" methyl substituted ring is much less successful in competing with the amide nitrogen (indazolone major product) than the anisyl ring (benzimidazolone predominates). On the other hand, the results of the photolysis of I strongly suggest that the formation of the benzimidazolones is due to a nitrene which does not discriminate between the reactivity of the two aromatic rings (Eq. (1)).

We had earlier shown that the thermal decomposition of VI (and of biphenylylcarbamoyl azide) in t-butyl and t-amyl alcohols gave the corresponding carbazates (IX) in very good yields: subsequent hydrolysis of these carbazates makes this

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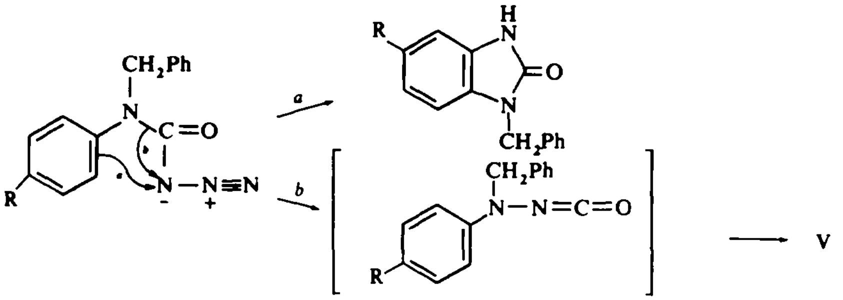
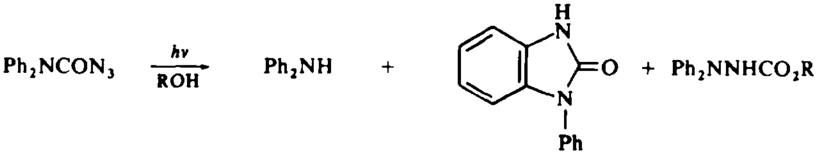
[*] Even in the photo-induced Curtius rearrangement,[17] a nitrene intermediate appears improbable.

[†] For examples of intramolecular trapping of acylnitrenes, see Ref 14. Again, only photolytic decomposition was successful in generating the acyl nitrenes.

SCHEME 1



sequence of reactions an excellent route to *pure* 1,1-diarylhydrazines.[18] The photolysis of VI in alcohols by means of a low pressure mercury lamp gave three products (see Table 1) which were identified as diphenylamine (VII), 1-phenylbenzimidazolone (VIII) and the corresponding carbazates IX (except in t-amyl alcohol). In benzene and tetrahydrofuran VII and VIII were formed while in cyclohexylamine other products incorporating the solvent were also isolated in addition to VII and VIII.



(3)

VI VII VIII IX

The absence of carbazate from the photolysis in t-amyl alcohol is significant and rules out N-diphenylaminoisocyanate (XI) as an intermediate in the reaction.[18,19] This is in agreement with Lwowski's suggestion[7] that a H-bonded azide and *not* a nitrene is responsible for the formation of this type of products. Presumably in the present case, steric hindrance of the bulky t-amyl group (this effect is already noticeable in isopropanol, see Table 1) would render very difficult the establishment of a hydrogen bond of any consequence.† Thus the excited azide would then lose nitrogen to give the nitrene, as indeed seems to be the case since the highest yield of VIII is obtained in t-amyl alcohol.

† It might be possible to rationalize the absence of t-amyl carbazate by the reaction of diphenylaminoisocyanate (XI) with traces of water, on the assumption that the reaction of XI with water is infinitely faster than with t-amyl alcohol. It would have to be assumed further that the other alcohols react almost as fast with XI as water would, since in all likelihood, traces of water are also present in these alcohols. However, several reasons make this possibility very unlikely. The solvents were dried and distilled prior to use and any water would be present in vanishingly small amounts, particularly in t-amyl alcohol. The presence of water might account for a lowered yield of the carbazate but not for its absence. Furthermore, the product of the reaction of XI with water, 1,1-diphenylhydrazine (or the carbohydrazide, see run 4, Table 1) was not isolated. Instead, the "missing" XI appeared as "unrearranged" diphenylcarbamoyl nitrene in the form of 1-phenylbenzimidazolone (VIII), formed in the highest yield (compared with the other alcohols). We thank Prof. M. Tashiro of Kyushu University for bringing this possibility of reaction with water to our attention.

TABLE 1. PHOTOLYSIS PRODUCTS OF DIPHENYLCARBAMOYL AZIDE[a]

Run	Solvent	Time (hr)	Products (%) VII	VIII	IX	Other products
1	Benzene	24	14	57	—	
2	Benzene (piperylene)	24	—	51[b]	—	Ph_2NCON_3 (39%)
3	Benzene (benzophenone)	38	—	44[b]	—	Ph_2NCON_3 (30%)
4	Tetrahydrofuran[c]	24	29	55	—	$(Ph_2NNH)_2CO$ (5%)[d]
5	Methanol	11	9	22	25	
6	Methanol (benzophenone)	24	—	30[b]	31[b]	Ph_2NCON_3 (18%)
7	Ethanol	20	19	35	22	
8	Isopropanol	24	21	35	14	
9	t-Amyl alcohol	12	12	45	—	
10	Cyclohexylamine	48	8	22	31[e]	$C_6H_{11}NHCONH_2$ (17%) $Ph_2NCONHC_6H_{11}$ (13%)[f]

[a] A 52·5 mM solution (200 ml) of the azide was used in each case except in run 1 where the concentration was 21 mM. All yields have been rounded to nearest whole number. During the photolyses, the temp ranged from 30–40°.

[b] These yields are calculated on the basis of azide not recovered.

[c] The solvent most likely contained some water which would account for the formation of $(Ph_2NNH)_2CO$.

[d] The yield of $(Ph_2NNH)_2CO$ should be doubled since it requires two azides to make one carbohydrazide.

[e] This figure represents the yield of 1,1-diphenyl-4-cyclohexylsemicarbazide, the product corresponding to the carbazates.

[f] Probably product of "dark" reaction, see Ref 21.

Of even greater interest is the formation of 1-phenylbenzimidazolone (VIII) coupled with the absence of 1-phenylindazolone (XII), the *major* product of the pyrolysis of VI in xylene.[*] This remarkable change in the nature of the products indicates that diphenylcarbamoyl nitrene (X) is the intermediate which cyclizes to VIII. The portion of photo-induced Curtius rearrangement that occurred, shows up as the carbazates as discussed above. Additional support for the nitrene mechanism comes from the work of Kametani and his group.[9] These authors found that in contrast to the *p*-anisyl case, there is essentially no difference between the "nucleophilicity" of the Me substituted ring[9a] and the corresponding unsubstituted benzene ring in *thermolyses*: thus the Curtius rearrangement (path *b*, Scheme I) predominates over displacement by the ring (path *a*, Scheme I). On the other hand, the photolysis of Ia and of Ib showed[9b] that the nitrene has a "levelling" effect on the difference in the reactivity between the methoxy and the methyl substituted rings.[9a] The presence of triplet quenchers piperylene and benzophenone had no effect on the yield of VIII while the formation of diphenylamine was completely repressed. These results clearly point to a *singlet* nitrene as the source of 1-phenylbenzimidazolone while the *triplet* nitrene is probably involved in the formation of diphenylamine as discussed below.

The surprising formation of diphenylamine has, to our knowledge, no precedent in carbamoyl azide decomposition. Lwowski and his group have reported related results in the photolysis of pivaloyl[16] and ethoxycarbonyl nitrenes;[20] similar products

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[*] Stolle[7a] reported an 88% yield in tetralin (no yield given for pyrolysis in xylene). We obtained a 90% yield of XII and *no* VIII could be isolated.

were detected in the decomposition of some sulfonyl azides.[21] The probability of a dissociation of VI into carbon monoxide and azido and diphenylamino radicals (Eq. (4)) is regarded as unlikely.[22] A more attractive candidate as precursor to diphenylamine is the triplet diphenylcarbamoyl nitrene as shown in Eq. (5). Indeed there is some precedent in the formation of ethoxy and cyanate radicals in the vapor phase flash photolysis of ethyl azidoformate;[16,20] similarly, the formation of iso-

$$Ph_2NCON_3 \longrightarrow N_3\cdot\ CO\ \cdot NPh_2 \longrightarrow Ph_2NH \qquad (4)$$

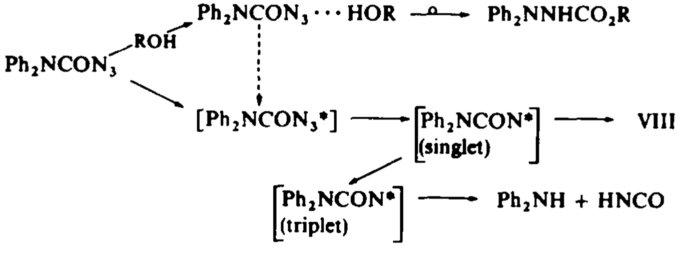
$$Ph_2NCON_3 \longrightarrow N_2 + Ph_2NCON \longrightarrow \cdot N{=}C{=}O + Ph_2N\cdot \longrightarrow Ph_2NH \qquad (5)$$

butene[22] from the photolysis of pivaloyl azide in solution has been viewed as arising by a radical decomposition of the nitrene. However, we believe that hydrogen abstraction by triplet X followed by dissociation into isocyanic acid and diphenylamino radical accounts best for the formation of diphenylamine. The isolation of

$$Ph_2NCO{-}\dot{\underset{\cdot}{N}} \xrightarrow{\text{solvents}} Ph_2NCO\dot{N}H \longrightarrow HNCO + Ph_2N\cdot \longrightarrow Ph_2NH \qquad (6)$$

cyclohexylurea from the photolysis in cyclohexylamine provides strong support for this path. The results obtained in the present study may be rationalized as shown in the scheme below.

SCHEME 2



EXPERIMENTAL*

Thermal decomposition of diphenylcarbamoyl azide.

A soln of 10·0 g (42·8 mmoles) diphenylcarbamoyl azide in 100 ml xylene was heated to reflux for 3 hr after which time the evolution of N_2 had subsided. Upon cooling, 8·0 g (90%) 1-phenylindazolone was obtained as colorless needles, m.p. 206–207°, lit[6a] m.p. 209°. Its IR spectrum was devoid of any C=O absorption and had a broad band at 2300–3100 cm^{-1} (H— bonded OH) and a small sharp band at 1620 cm^{-1} (C=N). The structure of XII is probably that of 3-hydroxy-1-phenyl indazole and this was supported by methylation of XII with MeI and diazomethane which gave the N-Me and a mixture of the N- and O-Me derivatives respectively.[23]

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* All m.ps. are uncorrected. The IR spectra were recorded on a Hitachi EPI-S2 infrared spectrophotometer neat or as KBr pellets. The elemental analyses were performed by Mr. M. Sekine of the Department of Chemistry of Ibaraki University, Mito, Japan.

Photolyses. The photolyses were carried out in an immersion type quartz apparatus under N_2, using a 10 W low pressure nercury lamp (Ricoh Kagaku Sagyo Co., UVL 300Q, max emission at 2537Å). The solvents were distilled prior to use. The progress of the photolyses was monitored by the disappearance of the azide band in the IR spectrum of an aliquot withdrawn periodically. The formation of colored materials, particularly in run 5 essentially stopped the photolysis after the time indicated in Table 1. In the photolyses with piperylene and benzophenone, an equivalent amount of these compounds was used.

The photolysates were then concentrated to a small volume under reduced pressure and chromatographed on Florisil. Diphenylamine, the carbazates and 1-phenylbenzimidazolone[24] were eluted with benzene, 4:1 benzene-ether and 1:1 benzene-ether respectively. The 1,1-diphenyl-4-cyclohexylsemicarbazide which precipitated from the photolysate after evaporation of cyclohexylamine and addition of benzene, was collected. The filtrate was concentrated and the residue chromatographed on Florisil to give diphenylamine, N,N-diphenyl-N-cyclohexylurea, additional amounts of 1,1-diphenyl-4-cyclohexylsemicarbazide, 1-phenylbenzimidazolone and cyclohexylurea which were eluted with benzene, 9:1 benzene-ether, 4:1 benzene-ether, 1:1 benzene-ether and 1:1 methanol-ether respectively. All products were identified by comparison with authentic samples.

Methyl 3,3-*diphenylcarbazate.* A soln of 2·38 g (10 mmoles) of VI in 50 ml of MeOH was heated under reflux for 28 days. Removal of the solvent left 2·40 g of colorless solid. One recrystallization from MeOH gave 2·00 g (83%) of pure product, m.p. 156–157°. (Found: C, 69·35; H, 5·93; N, 11·73. Calc for $C_{14}H_{14}N_2O_2$: C, 69·40; H, 5·82; N, 11·56%).

Isopropyl 3,3-*diphenylcarbazate.* Prepared as above by reflux for 5 days. Recrystallization from isopropanol gave an 82% yield of pure product, m.p. 131–133°. (Found: C, 71·35; H, 7·00; N, 10·58. Calc for $C_{16}H_{18}N_2O_2$: C, 71·08; H, 6·72; N, 10·36%).

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