Curtius and Lossen Rearrangements. II. Pivaloyl Azide

Siegfried Linke, G. Thomas Tisue,[1] and Walter Lwowski[2]

Contribution from the Research Center and the Chemistry Department, New Mexico State University, Las Cruces, New Mexico 88001. *Received June 12, 1967*

Abstract: Pivaloylnitrene, generated photolytically from pivaloyl azide, does not rearrange to *t*-butyl isocyanate at a detectable rate. Neither singlet nor triplet pivaloylnitrene are intermediates in the thermal or in the photo-induced Curtius rearrangement of pivaloyl azide. Both rearrangements are most likely concerted processes.

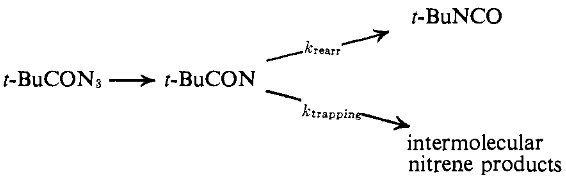
The mechanism of the Curtius rearrangement has been debated since Stieglitz[3] proposed its involving a carbonylnitrene intermediate.

$$\mathrm{RCON_3} \xrightarrow{\Delta} \mathrm{N_2} + \mathrm{RCON} \longrightarrow \mathrm{RN{=}C{=}O} \qquad (1)$$

Some authors have adopted this mechanism,[4] while others[5] prefer a concerted one. Hauser's[6] failure to trap the carbonylnitrene argues for the concerted mechanism, but can be explained by assuming a very short lifetime for the nitrene. The problem has been critically discussed by Smith,[7] who considers the possibility of a spectrum of mechanisms between the two extreme ones. More recently, it has been found that nitrenes can be trapped in the photolytic, but not in the thermolytic, decomposition of a wide variety of carbonyl azides.[8–13] This excludes carbonylnitrenes as intermediates in the thermal Curtius rearrangement, especially since it will be shown in this paper that thermolysis and photolysis can be conducted at temperatures that differ but little from each other. A preliminary account of a part of the work to be discussed below has appeared.[13] The product of the Curtius rearrangement, $\mathrm{RN{=}C{=}O}$, is found in all the reported[8–13] photolytic decompositions of carbonyl azides, $\mathrm{RCON_3}$. It thus seems possible that the photolytic Curtius rearrangement[14] involves a nitrene intermediate which partly rearranges and partly undergoes intramolecular[8,9,11] or intermolecular[10,12,13] reactions. Alternatively, the photolytic Curtius rearrangement could be a concerted process (or have another mechanism not involving a nitrene) which parallels the formation of trappable nitrene. In this paper, we shall show that the latter alternative applies, and that very little or none at all of the isocyanate formed in the photolysis of pivaloyl azide arises by way of rearrangement of pivaloylnitrene.

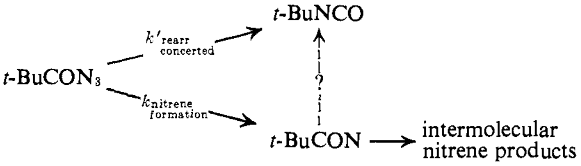
Results and Discussion

The reactions of pivaloylnitrene, briefly reported in a communication,[13] are described in the preceding paper.[15] To gain information on the photolytic Curtius rearrangement, we have accurately determined the yield of *t*-butyl isocyanate formed in photolyses of pivaloyl azide in the presence of efficient and of inefficient nitrene traps. If pivaloylnitrene rearranges to *t*-butyl isocyanate, its removal by nitrene traps should lower the isocyanate yield. The isocyanate yield should be affected little, however, if the nitrene is not the precursor of the isocyanate.



(2)

or



(3)

Thermolysis. In the preceding paper,[15] we reported that we could not find any nitrene products from the thermolyses of pivaloyl azide in several solvents. To complement this negative result, the yield of isocyanate from the thermolysis of pivaloyl azide in refluxing cyclohexane was measured and found to be 99.4%, quantitative within experimental error. Other thermolyses, in cyclohexene and in 2-methylbutane, were conducted at 28° and failed to give any nitrene products.[16] Photolysis at $-10°$ had given yields of nitrene products of 47 and 25%, respectively.[15] It does not seem possible that the temperature difference of 38° would have precluded trapping of the nitrene if it had been present. We conclude, therefore, that the thermal Curtius rearrangement does not involve the inter-

---

[1] National Institutes of Health Predoctoral Fellow, 1962–1965.

[2] To whom correspondence should be addressed at the Chemistry Department, New Mexico State University, Las Cruces, N. M. 88001.

[3] J. Stieglitz, *Am. Chem. J.*, 18, 751 (1896); F. Tiemann (*Ber.*, **24**, 4162 (1891)) had earlier proposed a carbonylnitrene as an intermediate in the Hofmann rearrangement.

[4] J. D. Roberts and M. C. Caserio, "Basic Principles of Organic Chemistry," W. A. Benjamin, Inc., New York, N. Y., 1964, p 656; L. F. Fieser and M. Fieser, "Advanced Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1961, p 502.

[5] J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 336; E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959, p 623.

[6] C. R. Hauser and S. W. Kantor, *J. Am. Chem. Soc.*, **72**, 4284 (1950).

[7] P. A. S. Smith, "Open-Chain Nitrogen Compounds," Vol. 2, W. A. Benjamin, Inc., New York, N. Y., 1966, p 220; P. A. S. Smith in "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 528.

[8] J. Apsimon and O. E. Edwards, *Proc. Chem. Soc.*, 461 (1961); *Can. J. Chem.*, **40**, 896 (1962); further data by Edwards quoted in ref 9.

[9] R. A. Abramovitch and B. A. Davis, *Chem. Rev.*, **64**, 149 (1964).

[10] L. Horner and A. Christmann, *Chem. Ber.*, **96**, 388 (1963); L. Horner, G. Bauer, and J. Dörges, *ibid.*, **98**, 2631 (1965).

[11] R. F. C. Brown, *Australian J. Chem.*, **17**, 47 (1964).

[12] R. Huisgen and J.-P. Anselme, *Chem. Ber.*, **98**, 2998 (1965).

[13] W. Lwowski and G. T. Tisue, *J. Am. Chem. Soc.*, **87**, 4022 (1965).

[14] L. Horner, E. Spietschka, and A. Gross, *Ann.*, **573**, 17 (1951).

[15] G. T. Tisue, S. Linke, and W. Lwowski, *J. Am. Chem. Soc.*, **89**, 6303 (1967).

[16] See Experimental Section of the preceding paper, ref 15.

mediacy of pivaloylnitrene, and it seems most probable to us that the rearrangement is concerted.

Photolysis. Pivaloyl azide was photolyzed, at −10°, in a variety of solvents and solvent mixtures, and the yields of *t*-butyl isocyanate and of intermolecular nitrene products were determined. The isocyanate yield could not accurately be measured by direct gas chromatography, because of the great volatility of this substance. The isocyanate was converted to *t*-butyl-*n*-butylurea by treatment with *n*-butylamine, and the urea was determined by vpc. The other products were determined in a separate aliquot of the reaction mixture, as described before.[15] The results of these experiments are given in Tables I–III. The data show the isocyanate yield to be practically the same under all conditions, while the yields of intermolecular nitrene products vary over a wide range, depending on the nature and concentrations of the substrates present.

Table I. Photolysis of Pivaloyl Azide in Various Solvents

	Yields,[a] %		
Solvent	*t*-BuNCO	C–H insertion product	Pivalamide
Cyclohexane	41.8, 39.9, 40.3, 43.2	20.6, 19.0, 19.9, 20.4	0.5
Cyclopentane	41.0, 43.3	13.4, 12.2	0.5
Neopentane	40.1, 39.4	0.2	0.7
Dichloromethane	43.2	...	0.4
Cyclohexene[b]	41.0	1.7, 1.2[b]	0.4
Benzene[c]	40.3	...	0.9

[a] Based on pivaloyl azide. [b] For the double-bond addition product, and its instability under the photolysis conditions, see ref 15. The figures for C–H insertion product given here are for 30% conversion.[15] [c] N-Pivaloylazepine, the addition product expected in analogy to the product from benzene and carbethoxynitrene, seems not to be stable under the photolysis conditions. It could not be isolated, but a nonvolatile oil was obtained (see Experimental Section). The reaction was not investigated further.

Table II. Photolysis of Pivaloyl Azide in Mixtures of Cyclopentane and Neopentane

Mole % cyclopentane in neopentane	Yields,[a] %			
	Isocyanate	N-Neopentylpivalamide	N-Cyclopentylpivalamide	Pivalamide
100	41.0, 43.3	...	13.4, 12.2	0.5
90	39.8	...	9.0	0.6
80	39.6	...	7.7	0.5
75	39.9	...	7.6	0.5
70	40.0	...	6.3	0.5
60	42.8	...	4.9	0.6
50	42.1	...	2.5	0.6
40	39.8	...	2.0	0.6
30	41.2	...	1.9	0.7
25	43.7	Trace	1.5	0.8
20	41.4	Trace	1.2	0.7
10	42.8	Trace	0.8	0.6
0	40.1, 39.4	0.2	...	0.7

[a] Based on pivaloyl azide.

The independence of the isocyanate yields from those of the nitrene products means that the nitrene cannot be a precursor of the isocyanate. Scheme 2 cannot apply, nor can the dashed arrow in scheme 3 represent a reaction competitive with those represented by solid arrows. To summarize our results, *neither the thermal nor the photoinduced Curtius rearrangements can involve a nitrene intermediate.*

Table III. Photolysis of Pivaloyl Azide in Mixtures of Cyclohexene and Cyclopentane[a]

Mole % cyclohexene in cyclopentane	Yields,[b] %				
	Isocyanate	N-(Cyclohex-2-enyl)pivalamide[c]	N-Cyclopentylpivalamide	Pivalamide	3,3'-Bis(cyclohexenyl)
100	41.0	6.8, 6.8	...	2.8[c]	0.3
77	39.8	6.8	...	ND[d]	0.4
68	40.7	6.8	...	ND	0.4
60	39.9	7.0, 6.7	...	ND	0.5
51	38.9	6.7	...	ND	0.5
43	39.7	6.6	...	ND	0.6
34	39.3	6.5	Trace	ND	0.6
26	39.8	6.2	Trace	ND	0.6
17	38.6	6.0	Trace	ND	0.7
8.5	39.6	5.2	0.8	ND	0.6
0	41.0	...	13.4, 12.2	0.5	...

[a] Yields after 24 hr of photolysis, see footnote *b*, Table I. [b] Based on pivaloyl azide. [c] This is in part decomposition product from the double-bond adduct, 7-pivaloyl-7-azabicyclo[4.1.0]heptane; see ref 15. [d] ND = not determined.

On paper, a rearrangement of a carbonylnitrene to an isocyanate looks facile. It is not yet understood why it should be so much slower than intermolecular reactions. One might argue that only the singlet nitrene can rearrange, and that the observed intermolecular reactions are those of the triplet. This is out of line, however, with the results on carbethoxynitrene. The latter inserts into C–H bonds only in its singlet state.[17,18] That the same is true for pivaloylnitrene is indicated by the experiments in cyclohexene–cyclopentane mixtures (Table III). The yields of N-cyclopentylpivalamide decrease rapidly with decreasing cyclopentane concentration, while the yields of product derived from the double-bond addition to cyclohexene remain practically constant. The reverse hypothesis, that only the triplet pivaloylnitrene rearranges to isocyanate, is rendered unlikely by the observation that no more isocyanate is formed in neopentane solution (where the triplet should accumulate due to the low reactivity of the singlet toward neopentane) (Table II). This leaves us with the conclusion stated above: pivaloylnitrene is not an intermediate in either type of Curtius rearrangement. Unless one wants to invent a new intermediate, neither singlet nor triplet nitrene, the Curtius rearrangements must be concerted.

Loosely related to our considerations is the question of the generality of our mechanism 3. Most likely, mechanism 3 (with the dashed arrow representing a very slow or nonexistent path) holds for all alkylcarbonyl azides. It might also hold for arylcarbonyl azides, but in view of the great migratory aptitude of aryl groups, future investigations might well show that some arylcarbonylnitrenes do in fact rearrange rapidly. To extend the generalization of our results to rearrangements similar to the Curtius rearrangement would be unsafe. Smith[19] has found that certain N-aryl-

---

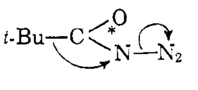
(17) W. Lwowski and F. P. Woerner, *J. Am. Chem. Soc.*, 87, 5491 (1965).

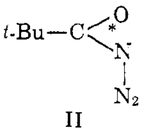
(18) W. Lwowski and J. Simson, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, Abstract O-163; J. Simson, Thesis, Yale University, 1967.

(19) P. A. S. Smith and E. Leon, *J. Am. Chem. Soc.*, 80, 4647 (1958); J. Vaughan and P. A. S. Smith, *J. Org. Chem.*, **23**, 1909 (1958).

imidoyl azides (such as the N-phenylbenzimdoylazide presumably formed in the thermolysis of 1,5-diphenyltetrazole) thermolyze to a mixture of benzimidazoles (intramolecular nitrene cyclization) and carbodiimides (an "imido-Curtius rearrangement"). This might very well be a case were an imidoylnitrene both rearranges and cyclizes.

Establishing the existence of two parallel mechanisms in the photolysis of pivaloyl azide raises the question of the detailed nature. The nitrene formation most likely involves excitation of the azide to the lowest singlet excited state, followed by loss of nitrogen. The rearrangement might occur, simultaneous with the loss of nitrogen, in that same electronically excited state of the azide, perhaps in those molecules that happen to be in a more suitable conformation I rather than II.


I


II

Another possibility is a competition between the dissociation of the excited azide (to give nitrene) and its internal conversion to a highly vibrationally excited molecule. The latter would either be quenched by collisions, or undergo normal, thermal, Curtius rearrangement. The photoinduced rearrangement would, then, involve only a special route to vibrationally activated azide (in a cool environment). Both intimate mechanisms would, of course, be in accord with the mechanism of scheme 3.

Experimental Section

The general techniques, authentic compounds, and pivaloyl azide have been described in the preceding paper.[15] Solvents and solvent mixtures used for the experiments were saturated with nitrogen; the cyclohexene was purified as before.[15]

***t*-Butyl isocyanate** was prepared, in 58% yield, by heating ethyl N-*t*-butylcarbamate[20] with powdered calcium hydroxide to 220°.[21] The thermal Curtius rearrangement of pivaloyl azide also gave pure *t*-butyl isocyanate.

N-*n*-Butyl-N′-*t*-butylurea was made by adding a solution of 1.46 g (0.2 mole) of *n*-butylamine in 10 ml of pentane to a solution of 1.98 g (0.2 mole) of *t*-butyl isocyanate in 10 ml of pentane, with cooling. An exothermic reaction occurred immediately. After 2 hr at room temperature, the solvent was removed. An almost quantitative yield of the urea crystallized upon refrigeration, mp 71–72°; infrared spectrum: NH at 3345 cm^{-1} (broad), CO at 1631 cm^{-1} (in CCl_4).

Anal. Calcd for $C_9H_{20}N_2O$: C, 62.75; H, 11.70; N, 16.26. Found: C, 62.66; H, 11.66; N, 16.14.

Photolyses were carried out, and the product yields determined as before.[15] The yields of *t*-butyl isocyanate were measured in a separate aliquot of the reaction mixtures by injecting 3 ml of *n*-butylamine at −10°. After 2 hr at −10°, and 1 hr at room temperature, the solvent was removed *in vacuo*. The residue was transferred to a 10-ml volumetric flask, and diluted to 10 ml with tetrahydrofuran. Vpc analyses were done on columns[15] A (160° column temperature) and B (146° column temperature).

Photolysis in Benzene. The photolysis was carried out as before[15] but since pure benzene would have frozen, a mixture of 45 ml of benzene and 5 ml of dichloromethane was used. During irradiation, the mixture turned light yellow. After evaporation of excess solvent and *t*-butyl isocyanate, an oily, nonvolatile residue remained. Its infrared spectrum (in CCl_4) showed absorptions at 3284, 2985, 1681, 1479, 1393, 1366, 1279, and 1242 cm^{-1}. The spectrum showed three multiplets at δ 1.25, 2.0, and 3.67.

Acknowledgment. We are greatly indebted to the National Science Foundation for generous support of this work.

[20] H. van Erp, *Rec. Trav. Chim.*, **14**, 17 (1895).

[21] B. Brauner, *Ber.*, **12**, 1874 (1879).

Unsaturated Macrocyclic Compounds. LI.[1]

1,6-Oxido[10]annulene[2]

Arnon Shani and Franz Sondheimer[3]

Contribution from the Daniel Sieff Research Institute,
the Weizmann Institute of Science, Rehovoth, Israel. *Received June 19, 1967*

Abstract: 9,10-Oxido-1,4,5,8,9,10-hexahydronaphthalene (**10**) on hydrolysis to 1,4,5,8,9,10-hexahydronaphthalene-*trans*-9,10-diol (**11**), followed by successive bromination and dehydrobromination, gives the tribromo oxide **13a** and the diene bromo oxide **14** instead of the anticipated 9,10-dihydronaphthalene-*trans*-9,10-diol (**5**). The oxide **10** on bromination and subsequent dehydrobromination yields 1,6-oxido[10]annulene (**20**), as well as 1-benzoxepin (**24**). In agreement with theory, the ten π-electron system **20** is shown to be an aromatic compound. Various reactions of **20** are described, including its nitration to the 2- and 3-nitro derivatives **27** and **26**. 1,6-Oxido[10]annulene (**20**) is easily converted to naphthalene derivatives, *e.g.*, by lithium aluminum hydride reduction, catalytic hydrogenation, and treatment with acids.

A variety of annulenes (monocyclic conjugated polyenes) and dehydroannulenes (monocyclic conjugated polyenynes) have been prepared in recent years.[4] These substances are expected to be aromatic, provided they contain $(4n + 2)$ out-of-plane π electrons, the carbon skeleton is reasonably coplanar, and the ring size is below a certain limit.[4]

---

[1] For Part L, see C. C. Leznoff and F. Sondheimer, *J. Am. Chem. Soc.*, **89**, 4247 (1967).

[2] Taken from the Ph.D. thesis of A. Shani, Weizmann Institute of Science, March 1965.

[3] Author to whom inquiries may be addressed at the Chemistry Department, University College, London, W.C. 1, England.

[4] For reviews, see F. Sondheimer, *Pure Appl. Chem.*, **7**, 363 (1963); F. Sondheimer, *Proc. Roy. Soc.* (London), **A297**, 173 (1967); F. Sondheimer, *et al.*, Special Publication No. 21, The Chemical Society, London, 1967, p 75.