

REACTIONS OF AMINES. XVI. 1-t-BUTYL-3,3-DIPHENYLAZIRIDINONE (1,2)

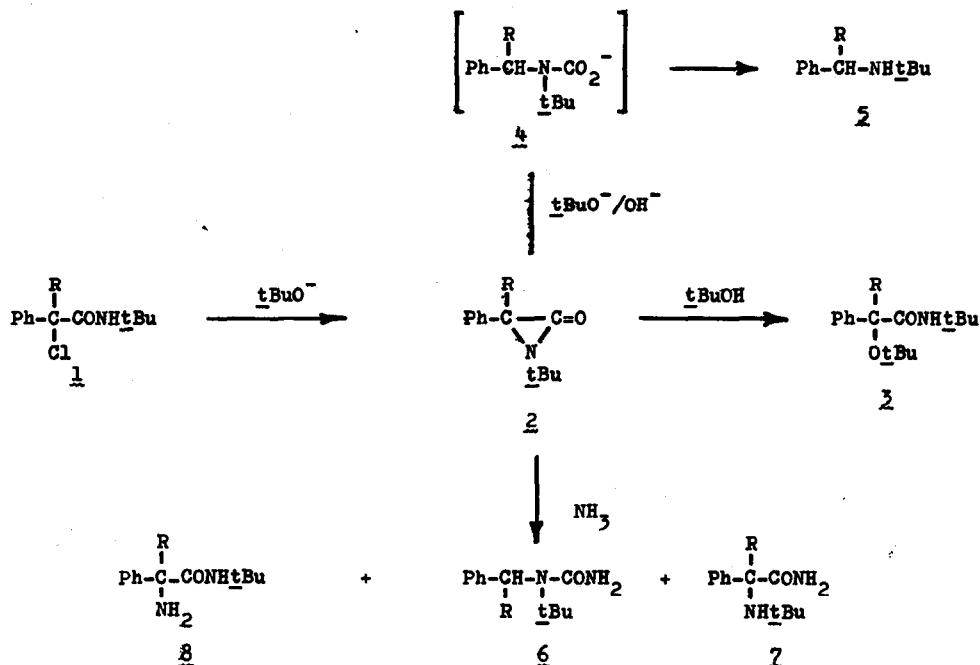
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Although a number of novel reactions which may proceed through 1-alkyl or 1-aryl derivatives of 3,3-diphenylaziridinone have been discovered (3-6), the actual isolation and characterization of  $\alpha$ -lactams with two aryl groups on carbon have not been reported. Indeed, Sheehan and Beeson (7) have recently reported that 1-t-butyl-3,3-diphenylaziridinone (2a) "has been observed only at low temperatures" and have suggested that the lability of 2a may be attributed to thermal instability. Neither of these statements is entirely correct, for about 2.5 years ago we found that 2a could be prepared and isolated in up to 65% yield from the reaction of N-t-butyl- $\alpha$ -chlorodiphenylacetamide (1a) with potassium t-butoxide (8) in ether (or toluene) provided that the reaction is carried out properly and quickly at ice-bath temperatures or below. Although in our hands this  $\alpha$ -lactam (m.p. 79-81°;  $\nu(\text{C=O})$  1847  $\text{cm}^{-1}$ ; 60 MHz nmr peaks at 441 (10H) and 77 (9H) Hz; purity of average crude sample > 95%) (11) was very reactive in most solutions, it could be kept as a solid in the freezer for periods of at least several months. One sample kept in the desiccator at room temperature had a half-life in excess of 16 days. Furthermore, the half-life varied considerably with sample purity; therefore, it could not be solely a function of thermal decomposition or isomerization but must also be a function of chemical reactivity (12). Deliberate pyrolysis of 2a at 105° gave benzophenone and t-butyl isocyanide as major products. The slow decomposition at room temperature gave little or no benzophenone, but gave a mixture of several products whose structures are currently under study (13).



Series a: R = Ph; series b: R = H

We had no difficulty in determining the mass spectrum of 2a which contains a reasonably strong molecular ion peak at  $m/e$  265 and which is best rationalized by a fragmentation pattern compatible with the assigned structure (14). Thus, 2a does not appear to be appreciably less stable thermally than the monophenyl lactam 2b reported previously (9,10), although 2a is much more reactive chemically.

The reactions of 2a, although not entirely unique, differ in some respects from those of the monophenyl lactam 2b. Thus, *N*-alkyl- $\alpha$ -chlorodiphenylacetamides have been reported (6) to react with sodamide in liquid ammonia to give products probably resulting from all three one-bond cleavage reactions of a presumed  $\alpha$ -lactam intermediate. The reactions of pure 2a support, in part, this earlier report, although it is clear from our experiments that the cleavage reagent is probably ammonia rather than sodamide. Thus, addition of 2a to liquid ammonia gave by 2-3 cleavage 62% of *N*-benzhydryl-*N*-*t*-butylurea (6a) (m.p. 110-112°; 60 MHz nmr peaks at 432 (10H), 365 (1H), 243 (2H), 92 (9H) Hz) (11). Minor products included about 10%

of the 1,3 cleavage product,  $\alpha$ -amino-N-t-butylidiphenylacetamide (8a) (m.p. 103-105°; 60 MHz nmr peaks at 434 (multiplet, 11H), 127 (2H), 74 (9H) Hz) (11) and a trace of what appeared to be the 1-2 cleavage product,  $\alpha$ -t-butylaminodiphenylacetamide (7a) (60 MHz nmr peak at 68 Hz). The reaction of 2a with methylamine, dimethylamine, and other amines gave one or more of the three one-bond cleavage products but the relative proportions of each depended upon the amine used and the reaction conditions (particularly the order of addition). The novel reactions of certain analogs of 1a with cyclic secondary amines at elevated temperatures reported recently (15) (and readily confirmed in this laboratory (13) with 1a) appear not to take place with 2a at low temperatures. Thus, the reactions of ammonia and the amines with this and other  $\alpha$ -lactams (13) are not simple and will be reported in detail in a later communication, as will other novel reactions of 2a and other  $\alpha$ -lactams.

Although 2a reacted with t-butyl alcohol to yield the 1-3 cleavage products,  $\alpha$ -t-butoxy-N-t-butylidiphenylacetamide (3a) (9,10) in essentially quantitative yield, it reacted with "aged" potassium t-butoxide (8,16) to give benzhydryl-t-butylamine (5a) (m.p. 53-54.5°; 60 MHz nmr peaks at 410-461 (10H), 302 (1H), 75 (1H), 64 (9H) Hz) (11) in up to 59% yield. Thus, 2a must have reacted with the potassium hydroxide in the reagent to give the carbamic acid salt 4a which was decarboxylated to 5a during workup. This is the first reported 2-3 cleavage caused by a reagent other than ammonia. No 1-2 or 1-3 cleavage product could be detected by nmr or infrared techniques. By way of contrast 2b reacted with "aged" potassium t-butoxide (8) to give only the 1-2 cleavage product, potassium  $\alpha$ -t-butylaminophenylacetate (m.p. 324-330°; 60 MHz nmr peaks in D<sub>2</sub>O at 442 (5H), 256 (1H), 69 (9H) Hz) (11).

Finally, lest it appear that 2-3 bond cleavages occur only with 3,3-diphenylaziridinones, we point out that 2b reacts with liquid ammonia to give a 58% yield of N-benzyl-N-t-butylurea (6b) (m.p. 131° dec.; 60 MHz nmr peaks at 454 (5H), 275 (sharp and broad singlets, 4H), 89 (9H) Hz) (11) by 2-3 bond cleavage and a 38% yield of  $\alpha$ -t-butylaminophenylacetamide (7b) (m.p. 94-95.5°; 60 MHz nmr peaks at 438 (5H), 392-423 (broad singlet, 2H), 255 (1H), 92-105 (broad singlet, 1H), 66 (9H) Hz) (11) by 1-2 bond cleavage. The reactions of 2b with ammonia and various amines were also dependent on reaction conditions; however, the two lactams 2a and 2b

showed marked quantitative differences in behavior toward the amines (13).

## REFERENCES

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7. J. C. Sheehan and J. H. Beeson, J. Am. Chem. Soc., 89, 366 (1967).
8. Since we are in part responsible for the use of potassium t-butoxide as base in the cyclization of  $\alpha$ -halo (9) and N-halo (10) amides, we should emphasize that our reasons for using this base were not precisely the same in the two cyclizations. N-Halo amides appear to require a very strong base;  $\alpha$ -halo amides do not and may be cyclized with other alkoxides or even powdered potassium hydroxide. In the latter cyclization potassium t-butoxide has the advantage that the t-butyl alcohol formed is a poor nucleophile, which does not attack rapidly the  $\alpha$ -lactam ring at low temperatures. There is surprisingly little difference in the cyclizations of some  $\alpha$ -halo amides using fresh and "aged" (containing potassium hydroxide and/or carbonate) potassium t-butoxide, an observation that requires careful interpretation of reported experimental results purportedly carried out with potassium t-butoxide.
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11. Correct elemental analyses were obtained for all new compounds reported here.
12. Although 2a could not be isolated from the reaction of N-t-butyl-N-chlorodiphenylacetamide with potassium t-butoxide, under proper conditions products derived from 2a could be isolated in good yield from the reaction mixture.
13. L. S. Endres, unpublished results.
14. R. G. Parker, unpublished results.
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16. The reactions of 2a with fresh potassium t-butoxide are more complex and are still under study.