p-Ethylphenylsodium was prepared by the slow dropwise addition of pure *p*-chloroethylbenzene (10.0 g., 0.071 mole) in 20 ml. of dry ethylbenzene to a sodium dispersion (3.5 g., 0.15 g. atom) covered by 75 ml. of ethylbenzene at 10° with high speed stirring under an atmosphere of dry nitrogen. High speed stirring was continued for 1 hour at 10° and for 20 hr. at room temperature. The carbonation, work-up esterification with diazomethane and analysis were all identical to the methods described previously.

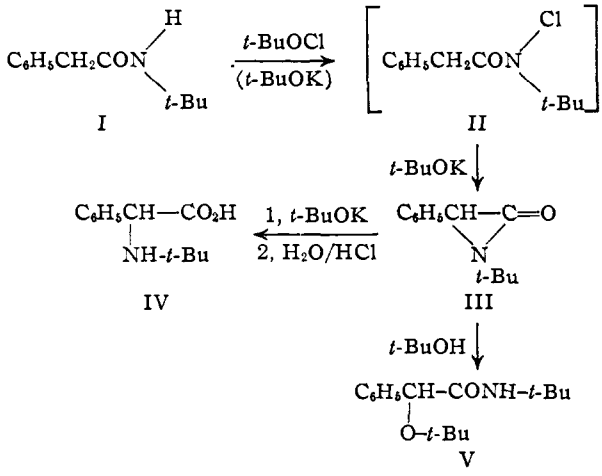
Acknowledgment.—The authors are grateful for financial assistance from the Petroleum Research Fund which made this work possible.

COMMUNICATIONS TO THE EDITOR

REACTIONS OF AMINES. X. 1-*t*-BUTYL-3-PHENYLAZIRIDINONE[1,2]

Sir:

In an earlier communication[1] we reported presumptive evidence for the existence of an α-lactam intermediate (III) (or some closely related substance (*vide infra*)) in the base-catalyzed rearrangement of N-chloro-N-*t*-butylphenylacetamide (I) to derivatives of phenylglycine (V). The present communication describes the isolation and characterization of this intermediate, which is believed to be the first authentic α-lactam to be so isolated and characterized.



In the earlier experiments potassium *t*-butoxide was employed as the base and benzene–*t*-butyl alcohol solution as solvent. Many subsequent experiments by several workers in this Laboratory yielded mixtures of what appeared to be 1-*t*-butyl-3-phenylaziridinone (III) and α-*t*-butoxy-N-*t*-butylphenylacetamide (V), but all attempts to separate the components either failed or resulted in the destruction of III. However, examination of the results of these and other experiments carried out on mixtures of III and V, as well as of II, III, and V, suggested that the successful isolation of III would require substantial completion of step II → III and minimization of step III → V. Accordingly, the base-solvent system was changed to potassium *t*-butoxide–toluene to reduce the concentration of *t*-butyl alcohol, and the quantities of reactants were adjusted so that the principal contaminant at the end of the reaction was unreacted (or regenerated) I, which was separated easily from III by virtue of the former's lower solubility in pentane.

In a typical experiment a solution of 3.4 g. of potassium *t*-butoxide in 250 ml. of toluene was added slowly with stirring over a period of 1 hr. to a solution of 5.7 g. of I and 3.3 g. of *t*-butyl hypochlorite in 120 ml. of toluene held at 5 ±5°.[3] The toluene was evaporated under vacuum at 0 ± 5°, and the residue was extracted with pentane. After 24 hr. in the freezer, the precipitated I was filtered off and the filtrate was concentrated to a small volume, yielding 1.75 g. (31%) of III, m.p. 29–31°. Samples III were recrystallized from pentane for analysis, m.p. 32–33° (Kofler) (Found for $C_{12}H_{15}NO$: C, 75.97; H, 8.02; N, 7.28; mol. wt., (thermistor method), 185, 186). The infrared spectrum showed a very strong ν(C=O) band at 1844 (CH_3CN), 1847 ($CHCl_3$), 1849 (CCl_4) or 1848 (Nujol mull) cm.$^{-1}$. Freshly recrystallized samples showed no significant absorption in the 1600–1800 cm.$^{-1}$ range, nor in the 3100–3500 cm.$^{-1}$ range.[4] In the n.m.r. spectrum[5] (CCl_4) of III peaks corresponding to the nine CH_3 protons appeared at 8.67 τ, the five aromatic ring protons at 2.63 τ, and the single proton of the α-lactam ring at 6.22 τ.

The purified α-lactam III appeared to be a moderately stable but reactive substance, which could be kept (dry) in the solid state for several months in the freezer or several days at room temperature without serious decomposition. It reacted with *t*-butyl alcohol in 2 hr. at room temperature to give V[1] as the sole product, and with a saturated solution of potassium *t*-butoxide in *t*-butyl alcohol with subsequent hydrolysis by aqueous hydrochloric acid to give IV[1] as the sole product.

The physical data, together with the two modes of ring cleavage, are compatible with the α-lactam structure assigned to III and are most easily rationalized in terms of that structure.[1] However,

(1) Paper IX, *J. Am. Chem. Soc.*, **83**, 4469 (1961).

(2) This work was supported in part by grant G-21405 of the National Science Foundation.

(3) Fortuitously, for this specific series of experiments the theoretical quantities (*assuming* 100% purity for reagents) were also the optimum quantities. In other experiments and with derivatives of III it has been found necessary to adjust either the amount of a given sample of base or of *t*-butyl hypochlorite for optimum yield and separation. For some analogs of III optimum quantities of reagents have yet to be found.

(4) Attempts to prepare KBr pellets under ordinary conditions led to destruction of the compound. However, by minimizing both the time and final pressure of the pressing operation, a moderately satisfactory KBr-pellet spectrum has been obtained for the *p*-chloroderivative of III (James Fuerholzer, unpublished results).

(5) The author is indebted to Dr. James P. Collman for the determination of the n.m.r. spectrum.

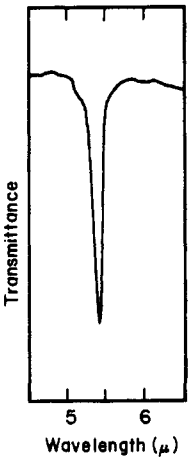
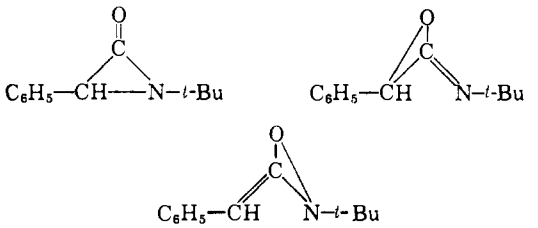


Fig. 1.—Infrared spectrum of 1-*t*-butyl-3-phenylaziridinone (in pentane solution).

as noted previously, the evidence accumulated to date cannot eliminate the alternative structures



(valence tautomers) or some more highly delocalized structure.[1,6] Probably no chemical technique would suffice to distinguish between the valence tautomers (if they exist independently as such) because of the ever-present possibility of interconversion prior to or during reaction. Nevertheless, the isolation of III of analytical and spectroscopical purity encourages one to think that its structure may be more rigorously defined by more sophisticated physical techniques (*e.g.*, X-ray analysis). The latter as well as the preparation and reactions of analogs of III are under study.

(6) See A. W. Fort, *J. Am. Chem. Soc.*, **84**, 2620 (1962), for references to the related problem of the structure of the intermediate in the Favorski reaction.

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C(19)-SUBSTITUTED STEROIDS. IV.[1] STUDIES OF LONG RANGE SHIELDING BY THE CARBONYL GROUP WITH NUCLEAR MAGNETIC DOUBLE RESONANCE AND NUCLEAR MAGNETIC TRIPLE RESONANCE AT 100 MC.

Sir:

We wish to report the examination of 3,3-dimethoxy-2β,19-epoxy-5α-androstan-17β-ol[1] I, 2β,-17β-dihydroxy-3,3-dimethoxy-5α- androstan - 19-oic acid 2,19-lactone II,[1] and 2β,19-epoxy-5α-cholestan-3-one[1] III by n.m.r. spectrometry and the demonstration of long range shielding effects of the carbonyl

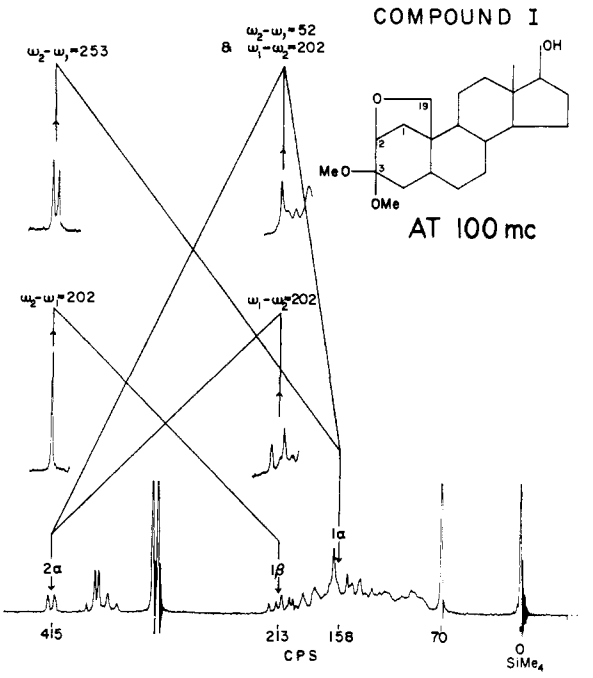

Fig. 1a.

group[2] in II and III by double resonance (n.m.d.r.)[3 a-f] and triple resonance (n.m.t.r.) techniques using Varian HR-100 spectrometer. These experiments were performed by modifying[4] the Varian-3521 integrator by breaking connection between modulation output and the probe sweep coils and inserting a 0.01 μfd capacitor, then the modulation index of 1.8 is reduced to a much lower number. Ordinary absorption spectra then are obtained by using either upper or lower 2 kc. (ω_1) sideband. By connecting an audio-oscillator to either the r.f. unit or the sweep coils additional field modulation at a variable frequency (ω_2) can make a portion of the r.f. power available for selective nuclear saturation and hence spin–spin decoupling or double resonance (n.m.d.r.). Similarly triple resonance (n.m.t.r.) was accomplished by using an additional oscillator. When operating on the lower 2 kc. sideband, protons whose chemical shifts are at higher applied field than those to which they are coupled may be decoupled by getting $\omega_2 - \omega_1$ approximately equal to the separation of the signals being decoupled. The frequency difference between ω_2 and ω_1 is not exactly equal to the chemical shift difference of the two groups of spin-coupled nuclei[5] although in general this discrepancy is small. The n.m.r. spectra are shown in Fig. 1 and the pertinent resonance values and coupling are given in Table I. All the samples were run as $CDCl_3$ solutions with tetramethylsilane added to act as an internal reference.

(1) Paper III in this series: R. Kwok and M. E. Wolff, *J. Org. Chem.*, in press. This investigation was supported in part by a PHS research grant (A-5016) from the National Institute of Arthritis and Metabolic Diseases, United States Public Health Service.

(2) Y. L. Crombie and J. W. Lown, *Proc. Chem. Soc.*, 299 (1961).

(3) (a) A. L. Bloom and J. N. Shoolery, *Phys. Rev.*, **97**, 1261 (1955). (b) W. A. Anderson, *ibid.*, **102**, 151 (1956). (c) J. D. Baldeschwieler, *J. Chem. Phys.*, **36**, 152 (1961). (d) J. P. Maher and D. F. Evans, *Proc. Chem. Soc.*, 208 (1961). (e) V. Royden, *Phys. Rev.*, **96**, 534 (1954). (f) R. Freeman and D. H. Whiffen, *Mol. Phys.*, **4**, 321 (1961).

(4) Varian Technical Information Bulletin, Vol. III, No. 3, ins. 1471.

(5) W. A. Anderson and R. Freeman, *J. Chem. Phys.*, July 1 (1962).