

geometry of the cation is important for the computation of delocalization energy, charge density distribution, and bond orders. With this in mind, a crystallographic investigation of *sym*-triphenylcyclopropenyl perchlorate (TPP<sup>+</sup>ClO<sub>4</sub><sup>-</sup>) was undertaken. A microcrystalline sample of this salt was kindly supplied by Professor Ronald Breslow of Columbia University.

**Experimental.**—Single crystals of *sym*-triphenylcyclopropenyl perchlorate (C<sub>21</sub>H<sub>15</sub>ClO<sub>4</sub>) adequate for the present investigation were crystallized from acetonitrile. The crystals are monoclinic, elongated along *b*. The following unit-cell parameters were determined from oscillation and Weissenberg photographs using Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ):  $a = 9.97 \text{ \AA}$ ,  $b = 12.05 \text{ \AA}$ ,  $c = 17.28 \text{ \AA}$ , and  $\beta = 120^\circ$ . The space group is P2<sub>1</sub>/c. Equi-inclination Weissenberg photographs of the ten levels,  $h0l$ – $h9l$ , were collected employing the multiple film technique. Intensities were eye-estimated by comparison with a calibrated intensity strip and the usual Lorentz and polarization corrections applied. Photometered unidimensionally integrated Weissenberg  $0kl$  and  $2kl$  data were used to correlate the separate layers.

**Structure Determination.**—The molecular orientation in the crystal was clearly indicated by the spectra  $\bar{3}014$  and  $602$ . The occurrence of high vector density at  $\frac{1}{2}, 0$ ;  $0, \frac{1}{2}$ ; and  $\frac{1}{2}, \frac{1}{2}$  in addition to the origin peak in the ( $h0l$ ) Patterson projection limited the possible positions of the molecule in the unit-cell. In the Harker section of the 3-dimensional Patterson function there are four outstandingly high peaks. These are evidently Cl–Cl interactions, one pair being Harker peaks and the other non-Harker. This feature indicates that the Cl atoms are located in or near the glide planes. Preliminary structure factor calculations and packing considerations were used as a validity check.

Approximate O atom coordinates were taken from a partial  $F_o$  synthesis in the region of ClO<sub>4</sub><sup>-</sup> calculated with phases based on the Cl position. Further structure factor–Fourier computations with the Cl and 4 O atoms showed many peaks distributed in hexagonal and fragmented hexagonal pattern throughout the unit cell. In this conglomeration of peaks it was possible to identify quite distinctly the cyclopropenyl ring and the phenyl group attached to C-1. Inclusion of these 9 carbon atoms in the next round of structure factor and Fourier calculation yielded no new information. At this stage it was decided to compute a set of structure factors assuming an essentially planar TPP cation fitted as indicated by the 3-dimensional Patterson function. The observed slight decrease in the *R* factor was disturbing. Since the shifts in O atom coordinates had been small, it was suspected that their positions might be in error. Accordingly, the oxygen atoms were omitted in the following structure factor calculation. The *R* factor decreased dramatically and the  $F_o$  synthesis indicated the correct oxygen positions. Subsequent refinement was by full matrix least squares and the structure converged rapidly to the present *R* value of 13%. Further refinement of the structure is in progress.

**Discussion.**—The structure is composed of TPP cations and ClO<sub>4</sub> anions. The center of the cyclopropenyl group is coincident with the 2<sub>1</sub> axes, sandwiched between the anions, while the anions (nuts) are tightly held by pairs of cations (nutcrackers). The cyclopropenyl ring and the three phenyl atoms attached to it lie approximately in a plane. The average C–C distance in the cyclopropenyl ring is 1.40  $\text{\AA}$ , and the

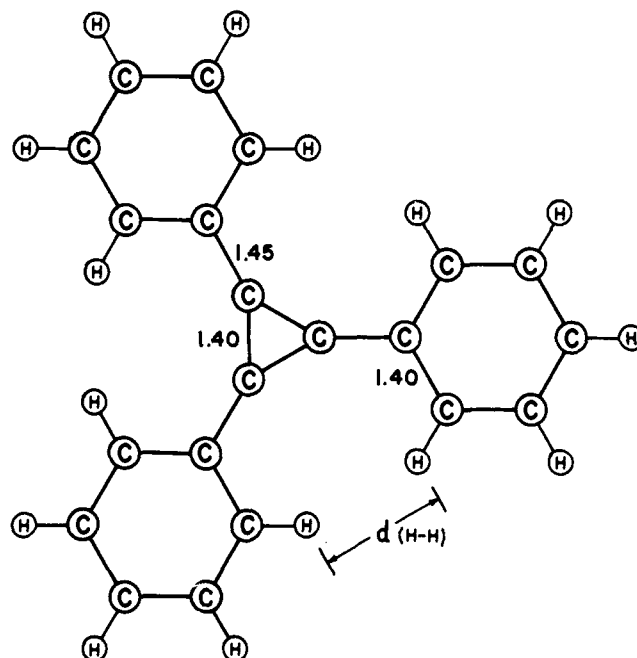


Fig. 1.— $d_{\text{H-H}} = 2.18 \text{ \AA}$  for a C–H distance of 1.0  $\text{\AA}$  and C–C distances as shown, assuming a planar configuration.

average exocyclic C–C "single" bond length is 1.45  $\text{\AA}$ . The *sym*-triphenylcyclopropenyl cation has been assumed planar.<sup>3</sup> While this would result in rather severe compression of H atoms, the uncertainty in the C–C bond lengths was felt to be sufficient to relieve it. Contrary to these earlier assumptions, the *sym*-triphenylcyclopropenyl cation as a whole is nonplanar; the phenyl groups are twisted out of the plane of the cyclopropenyl group at an average angle of  $21^\circ$ . From these dimensions and an assumed C–H length of 1  $\text{\AA}$ , the calculated "ortho" H–H distance for a planar TPP cation is 2.18  $\text{\AA}$ , about 0.2  $\text{\AA}$  shorter than the sum of the van der Waals radius for hydrogen. The observed nonplanarity is just sufficient to accommodate these atoms with a normal radius.

**Acknowledgment.**—M. S. is indebted to Professor G. A. Jeffrey, University of Pittsburgh, for his encouragement and the award of a Research Associateship during the tenure of which the experimental work was performed. He is grateful to Professor Ronald Breslow, Columbia University, for a lavish supply of the sample. We wish to thank the National Institutes of Health and the U. S. Public Health Service for Grants GM-10828 E1423, respectively.

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## Reactions of Amines. XII. The Structure of $\alpha$ -Lactams<sup>1,2</sup>

Sir:

The intermediate isolated in the Favorskii-like rearrangement of *N*-*t*-butyl-*N*-chlorophenylacetamide **1** has been assigned tentatively the  $\alpha$ -lactam structure, 1-*t*-butyl-3-phenylaziridinone (**3**).<sup>3</sup>

(1) Paper XI: *J. Org. Chem.*, **28**, 2369 (1963).

(2) This work was supported in part by Grant G-21405 from the National Science Foundation and by grants from the John Simon Guggenheim Memorial Foundation and the University of Nebraska Research Council to H. E. B.

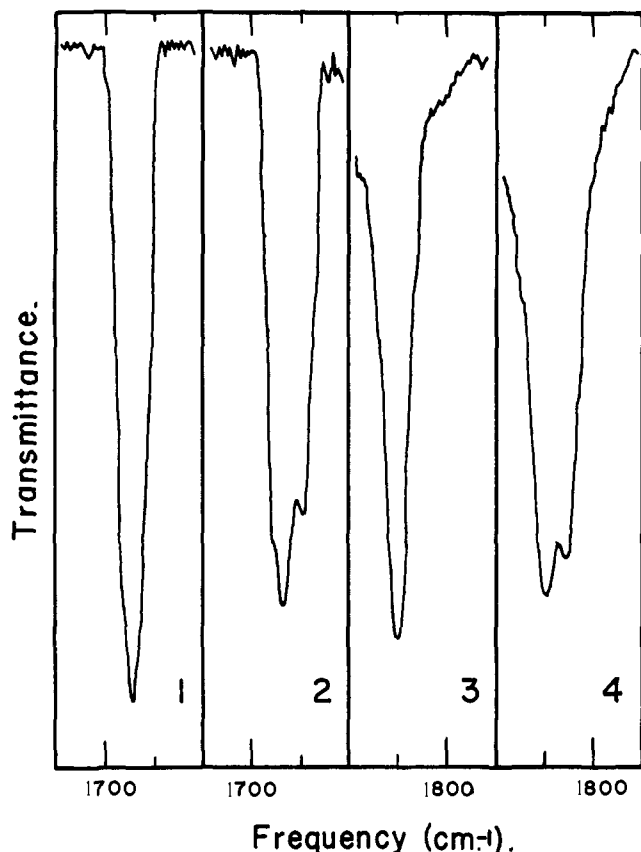
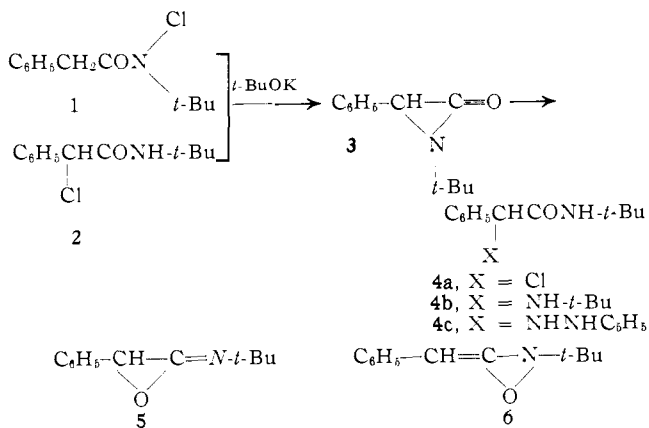


Fig. 1.—Infrared spectra: 1, compound 1; 2, compound 1 containing about 50% O<sup>18</sup>; 3, compound 3; 4, compound 3 containing about 50% O<sup>18</sup>. All spectra determined in methylene chloride solution.

If one concurs with the increasing acceptance of a mesomeric dipolar structure for the Favorskii intermediate,<sup>4-6</sup> an alternative structure for this  $\alpha$ -lactam would be one with extensive delocalization of the bonding electrons and with the  $\alpha$ -carbon atom in the  $sp^2$  configuration.<sup>4,7</sup> As noted previously,<sup>3</sup> other localized



(3) H. E. Baumgarten, *J. Am. Chem. Soc.*, **84**, 4975 (1962).

(4) See A. W. Fort *ibid.*, **84**, 4975 (1962), for a detailed discussion of the geometry of such an intermediate.

(5) See H. O. House and W. F. Gilmore *ibid.*, **83**, 3972, 3980 (1961), for the first compelling evidence for the existence of such an intermediate in some Favorskii reactions and references to earlier work.

(6) Although it now appears that a delocalized intermediate of some sort may be involved in Favorskii reactions run under certain conditions, there is no compelling evidence indicating whether or not such an intermediate (1) is always involved or (2) precedes or follows the formation of a localized intermediate.

(7) The suggested resonance picture<sup>4</sup> of the delocalized intermediate appears to be unnecessarily confused, involving contributions from structures with peculiar or radically different geometries and with singlet and triplet configurations of the same electron pair.

alternatives (valence tautomers) include the  $\alpha$ -imino lactone 5 and the benzal oxazirine 6. Certainly, much of the known chemistry<sup>3,8,9</sup> of the  $\alpha$ -lactams can be accommodated by a delocalized structure, as can our recent observations that 3 reacts readily with aqueous or ethanolic hydrogen chloride to form N-*t*-butyl- $\alpha$ -chlorophenylacetamide<sup>10</sup> (4a) (*vide infra*), with *t*-butylamine to form  $\alpha$ -*t*-butylamino-N-*t*-butylphenylacetamide<sup>10</sup> (4b, m.p. 102–103°. *Anal.* Found: C, 73.29; H, 9.89; N, 10.47), and with phenylhydrazine to form N-*t*-butyl- $\alpha$ -phenylhydrazinophenylacetamide<sup>10</sup> (4c, m.p. 170–171°. *Anal.* Found: C, 72.56; H, 7.83; N, 13.93). However, as pointed out previously,<sup>3</sup> chemical evidence alone may not suffice to determine the nature of the  $\alpha$ -lactam because of the possibility of tautomeric conversions, solvent-promoted ionizations,<sup>5</sup> etc.

It would appear that, if the  $\alpha$ -lactam (as isolated) has the delocalized structure or if its formation goes through a delocalized intermediate of any substantial lifetime, it should *not* be possible to prepare an optically active  $\alpha$ -lactam. To examine this possibility ( $\pm$ )-mandelic acid was treated with thionyl chloride and the resulting ( $\pm$ )- $\alpha$ -chlorophenylacetyl chloride was converted into ( $\pm$ )-N-*t*-butyl- $\alpha$ -chlorophenylacetamide<sup>10</sup> (2, m.p. 126.5–127.5°. *Anal.* Found: Cl, 15.51). Cyclization of the  $\alpha$ -chloroamide using the technique described previously<sup>3</sup> for the N-chloroamide gave an 11–13.5% yield of ( $\pm$ )-3 (along with 45–51% of recovered 2), whose physical and chemical properties were identical with those reported previously.<sup>11</sup> Repetition of this sequence with D-(–)-mandelic acid ( $[\alpha]_D^{26} -147.7^\circ$  ( $c$  1.00, water)) gave (+)-2 ( $[\alpha]_D^{26} +11.8^\circ$  ( $c$  1.87, CHCl<sub>3</sub>)), and cyclization of the latter gave a 15.5% yield of (–)-3 ( $[\alpha]_D^{28} -32.4^\circ$  ( $c$  1.65, CCl<sub>4</sub>)). The infrared spectrum of the product indicated it to be essentially free of the starting material or decomposition products. Inasmuch as (+)-2 is very easily racemized, it was not possible to determine from these experiments the optical purity of the (–)-3. Neither was it possible to assign a definite configuration to (–)-3; however, based on the known stereochemistry of D-(+)- $\alpha$ -chlorophenylacetamide<sup>12</sup> prepared from D-mandelic acid and of several Favorskii reactions, it seems probable that (–)-3 has the L-configuration. Nevertheless, on the basis of the reasoning cited before, the preparation of an optically active  $\alpha$ -lactam would appear to eliminate the delocalized structure as well as the optically symmetrical structure 6 and would indicate that any delocalized precursor of 3 must cyclize very rapidly.

There remain, of course, the valence tautomers 3 and 5. To distinguish between these the original preparation<sup>3</sup> of the  $\alpha$ -lactam was repeated using 1 containing slightly less than 50% of O<sup>18</sup>. The starting material showed (Fig. 1) a doublet  $\nu(\text{C}=\text{O})$  band at 1668 and 1645  $\text{cm}^{-1}$  (CH<sub>2</sub>Cl<sub>2</sub>). The  $\alpha$ -lactam 3, obtained in 24% yield, also showed a doublet  $\nu(\text{C}=\text{O})$  band at 1848 and 1827  $\text{cm}^{-1}$  (CH<sub>2</sub>Cl<sub>2</sub>). This result is most easily rationalized on the basis of structure 3.<sup>13</sup>

Also to be accounted for in any final structural assignment is the C<sup>13</sup>-H coupling constant for the  $\alpha$ -C-H of

(8) H. E. Baumgarten, R. L. Zey, and U. Krolls, *J. Am. Chem. Soc.*, **83**, 4469 (1961).

(9) J. C. Sheehan and J. W. Frankenfeld, *ibid.*, **83**, 4792 (1961).

(10) Structural assignment supported by infrared and n.m.r. spectra.

(11) This appears to be the first recorded example of the successful isolation of an  $\alpha$ -lactam using Sarel's reaction (*cf.* S. Sarel and H. Leader, *J. Am. Chem. Soc.*, **82**, 4752 (1960), and J. C. Sheehan and J. W. Frankenfeld, *ibid.*, **83**, 4792 (1961)). This reaction gives lower yields of the  $\alpha$ -lactam (using the same reaction conditions) than that starting from the N-chloroamide but the product is more nearly pure.

(12) K. Mislow and M. Heffler, *ibid.*, **74**, 3668 (1952).

(13) *Cf.* S. Pinchas, D. Samuel, and M. Weiss-Brodsky, *J. Chem. Soc.*, 2666 (1961).

3, which is given in Table I along with other pertinent data. The observed value is consistent with those for related azirine derivatives and suggests that the *s*-character of the  $\alpha$ -carbon atom is approximately 34%.

TABLE I  
C<sup>13</sup>-H COUPLING CONSTANTS

Compound	Group	$J_{C^{13}H}$ , c.p.s. <sup>a</sup>
$\alpha$ -Lactam 3	Ring CH	$168.5 \pm 0.5$
	<i>t</i> -Bu	126
N-Methylallenimine <sup>b</sup>	Ring CH <sub>2</sub>	169
	Olefinic CH <sub>2</sub>	162
	N-CH <sub>3</sub>	135
2,2-Dimethylethylenimine	Ring CH <sub>2</sub>	166
Ethylenimine	Ring CH <sub>2</sub>	$168.1 \pm 0.5^c$
Ethylene oxide	Ring CH <sub>2</sub>	$175.8 \pm 0.5^c$
Cyclopropane	Ring CH <sub>2</sub>	161 <sup>d</sup>

<sup>a</sup> Determined with neat liquid using a Varian A-60 spectrometer. <sup>b</sup> We are indebted to Professor J. D. Roberts for a sample of this compound. <sup>c</sup> F. S. Mortimer, *J. Mol. Spectry.*, **5**, 199 (1960). <sup>d</sup> N. Muller and D. E. Pritchard, *J. Chem. Phys.*, **31**, 768, 1471 (1959).

Although individual items among this experimental evidence and that cited earlier, taken one at a time, can be rationalized reasonably well on the basis of one or another of the alternative structures, consideration of the whole of the data appears to lend substantial support to the  $\alpha$ -lactam structure. The results do *not* rule out the possibility that a delocalized intermediate may be involved in some of the further reactions of 3.<sup>6</sup> Experiments exploring this possibility (among others) are in progress.

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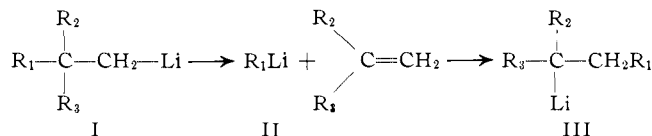
RECEIVED JULY 19, 1963

### Carbanions. VI. The Mechanism of Rearrangement of 2,2,2-Triphenylethyllithium and 2,2,3-Triphenylpropyllithium

Sir:

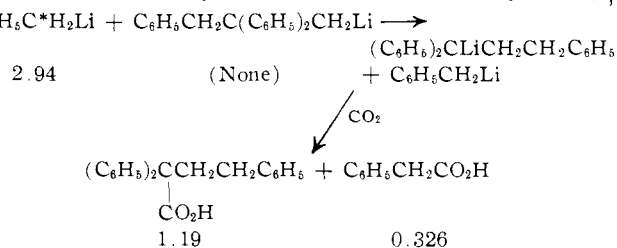
A 1,2-shift of phenyl has been observed in 2,2,2-triphenylethyl derivatives of sodium,<sup>1,2</sup> potassium,<sup>3</sup> and lithium.<sup>3</sup> An analogous migration of phenyl has been observed in 2,2-diphenylpropyllithium and -potassium and of phenyl in preference to *p*-tolyl in 2-phenyl-2-(*p*-tolyl)-propyllithium.<sup>4</sup> Finally, a 1,2-migration of benzyl has been observed in 2,2,3-triphenylpropyllithium.<sup>5</sup> These rearrangements have been assumed, implicitly or explicitly, to be intramolecular in character.

By analogy with recent work<sup>6</sup> on the Wittig rearrangement of ethers, an elimination-readdition mechanism seems possible. Thus, the organolithium compound I could eliminate an organolithium compound II to form an olefin which could combine with II in the inverse manner to give the final product of rearrangement III. The general argument<sup>4</sup> in opposition to such a mechanism is that if addition of organolithium compound II to the olefin were possible, then the more basic organo-



lithium compound I, which is present initially in high concentration, should compete successfully in addition to the olefin; however, no products corresponding to addition of I have been found. As a further test for the elimination-readdition mechanism, Zimmerman and Zweig<sup>4</sup> obtained little, if any, reaction of *p*-tolyl-lithium with  $\alpha$ -methylstyrene using conditions under which 2-phenyl-2-(*p*-tolyl)-propyllithium had undergone much rearrangement.

We wish to report some experiments pertaining to the elimination-readdition mechanism for rearrangement of 2,2,2-triphenylethyllithium and 2,2,3-triphenylpropyllithium. A preliminary experiment, in which 1,1-diphenylethene was added to about a half-molar equivalent of 2,2,3-triphenylpropyllithium in tetrahydrofuran at  $-65 \pm 5^\circ$  and the mixture warmed to  $0^\circ$  for 10 min. under the general conditions required for rearrangement,<sup>5</sup> gave after carbonation only 3% recovery of 1,1-diphenylethene and much ill-defined polymeric material. This experiment must be regarded as indecisive, since the concentration of 1,1-diphenylethene was doubtlessly much higher than that likely to exist during rearrangement of 2,2,3-triphenylpropyllithium. Accordingly, benzylithium was prepared by the procedure of Gilman<sup>7</sup> from benzyl methyl ether- $\alpha$ -C<sup>14</sup>. A tetrahydrofuran solution (150 ml.) containing 11.2 mmoles of radioactive benzylithium at  $-65^\circ$  was added to 450 ml. of a tetrahydrofuran solution containing 24.3 mmoles of 2,2,3-triphenylpropyllithium<sup>5</sup> at the same temperature and the well stirred mixture was allowed to warm to  $0^\circ$  and kept at this temperature for 30 min. before carbonation.<sup>8</sup> The initial specific activity of the starting benzylithium was determined by carbonation of a portion of the same preparation of benzylithium and assaying the resulting benzoic acid. In the following reaction sequence the activities of reactants and products are indicated below each compound assayed in units of microcuries per millimole. From this experiment it is obvious that the rearranged organolithium compound gained radioactivity at the expense of the benzylithium; therefore, very likely,



a benzyl group in a triphenylpropyllithium (or compound derived therefrom) exchanged with a benzyl group of benzylithium. The 1,1,3-triphenylpropyllithium produced, however, is *not* at radiochemical equilibrium with the benzylithium in the solution at the end of this experiment, since its

(7) H. Gilman and H. A. McNinch, *ibid.*, **26**, 3723 (1961); H. Gilman and G. L. Schwebke, *ibid.*, **27**, 4259 (1962).

(8) The concentrations of the organolithium compounds were determined by the double titration technique [H. Gilman and A. H. Haubein, *J. Am. Chem. Soc.*, **66**, 1515 (1944)]. The radiochemical determinations were by the wet combustion method [O. K. Neville, *ibid.*, **70**, 3501 (1948)] with the oxidizers prepared according to Van Slyke and co-workers [D. D. Van Slyke, J. Plazin, and J. R. Weisiger, *J. Biol. Chem.*, **191**, 209 (1951)]. A vibrating-reed electrometer (Applied Physics Corp., Model 31) was used to assay the radioactive carbon dioxide. Benzoic acid-carboxyl-C<sup>14</sup> (from Tracerlab, Inc.) was used to prepare benzyl methyl ether- $\alpha$ -C<sup>14</sup>. The uniformly labeled chlorobenzene-C<sup>14</sup> was from New England Nuclear Corp.

- (1) E. Grovenstein, Jr., *J. Am. Chem. Soc.*, **79**, 4985 (1957).
- (2) H. E. Zimmerman and F. J. Smentowski, *ibid.*, **79**, 5455 (1957).
- (3) E. Grovenstein, Jr., and L. P. Williams, Jr., *ibid.*, **83**, 412 (1961).
- (4) H. E. Zimmerman and A. Zweig, *ibid.*, **83**, 1196 (1961).
- (5) E. Grovenstein, Jr., and L. P. Williams, Jr., *ibid.*, **83**, 2537 (1961).
- (6) U. Schoellkopf and W. Fabian, *Ann.*, **642**, 1 (1961); U. Schoellkopf and D. Walter, *ibid.*, **654**, 27 (1962); P. T. Lansbury and V. A. Pattison, *J. Am. Chem. Soc.*, **84**, 4295 (1962); P. T. Lansbury and V. A. Pattison, *J. Org. Chem.*, **27**, 1933 (1962).