This study indicates the major role which a low frequency vibrational mode with moderately large transition moment plays in the static polarizability of quinone. The results suggest that similar behavior may be found in other molecules, especially some of those discussed by Meredith, *et al.*,[4] and Hammick, *et al.*,[6] which have anomalously large $P_T - P_E$.

Acknowledgment.—We wish to thank the Perkin-Elmer engineering department and especially Mr. R. A. Anacreon for making the Model 301 spectrometer available to us for measurements in the 75-300 cm.$^{-1}$ region.

[14] This band was found by Cartwright and Errera at 120 cm.$^{-1}$, as reported by Hammick, *et al.*[6] Coop and Sutton,[5] together with Hammick, *et al.*, suggested correctly that this band makes a significant contribution to the atomic polarization and attempted to interpret the infrared datum in terms of one dimensional oscillators. They were forced to assume the existence of *two* independent *in plane* oscillators to obtain agreement with the observed frequency.

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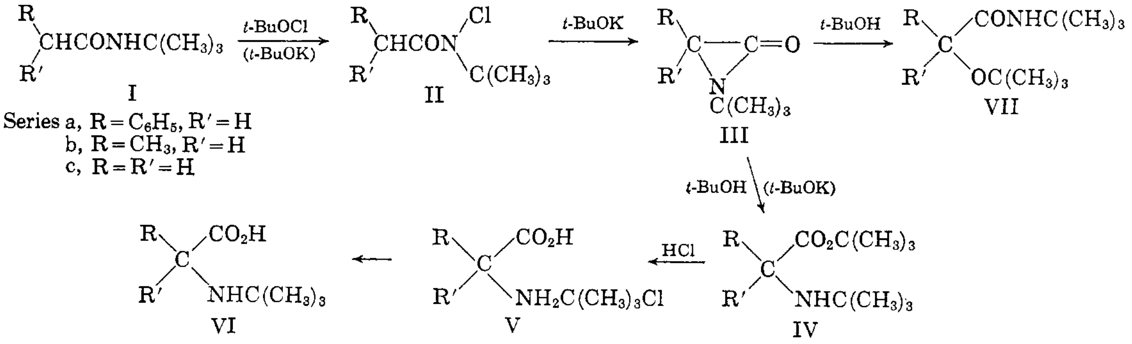
REACTIONS OF AMINES. IX. THE REARRANGEMENT OF N-*t*-BUTYL-N-CHLOROAMIDES[1,2]

Sir:

Sheehan and Frankenfeld[3] have established that, although they probably are intermediates in the Favorskii-like, sodium hydride-catalyzed rearrangement of certain α-chloroanilides, azirdinones (α-lactams) are not found among the final products of the rearrangement, as claimed earlier by Sarel and Leader,[4] but are converted under the conditions employed to oxindole and indoxyl derivatives. This communication describes the formation of α-*t*-butylaminoacids (VI) through the Favorskii-like rearrangement of N-*t*-butyl-N-chloroamides (II) and offers presumptive evidence for the existence of α-lactams (III) as moderately stable intermediates under the more favorable conditions of this rearrangement.



Series a, R = C$_6$H$_5$, R′ = H
b, R = CH$_3$, R′ = H
c, R = R′ = H

In a typical experiment N-*t*-butylphenylacetamide (Ia) (ν(C═O) 1647 cm.$^{-1}$ (KBr); ν(C═O) 1661 cm.$^{-1}$, ν(N—H) 3420 cm.$^{-1}$ (CHCl$_3$)) was converted into N-*t*-butyl-N-chlorophenylacetamide (IIa) (ν(C═O) 1670 cm.$^{-1}$ (CHCl$_3$)) by treatment with *t*-butyl hypochlorite and a trace of potassium *t*-butoxide. In general the N-chloroamide was not isolated but was rearranged by addition *to* potassium *t*-butoxide (in *t*-butyl alcohol) or by addition *of* the same reagent. In the former instance the N-chloroamide was added to two equivalents of cold potassium *t*-butoxide giving, after isolation, a crude ester (presumably (IVa) (ν(C═O) 1749 cm.$^{-1}$ (liquid film)) as a viscous oil. Hydrolysis of the ester with concentrated hydrochloric acid gave a 72% yield of N-*t*-butylphenylglycine hydrochloride (Va) (as the methanolate, m.p. 207–208° (dec.) with a characteristic gas evolution (loss of methanol?) at 126–127°, from methanol–ether; found for C$_{13}$H$_{22}$NO$_3$Cl: C, 57.05; H, 7.87; N, 5.23). The yield of Va from once-distilled IIa was 68%. The free amino acid VIa could be obtained by ion exchange (m.p. 152–153°; found for C$_{12}$H$_{17}$NO$_2$: C, 69.33; H, 8.34; N, 6.40). Both products were identical with authentic samples prepared by the Strecker synthesis.

By similar treatment N-*t*-butylpropionamide (Ib) and N-*t*-butylacetamide (Ic) gave 49 and 30% yields of N-*t*-butylalanine (VIb) and N-*t*-butylglycine (VIc), respectively (VIb, m.p. 201–202°; found for C$_7$H$_{15}$NO$_2$: C, 57.67; H, 10.49; N, 9.80. VIc methyl ester hydrochloride, m.p. 171–172°; found for C$_7$H$_{16}$NO$_2$Cl: C, 46.05; H, 8.88; N, 7.43).

In several experiments the course of the reaction was followed by periodic infrared analysis of samples from the reaction mixture. Dropwise addition over a 2-hr. period of 0.1 mole of potassium *t*-butoxide in 100 ml. of *t*-butyl alcohol to a cold solution (ice-bath) of 0.1 mole of Ia and 0.1 mole of *t*-butyl hypochlorite in 225 ml. of benzene caused these spectral changes. Upon addition of the first few drops of base, there was a slight high-frequency shift due to N-chlorination. Continued addition of base caused a band to appear at 1847 cm.$^{-1}$. This band grew in intensity as base was added while the band at 1670 cm.$^{-1}$ broadened somewhat and decreased in intensity. The intensity of the 1847 cm.$^{-1}$ band reached a maximum when just slightly less than one equivalent of base had been added. Addition of further base caused a sudden marked change in the color of the solution (from pale blue-gray to pale tan), complete disappearance of the 1847 cm.$^{-1}$ band and the appearance of an ester carbonyl band at 1749 cm.$^{-1}$ (see Fig. 1).

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[1] This work was supported in part by grant G-11339 of the National Science Foundation.

[2] Part VIII, *J. Org. Chem.*, **26**, 1533 (1961).

[3] J. C. Sheehan and J. Frankenfeld, *J. Am. Chem. Soc.*, **83**, in press (1961).

[4] S. Sarel and H. Leader, *ibid.*, **82**, 4752 (1960).

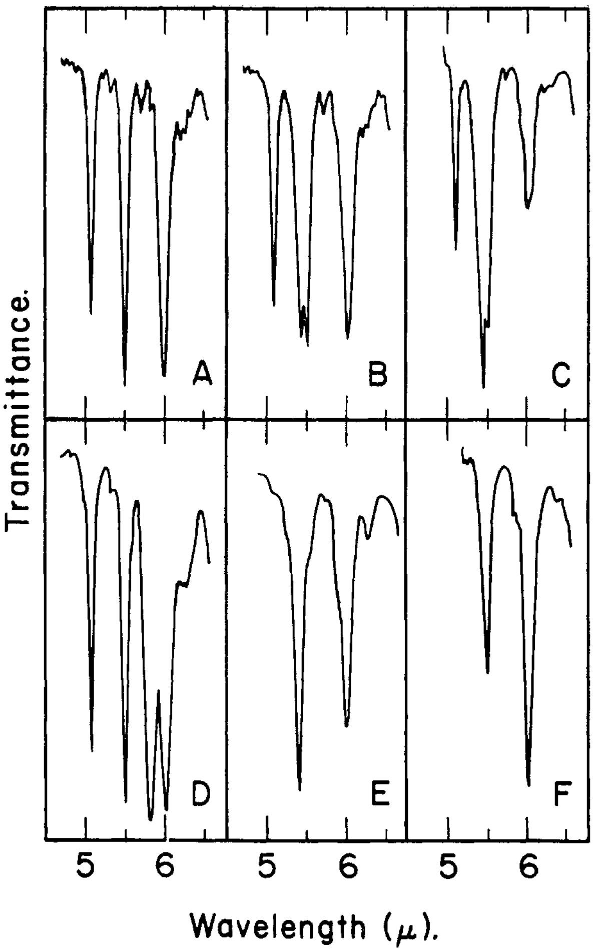
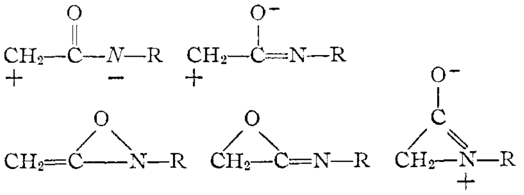


Fig. 1.—Infrared spectra: A, saturated solution of Ia in benzene (benzene peaks at 5.09 μ and 5.51 μ); B, after addition of 1 equiv. of *t*-butyl hypochlorite and 0.5 equiv. of potassium *t*-butoxide; C, after addition of 1 equiv. of potassium *t*-butoxide; D, after addition of slightly more than 1 equiv. of potassium *t*-butoxide; E, after evaporation of solution of curve C to dryness and extraction of solids with pentane; F, mixture of curve E after two weeks in freezer. Curves A-D were determined for chloroform sloutions, curves E and F for pentane solutions.

An intermediate absorbing at 1843 cm.$^{-1}$ ($CHCl_3$) was observed as a mixture with other materials from the reaction of N-*t*-butyl-N-chloroacetamide (Ic) with potassium *t*-butoxide.

One reasonable explanation of these observations is that the reaction follows the path I → V and that the band at 1847 cm.$^{-1}$ is due to the aziridinone intermediate IIIa.[5] Attempts to isolate this intermediate by addition of slightly less than one equivalent of potassium *t*-butoxide in IIa have not been successful. However, a roughly 1:1 mixture (based on relative intensities of the ν(C=O) bands) of two products thought to be IIIa and α-*t*-butoxy-N-*t*-butylphenylacetamide (VIIa) has been obtained. Attempts to separate the two substances have resulted in destruction of the component absorbing at 1847 cm.$^{-1}$. The latter (as a mixture with VIIa) is very short-lived in the presence of water or hydroxylic solvents at room temperature but may be kept in the solid state or in dry pentane solution in the freezer for several weeks with only gradual loss of the high frequency component. The position of the 1847 cm.$^{-1}$ band is little affected by the dielectric constant of the solvent, being essentially unchanged in *cold* chloroform, methylene chloride, benzene, pentane, acetonitrile or methanol. The band disappears completely in methanol after 20 minutes at 5° and after 5 minutes at room temperature. If the mixture is allowed to stand at room temperature for one day in *t*-butyl alcohol, the principal product is VIIa (m.p. 107–108°, ν(C=O) 1669 cm.$^{-1}$, ν(N—H) 3398 cm.$^{-1}$ ($CHCl_3$); found for $C_{16}H_{25}NO_2$: C, 73.20; H, 9.41; N, 5.00)).

Although it appears reasonable that the intermediate in this new rearrangement may have the aziridinone structure (III), a number of resonance forms can be written for III, of which five (other than III) are reproduced below.



Examination of these forms (the spectral properties of which may be difficult to predict) will suggest that further evidence will be required before the appropriate structure can be selected. The similarity of the present situation to that encountered in the Favorskii rearrangement will be obvious.[6,7]

The difference in behavior of the intermediate toward *t*-butyl alcohol and toward *t*-butoxide ion is also characteristic of the Favorskii rearrangement.[6,7]

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[5] Estimated ν(C=O) for α-lactams is 1830–1850 cm.$^{-1}$.

(6) H. O. House and W. F. Gilmore, *J. Am. Chem. Soc.*, **83**, 3972, 3980 (1961).

(7) A. W. Fort, Abstracts of Papers, Meeting of the American Chemical Society, Sept. 4, 1961, Chicago, Ill., p. 19-Q.

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RECEIVED JUNE 5, 1961

EXCHANGE OF HYDROGEN BETWEEN WATER AND THE HYDROBORATE ION

Sir:

We wish to report evidence for the exchange of hydrogen between hydroborate ions and water in aqueous hydroborate solutions. Exchange takes place by two different paths. The exchange rate corresponding to one path is independent of *p*H and is measurable at elevated temperatures in solutions of very high *p*H (~14). The exchange corresponding to the other path is acid-catalyzed and is detectable in solutions undergoing hydrolysis at ordinary temperatures.

The *p*H-independent exchange reaction was studied by measuring the exchange between D_2O (99.82%) and potassium hydroborate (0.4 *M*) in solutions which were 1, 3 and 5 *M* in sodium deuteroxide and in which the ionic strength was brought to 5.4 *M* with sodium chloride. These solutions were held in a thermostated bath and