quency observed in the Raman spectrum, though a search was made for it; however, this is considerably below the limit of reliability of the potassium bromide optics used and the apparent absence is suggestive at the very most. The only observed coincidence between the infrared spectrum of the vapor and the Raman spectrum is the 465 cm.$^{-1}$ frequency, which had been assigned previously[5] as the F_2 fundamental on the basis of a force constant analysis. This coincidence confirms both the tetrahedral structure and the frequency assignment.

There also seemed to be weak absorption by P_4 vapor in the region from 1240 to 1290 cm.$^{-1}$; however, it was obscured by erratic general absorption in the region, which became very strong at temperatures above 250° and was caused by red phosphorus sporadically deposited on the windows. There are several allowed combination bands which can account for this weak P_4 absorption.

The appearance of the totally symmetric vibration ν_1 at 602 and 604 cm.$^{-1}$ in the solid and CS_2 solution spectra, respectively, and the presence of weak absorption at 959 cm.$^{-1}$ in the solid are attributed to selection rule violations caused by intermolecular forces. An alternate interpretation in terms of a pyramidal structure, a slightly distorted tetrahedron, was considered in detail prior to obtaining a satisfactory spectrum for the vapor, and was found to be compatible with other available experimental data. However, the conditions under which the vapor spectrum was later obtained were such that the absence of absorption in the vicinity of 605 cm.$^{-1}$ is almost certain evidence that the corresponding vibrational mode is not infrared active in the vapor.

The resolution, stability and general performance of the spectrometer with the modified primary optics and heated cell were comparable to that of the normal instrument used for the spectra of the solid and solutions; a slight decrease in available light was compensated for by increasing slit widths 5 to 10%. When vaporized, the sample was equivalent to a thickness of 1.3 mm. of the solid, about three times that which gives readily detectable absorption at 602 cm.$^{-1}$ in the solid. Spectra were obtained at temperatures up to 280° where all of the phosphorus was vaporized and the pressure in the cell was nearly one atmosphere, without a trace of absorption at 605 or at 959 cm.$^{-1}$. Moreover, at 170° when the vapor pressure is of the order[1] of 6 to 10 cm., all of the bands were clearly present. The resulting conclusion that the selection rules are violated is substantiated by a high value, about[1] 22.8, of Trouton's constant for phosphorus and by the presence of complexes and molecular chains in carbon disulfide solution,[1] both facts indicative of strong intermolecular attraction.

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Decomposition of Amine Picrates with Ethanolamine

BY IRVING ALLAN KAYE, IRVING C. KOGON AND WILLIAM BURLANT

Amines, especially thermolabile or air-sensitive liquids yielding oily or hygroscopic salts, are frequently purified through their picrates. The recovery of the base, usually accomplished by decomposing the salt with an inorganic base, is complicated by the low water-solubility of sodium, potassium and ammonium picrates. This difficulty may be overcome by using lithium hydroxide.[1]

We have found that the more economical ethanolamine forms a picric acid salt which is extremely soluble in water and have used this base, following previously described directions,[1,2] in recovering numerous amines of varied structure.

[1] Burger, THIS JOURNAL, **67**, 1615 (1945).

[2] Weiner and Kaye, *J. Org. Chem.*, **14**, 868 (1949).

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The Lead Tetraacetate Oxidation of Pregnenolone Benzoate

BY O. MANCERA

Recently Giral[1] described the lead tetraacetate oxidation of pregnenolone benzoate to a product, $C_{30}H_{38}O_5$, m. p. 175–176°, $[\alpha]_D$ +161° (chloroform), formulated as Δ^5-pregnen-3β,21-diol-20-one 3-benzoate 21-acetate.

A calculation of the molecular rotation differences yields a value of +628 for the contribution of the benzoyl group of Giral's product (Table I), in complete disagreement with such values reported by Barton.[2]

Some time ago we had investigated the lead tetraacetate oxidation of pregnenolone benzoate and obtained in 39% yield a product, $C_{30}H_{38}O_5$, m. p. 200–201°, $[\alpha]^{20}_D$ +48.95° (chloroform), shown to be Δ^5-pregnen-3β,21-diol-20-one 3-benzoate 21-acetate by comyarison with an authentic specimen prepared by benzoylation of Δ^5-pregen-3β,21-diol-20-one 21-acetate. The molecular rotation differences given in Table I are in good agreement with the values expected on the basis of earlier work.[2]

TABLE I

Substance	$[\alpha]_D$	$[M]_D$	$[M]_D$ contribution of the 3-benzoyl group[a]
Giral's product	+161	+770	+628
Δ^5-Pregnen-3β,21-diol-20-one 3-benzoate 21-acetate	+ 49	+234	+ 92
Δ^5-Pregnen-3β,21-diol-20-one 21-acetate	+ 38	+142	...

[a] Barton (ref. 2) reported +81 ± 16.

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[1] Giral, THIS JOURNAL, **72**, 1913 (1950).

[2] Barton, *J. Chem. Soc.*, 813 (1945).