

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 previously⁵ 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 order¹ 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, about¹ 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.

THE NOYES CHEMICAL LABORATORY
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RECEIVED JULY 13, 1950

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 Giral¹ described the lead tetraacetate oxidation of pregnenolone benzoate to a product, $\text{C}_{30}\text{H}_{38}\text{O}_5$, m. p. 175 – 176° , $[\alpha]_D +161^\circ$ (chloroform), formulated as Δ^5 -pregnen- $3\beta,21$ -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, $\text{C}_{30}\text{H}_{38}\text{O}_5$, m. p. 200 – 201° , $[\alpha]_D^{20} +48.95^\circ$ (chloroform), shown to be Δ^5 -pregnen- $3\beta,21$ -diol- 20 -one 3-benzoate 21-acetate by comparison with an authentic specimen prepared by benzylation of Δ^5 -pregnen- $3\beta,21$ -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- $3\beta,21$ -diol- 20 -one 3-benzoate 21-acetate	+ 49	+234	+ 92
Δ^5 -Pregnen- $3\beta,21$ -diol- 20 -one 21-acetate	+ 38	+142	...

^a Barton (ref. 2) reported $+81 \approx 16$.

- (1) Giral, *THIS JOURNAL*, **73**, 1913 (1950).
(2) Barton, *J. Chem. Soc.*, 813 (1945).

Speculations as to the nature of Giral's product,¹ have led to no fruitful conclusions unless he possessed a mixture whose rotation was determined incorrectly.³

Experimental

A vigorously stirred and boiling solution of 5 g. of pregnenolone benzoate (m. p. 192–193°, $[\alpha]^{20D} +47.4$) in 75 cc. of glacial acetic acid was treated over a period of 1.5 hours with a mixture of 5 g. of lead tetraacetate and 75 cc. of glacial acetic acid. After cooling and diluting with water, the precipitate (5.2 g.) was collected and dried. Several crystallizations from methanol–chloroform afforded 1.25 g. (22%) of substantially pure Δ^5 -pregnen-3 β ,21-diol-20-one 3-benzoate 21-acetate.

The combined mother liquors were refluxed for 45 minutes with 175 cc. of alcohol, 0.53 g. of semicarbazide hydrochloride and 0.75 g. of sodium acetate,⁴ the solution cooled and the semicarbazone of pregnenolone benzoate was filtered; yield 1.53 g. (27%), m. p. 260–263°. The alcoholic solution was evaporated to dryness and the residue was recrystallized from methanol–chloroform to yield an additional 0.4 g. of the 3-benzoate-21-acetate together with 0.57 g. of the same product obtained on chromatographing the mother liquors on 80 g. of ethyl acetate washed alumina. The analytical sample crystallized from methanol–chloroform as colorless needles with m. p. 200–201° (Kofler), $[\alpha]^{20D} +48.95^\circ$ (chloroform), identical in all respects with an authentic specimen prepared by benzylation of Δ^5 -pregnen-3 β ,21-diol-20-one 21-acetate.

Anal. Calcd. for $C_{30}H_{48}O_5$: C, 75.28; H, 8.00. Found: C, 74.96; H, 8.12.

Acknowledgment.—We wish to thank Syntex, S. A., for a generous gift of pregnenolone benzoate and 21-acetoxypregnenolone.

(3) An error in the rotation of Giral's product might explain his results, since some of the by-products in our lead tetraacetate oxidation showed relatively sharp melting points in the neighborhood of 170° but exhibited $[\alpha]^{20D}$ of around +47°.

(4) Lead tetraacetate oxidations of various pregnenolone esters have demonstrated that unreacted ketone can be separated nearly quantitatively from the rest of the reaction mixture by treatment with a limited amount of semicarbazide. The corresponding 21-acetoxy derivatives do not form a semicarbazone. (Private communication from the research laboratories of Syntex, S. A.)

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A New Synthesis of Dibenzoselenophene¹

BY JAMES D. McCULLOUGH, TOD W. CAMPBELL AND
EDWIN S. GOULD

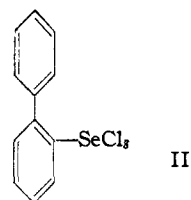
During work carried out in this Laboratory in attempts to resolve unsymmetric cyclic selenoxides, it became necessary to prepare a large quantity of dibenzoselenophene (I). The synthetic methods appearing in the literature^{2,3,4} involve either low yields or a number of time-consuming steps. However, the method of Behagel and Hofmann, in which the compound was obtained by treatment of *o*-biphenylselenium trichloride (II) with potas-

(1) Based on research performed under Task Order I of Contract N6-onr-275 between the Office of Naval Research and the University of California, Los Angeles.

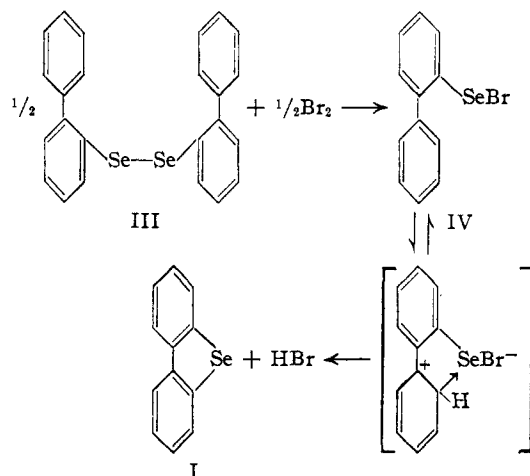
(2) N. M. Cullinane, A. G. Rees and C. A. Plummer, *J. Chem. Soc.*, 151 (1939).

(3) C. Courtot and A. Monyamedi, *Compt. rend.*, **199**, 531 (1934).

(4) O. Behagel and K. Hofmann, *Ber.*, **72B**, 582 (1939).



sium hydroxide in methanol, suggested that the corresponding tribromide, which presumably could be prepared more conveniently, might also yield dibenzoselenophene when treated with base. Although addition of bromine to a carbon tetrachloride solution of di-(*o*-biphenyl) diselenide (III) yields a brick-red precipitate as stated by Behagel and Hofmann, the material rapidly loses hydrogen bromide and the result is apparently a mixture of dibenzoselenophene dibromide and bromodibenzoselenophene dibromide. This latter conclusion is based on our experimental equivalent weights⁵ which range from 204 to 212 and from the fact that the solutions resulting from the titration are colorless rather than of the orange arylselenide color which normally results in the titration of an arylselenium tribromide. The theoretical equivalent weights are 157.4 for *o*-biphenylselenium tribromide, 195.5 for dibenzoselenophene dibromide and 235.5 for bromodibenzoselenophene dibromide. Although we were unable to isolate a compound whose properties and composition indicate it to be *o*-biphenylselenium tribromide, it was observed that dibenzoselenophene is formed in good yield when a solution containing equimolar amounts of di-(*o*-biphenyl) diselenide (III) and bromine in carbon tetrachloride is kept at 70° for 48 hours. Indeed, by the correct choice of conditions, the yield of dibenzoselenophene becomes essentially quantitative. Since the diselenide (III) can be made in good yield by a two-step synthesis from *o*-aminobiphenyl, which is readily available, the new synthesis appears to be more direct than any other described up to this time.



(5) J. D. McCullough, T. W. Campbell and N. J. Krisnevich, *Ind. Eng. Chem., Anal. Ed.*, **18**, 638 (1946).