ether, 0.12 g. (0.00137 mole) of morpholine was added, and the solution allowed to stand at room temperature for two days. Cooling the solution caused the crystallization of 0.205 g. (66% yield) of product, m.p. 85–87°. When admixed with the amide XI there was no depression of m.p.

**C. From β-Benzoylpropionic Acid.**[9]—A 0.50-g. sample of the acid and 0.50 g. of morpholine were mixed and heated in an open tube at 160–170° for two hours. The reaction mixture was cooled and mixed with water. The water insoluble crystalline material melted at 86–88°; mixed m.p. with XI, 86-87°.

**γ-Phenylbutyromorpholide (XII). a.**—A 0.52-g. sample of the amide XI was dissolved in 75 ml. of abs. ethanol and shaken at room temperature for 1.5 hr. under 43 lb./in.$^2$ of hydrogen in the presence of 10% palladium-on-charcoal. Evaporation of the solvent left an oil which crystallized from petroleum ether (b.p. 60°), wt. 0.165 g., m.p. 41–42°.

*Anal.* Calcd. for $C_{14}H_{19}NO_2$: C, 72.07; H, 8.21; N, 6.00. Found: C, 72.14; H, 8.11; N, 6.19.

**b.**—A 2.5-g. sample of γ-phenylbutyric acid was warmed with 5.5 g. of thionyl chloride for ten minutes. The excess thionyl chloride was removed under reduced pressure and the residue treated with 5.0 g. of morpholine in benzene. After standing for a few minutes the benzene solution was washed with water and dilute sodium carbonate solution, dried over anhyd. $MgSO_4$ and evaporated to an oily residue. This oil was crystallized from petroleum ether to produce 2.6 g. (73%) of γ-phenylbutyromorpholide, m.p. 41–42°. This product gave no precipitate with dry HCl in dry ether.

**γ-Phenyl-γ-morpholinobutyric Acid (XIII).**—A 2.0-g. (0.0123 mole) of γ-phenyl-γ-butyrolactone[7] was dissolved in 10 ml. of dry ether and 1.075 g. (0.0123 mole) of morpholine added. After standing at room temperature for fifteen hours a colorless oil had separated. Cooling produced a solid which was recrystallized from a mixture of benzene and dry ether to give 2.55 g. of a colorless product, m.p. 94–96°.

*Anal.* Calcd. for $C_{14}H_{19}NO_3$: C, 67.44; H, 7.68; N, 5.62. Found: C, 67.32; H, 7.63; N, 5.31.

This amino acid produced a hygroscopic hydrochloride when treated with dry hydrogen chloride gas in ether solution. Recrystallization from methanol gave colorless crystals, m.p. 176–177°, identical with morpholine hydrochloride, as shown by a mixed m.p. experiment.

LINCOLN, NEBRASKA

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[9] L. F. Somerville and C. F. H. Allen, "Organic Syntheses," Col. Vol. II, 2nd ed., John Wiley & Sons, Inc., New York, N. Y., 1943, p. 81.

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[CONTRIBUTION FROM AVERY LABORATORY, UNIVERSITY OF NEBRASKA]

# Reactions of β-Benzoylacrylic Acid and its Methyl Ester with Hydrazines. Absorption Spectra Studies[1]

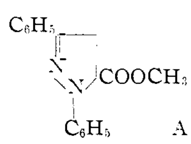
BY NORMAN H. CROMWELL, KENNETH E. COOK AND PAUL L. CREGER

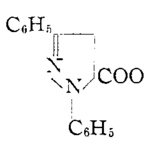
RECEIVED APRIL 5, 1956

The reaction products of phenylhydrazine with α-amino-β-benzoylpropionic acid and its methyl ester have been found to be the phenylhydrazones of β-benzoylacrylic acid and the methyl ester. Ultraviolet and infrared spectra comparisons of these products with the corresponding *unsym*-methylphenylhydrazones and with authentic pyrazolines gave definitive evidence for the structures.

In a previous study[1,2] some amine adducts of β-benzoylacrylic acid and its methyl ester were prepared and evidence was found to establish their structures as α-amino-γ-ketoacids and α-amino-γ-ketoesters. In the present study it has been found that such compounds react with phenylhydrazine to expel the amino grouping and produce the phenylhydrazones of β-benzoylacrylic acid and methyl β-benzoylacrylate, respectively, contrary to our earlier conclusions.[1]

The treatment of methyl α-morpholino-β-benzoylpropionate[2] with phenylhydrazine under mild conditions failed to yield a solid derivative. However, when this amino keto ester, or the corresponding amino keto acid,[2] was warmed with phenylhydrazine in glacial acetic acid, brilliant yellow colored products were produced which elemental analysis indicated to be the phenylhydrazones I and II of methyl β-benzoylacrylate and β-benzoylacrylic acid, respectively, or possibly the isomeric pyrazolines A and B. These products I and II failed to give positive Knorr[3] or Raiford[4] pyrazoline tests.


A


B

The same phenylhydrazine derivatives I and II resulted from the reactions of methyl β-benzoylacrylate and β-benzoylacrylic acid, respectively, and phenylhydrazine under conditions identical with those described above. The phenylhydrazine derivative I was also obtained when compound II was allowed to react with diazomethane.

Heating the phenylhydrazine derivative II of β-benzoylacrylic acid with acetic anhydride and sodium acetate gave an excellent yield of a colorless product which elemental analysis and absorption spectra studies suggested was 2,6-diphenyl-3-pyridazinone (III). Although β-benzoylacrylic acid had been reported[5] as reacting with phenylhydrazine to produce a phenylhydrazone it seemed important to obtain definitive evidence for these structures I and II, and to eliminate the possibility that these derivatives might be the pyrazolines, A and B. It appeared this could be accomplished best by careful absorption spectra comparisons with compounds of definite structure. For this purpose the methylphenylhydrazones IV and V of methyl β-benzoylacrylate and β-benzoylacrylic acid were prepared for the first time.

The infrared spectra studies (see Table I) showed some close similarities and an important difference

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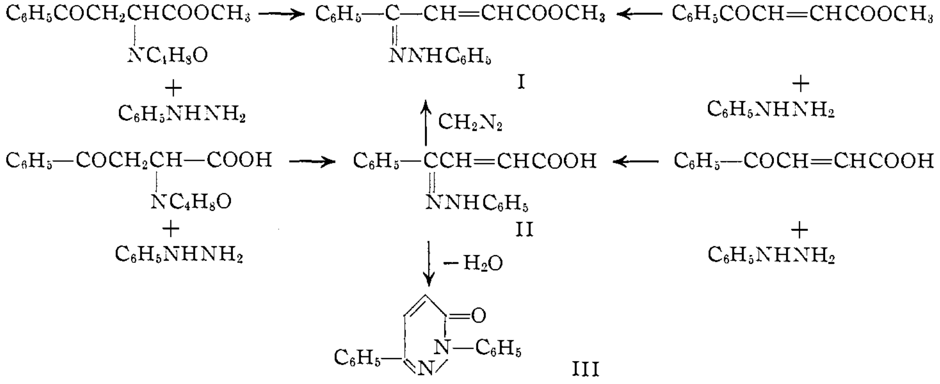
[1] Presented in part at the 128th meeting of the American Chemical Society, Minneapolis, Minn., Sept. 1955.

[2] N. H. Cromwell, P. L. Creger and K. E. Cook, THIS JOURNAL, **78**, 4412 (1956).

[3] L. Knorr, *Ann.*, **238**, 200 (1887).

[4] L. C. Raiford and W. J. Peterson, *J. Org. Chem.*, **1**, 544 (1937).

[5] T. Kozniewski and L. Marchlewski, *Chem. Zentr.*, **77** [II], 1190 (1906).

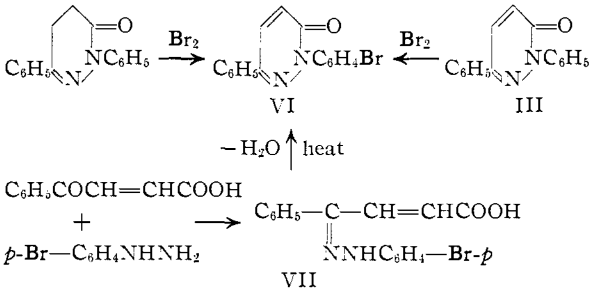


for the spectra of the hydrazone esters I and IV and for the hydrazone acids II and V. Thus these esters both showed conjugated ester carbonyl bands, 1704–1697 cm.$^{-1}$, C=C and/or C=N bands 1627–1618 cm.$^{-1}$, phenyl bands, 1603–1597 cm.$^{-1}$, and unassigned bands 1543–1527, but only the hydrazone I had an N–H band at 3312 cm.$^{-1}$. The hydrazone acids II and V showed similar relationships, both having conjugated carboxylic acid carbonyl bands, 1673–1670 cm.$^{-1}$, C=C and/or C=N bands, 1618–1610 cm.$^{-1}$, phenyl bands, 1600–1595 cm.$^{-1}$, and unassigned bands, 1537–1525 cm.$^{-1}$, but only II had an N–H band at 3312 cm.$^{-1}$. Two known pyrazolines, 1,3,5-triphenyl-4-benzylaminopyrazoline[6] and the corresponding 4-cyclohexylamino derivative[6] were found to have N–H bands 3320–3308 cm.$^{-1}$ and phenyl bands 1598–1597 cm.$^{-1}$. These authentic pyrazolines had no bands in the 1630–1610 cm.$^{-1}$, nor the 1540–1525 cm.$^{-1}$ regions of the spectrum. Similar results have been reported previously[7] for 1,5-diphenyl-3-*p*-tolylpyrazoline and its 4-benzylamino derivative.

A comparison of the ultraviolet spectra of the hydrazone derivatives I, II, IV and V (see Table I) with the spectra of known pyrazolines[6,8] gives further indication that the former are not pyrazolines. Nevertheless, there is considerable similarity between the ultraviolet spectra of the hydrazones and these pyrazolines. This might be expected since the major chromophoric grouping in both classes of compounds is the arrangement (Aryl—C=N—N—Aryl). The cross-conjugated α,β-unsaturated carbonyl grouping present in the hydrazone derivatives I, II, IV and V does not greatly affect the location of the ultraviolet maxima in these compounds, but variations in the extinction coefficients are observed.

A survey of the literature shows that several investigators have prepared pyridazinones by heating various hydrazone derivatives of γ-keto-α,β-unsaturated acids.[9] Various pyridazinones also have been obtained[9b,10] by removing two hydrogen atoms from the dihydropyridazinones prepared by heating γ-keto acids with hydrazines.

In an attempt to prepare the pyridazinone III by bromination and dehydrobromination of the known 2,6-diphenyldihydropyridazinone-3[11] we obtained instead, 2-(*p*-bromophenyl)-6-phenyl-3-pyridazinone (VI). Overend and Wiggins[9b] had previously shown that substitution of bromine in the *p*-position of the 2-phenyl group as well as bromination followed by dehydrobromination in the ring is to be expected in such reactions. The pyridazinone VI was also obtained by the bromination of pyridazinone III and from the *p*-bromophenylhydrazone derivative VII of β-benzoylacrylic acid.



Attempts to prepare the pyridazinone III by oxidation of the corresponding dihydropyridazinone with nitrous acid[10c] or potassium permanganate[10b] left most of the starting material unchanged.

The infrared spectrum of the *p*-bromophenylhydrazone VII showed an N–H band at 3340 cm.$^{-1}$, a conjugated carboxylic acid carbonyl band at 1680 cm.$^{-1}$, a C=C and/or C=N band at 1628 cm.$^{-1}$ and a phenyl band at 1595 cm.$^{-1}$. The ultraviolet spectrum of VII was similar to that of II. The infrared spectra of the pyridazinones III and VI were quite similar, with strong amide–carbonyl bands at 1667 and 1663 cm.$^{-1}$ and phenyl bands at 1590 and 1597 cm.$^{-1}$, respectively. The ultraviolet spectra (see Table I) of the two pyridazinones III and VI were also similar, as was to be expected by reference to the findings of Overend and Wiggins.[9b]

**Acknowledgment.**—This investigation was supported in part by a grant from the National Science Foundation, NSF-G1091.

## Experimental

**Methyl β-Benzoylacrylate Phenylhydrazone (I). A. From α-Morpholino-β-benzoylpropionate.**—A solution of 1.08 g. of phenylhydrazine and 2.77 g. of the amino keto ester in 20 ml. of glacial acetic acid was heated on a steam-bath for one hour. The bright yellow solution was poured

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[6] N. H. Cromwell, *et al.*, THIS JOURNAL, **73**, 1044 (1951).

[7] N. H. Cromwell, *et al.*, *ibid.*, **71**, 3337 (1949).

[8] N. H. Cromwell and H. Hoeksema, *ibid.*, **71**, 716 (1949).

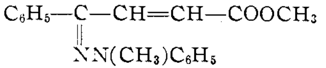
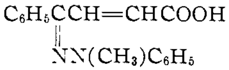
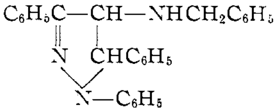
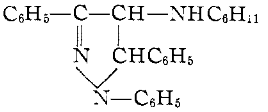
[9] (a) L. Wolff, *Ann.*, **264**, 251 (1891); (b) W. G. Overend, L. M. Turton and L. F. Wiggins, *J. Chem. Soc.*, 3505 (1950).

[10] (a) F. Ach, *Ann.*, **253**, 48 (1889); (b) C. Paal and J. Ubber, *Ber.*, **36**, 497 (1903); (c) C. Paal and C. Koch, *ibid.*, **36**, 2538 (1903).

[11] J. Biedermann, *ibid.*, **24**, 4081 (1891).

TABLE I

SUMMARY OF ULTRAVIOLET AND INFRARED SPECTRA

| Structure | Ultraviolet max.[a] λ, mμ | $\epsilon \times 10^{-3}$ | Infrared bands[b] Band | Wave no., cm. |
|---|---|---|---|---|
| I | 242<br>293<br>302<br>367 | 14.1<br>5.00<br>4.80<br>31.0 | N-H<br>Ester C=O<br>C=C/C=N<br>Phenyl | 3312<br>1704<br>1627<br>1603<br>1543 |
| II | 241<br>293<br>303<br>363 | 13.3<br>5.23<br>5.27<br>25.2 | N-H<br>Acid C=O<br>C=C/C=N<br>Phenyl | 3312<br>1673<br>1618<br>1600<br>1537 |
| VII | 231<br>250<br>315<br>349 | 13.4<br>11.6<br>15.0<br>30.6 | N-H<br>Acid C=O<br>C=C/C=N<br>Phenyl | 3340<br>1680<br>1628<br>1595<br>1547 |
|  $C_6H_5-\underset{\underset{NN(CH_3)C_6H_5}{\Vert}}{C}-CH=CH-COOCH_3$<br>IV | 247<br>369 | 17.7<br>20.7 | Ester C=O<br>C=C/C=N<br>Phenyl | 1697<br>1618<br>1597<br>1527 |
|  $C_6H_5\underset{\underset{NN(CH_3)C_6H_5}{\Vert}}{C}CH=CHCOOH$<br>V | 248<br>367 | 14.78<br>17.55 | Acid C=O<br>C=C/C=N<br>Phenyl | 1670<br>1610<br>1595<br>1525 |
|  | 242[c]<br>310<br>360 | 16.7<br>6.96<br>19.4 | N-H<br>Phenyl | 3320<br>1597<br>1510 |
|  | 242[c]<br>355 | 15.3<br>18.9 | N-H<br>Phenyl | 3308<br>1598<br>1592<br>1557<br>1508 |
| III | 250<br>331 | 17.8<br>4.70 | Amide C=O<br><br>Phenyl | 1667<br>1650<br>1590 |
| VI | 242<br>335 | 16.9<br>4.5 | Amide C=O<br>Phenyl | 1663<br>1597<br>1577 |

[a] Ultraviolet spectra were determined at 25° using 95% ethanol solutions and a Cary recording ultraviolet spectrophotameter, Model 11. [b] All infrared spectra were obtained with a Perkin-Elmer recording instrument, Model 21, employing sodium chloride optics and Nujol mulls. [c] See ref. 6.

onto cracked ice. The sticky solid was recrystallized from aqueous methanol to give bright yellow leaflets; m.p. 152–154°; yield 1.50 g. (54%). This compound I gave negative Raiford[4] and Knorr[3] tests for the pyrazoline nucleus.

*Anal.* Calcd. for $C_{17}H_{16}N_2O_2$: C, 72.86; H, 5.58; N, 9.96. Found: C, 72.83; H, 5.75; N, 9.99.

**B. From Methyl β-Benzoylacrylate.**—The acetic acid reaction mixture was allowed to stand for 12 hours at room temperature. Isolation of the product I as before gave a 50% yield; m.p. 150–153°, identical with the product obtained from the amino keto ester.

**C. From β-Benzoylacrylic Acid Phenylhydrazone** (II) **and Diazomethane.**—An ether solution of the acid II on treatment with an ether solution of diazomethane gave a near quantitative yield of the ester I, m.p. 152–154°.

**β-Benzoylacrylic Acid Phenylhydrazone** (II). **A. From α-Morpholino-β-benzoylpropionic Acid.**—A mixture of 2.63 g. (0.01 mole) of the amino keto acid and 1.08 g. (0.01 mole) of phenylhydrazine in 30 ml. of glacial acetic acid was heated on a steam-bath for 30 minutes. The product was worked up in the usual way to give 2.19 g. (82% yield) of bright yellow needles, m.p. 197–197.5° dec. This material II gave negative Knorr[3] and Raiford[4] tests for the pyrazoline nucleus. It was soluble in dilute sodium hydroxide from which it precipitated unchanged when acidified with dil. hydrochloric acid.

*Anal.* Calcd. for $C_{16}H_{14}N_2O_2$: C, 72.16; H, 5.30; N, 10.52. Found: C, 72.32; H, 5.30; N, 10.23.

**B. From β-Benzoylacrylic Acid.**—To 3.80 g. (0.02 mole) of β-benzoylacrylic acid in 20 ml. of glacial acetic acid was added 2.16 g. (0.02 mole) of phenylhydrazine. Almost immediately upon the addition of the phenylhydrazine a voluminous, light-yellow solid separated which soon redissolved. After standing at room temperature for 24 hours the reaction mixture was worked up to yield 4.84 g. (91% yield) of II, m.p. 195–197° dec.

**2,6-Diphenyl-3-pyridazinone** (III).—A solution of 3.0 g. of II in 65 ml. of acetic anhydride and 3.0 g. of sodium acetate was heated under reflux for 40 minutes. The reaction mixture was cooled and poured into 400 ml. of cold water. The crude precipitated material was recrystallized from methanol and water to give 2.73 g. (98% yield) of colorless needles, m.p. 150–151°.

*Anal.* Calcd. for $C_{16}H_{12}N_2O$: C, 77.40; H, 4.87; N, 11.29. Found: C, 77.71; H, 4.80; N, 11.40.

This product III did not give a positive Raiford test[4] for a pyrazoline nucleus. It melted without decomposition and was insoluble in dil. aqueous sodium hydroxide in contrast with the behavior of the starting material II.

**Methyl β-Benzoylacrylate Methylphenylhydrazone** (IV).—A 1.90-g. sample of methyl β-benzoylacrylate was mixed at room temperature with 1.22 g. (one equiv.) of *unsym*-methylphenylhydrazine in 7 ml. of glacial acetic acid. The reaction mixture was cooled and allowed to stand in the ice-chest for 24 hr. The yellow-orange colored product was recrystallized from methanol and benzene, wt. 2.0 g., m.p. 106–108°.

*Anal.* Calcd. for $C_{18}H_{18}N_2O_2$: C, 73.45; H, 6.16; N, 9.52. Found: C, 73.16; H, 5.91; N, 9.51.

**β-Benzoylacrylic Acid Methylphenylhydrazone** (V).—A 3.8-g. sample of β-benzoylacrylic acid was mixed with 2.63 g. (one equiv.) of *unsym*-methylphenylhydrazine in 14 ml. of glacial acetic acid and the solution held at near room temperature by cooling with cold water. After standing in the ice-chest for 24 hr. the orange colored crystalline solid was removed and recrystallized from a mixture of benzene and methanol, wt. 4.32 g., m.p. 176–177° dec.

*Anal.* Calcd. for $C_{17}H_{16}N_2O_2$: C, 72.84; H, 5.75; N, 9.99. Found: C, 72.64; H, 5.73; N, 9.86.

**2-(*p*-Bromophenyl)-6-phenyl-3-pyridazinone (VI). A. From 2,6-Diphenyl-4,5-dihydro-3-pyridazinone.**[11]—A 1.52-g. (0.006 mole) sample of the dihydropyridazinone in 2.7 ml. of anhyd. glacial acetic acid was treated dropwise with 1.7 g. (0.010 mole) of bromine. A flocculent, yellow colored solid formed rapidly in the cooled solution and hydrogen bromide was evolved. This solid redissolved in two hours. The reaction mixture was allowed to stand at room temperature for 24 hr. and then 10 ml. of ether was added to precipitate a colorless crystalline solid. This was refluxed with 1.72 g. of anhyd. sodium acetate in 20 ml. of anhyd. glacial acetic acid. The solvent was removed under reduced pressure and the residue extracted with chloroform. Evaporation of the chloroform solution produced a colorless product which was recrystallized from benzene and 95% ethanol; wt. 1.20 g. (80% yield); m.p. 175–177°.

*Anal.* Calcd. for $C_{16}H_{11}N_2OBr$: C, 58.75; H, 3.39; N, 8.56. Found: C, 59.05; H, 3.48; N, 8.60.

**B. From 2,6-Diphenyl-3-pyridazinone** (III).—A 1.0-g. sample of the pyridazinone was dissolved in the minimum amount of hot anhyd. glacial acetic acid. The cooled solution was treated with 0.645 g. (one equiv.) of bromine and allowed to stand at room temperature for 24 hr. The reaction mixture was worked up as described above to give 0.5 g. of unchanged starting material and 0.21 g. of the expected product VI, m.p. 174–176°.

**C. From β-Benzoylacrylic Acid *p*-Bromophenylhydrazone.**—The *p*-bromophenylhydrazone (VII) of β-benzoylacrylic acid was obtained from β-benzoylacrylic acid and *p*-bromophenylhydrazine in glacial acetic acid in a 90% yield by allowing the reaction mixture to stand at room temperature for ten hours; recrystallized from 95% ethanol, yellow crystals, m.p. 201–203° dec.

*Anal.* Calcd. for $C_{16}H_{13}N_2O_2Br$: C, 55.66; H, 3.79; N, 8.12. Found: C, 55.99; H, 4.04; N, 8.30.

A 0.4-g. sample of the hydrazone VII was refluxed in 8 ml. of acetic anhydride for 40 minutes, cooled and poured into cold water. This mixture precipitated a tan colored solid after standing for 12 hr., which was recrystallized from ethanol and benzene to give 0.22 g. of colorless crystals, m.p. 174–176°, mixed with VI as prepared under A, m.p. 175–176°.

LINCOLN, NEBRASKA

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF VIRGINIA]

# Nuclear Substituted 3,4-Dihydroxyphenethylamines and Related Derivatives

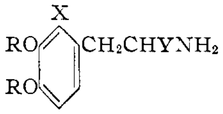
BY ALFRED BURGER AND RICHARD D. FOGGIO[1]

RECEIVED MARCH 14, 1956

The synthesis of several 2-methyl- and 2-chloro-3,4-dihydroxyphenylalkyl- and alkanolamines, and of 5-methylpapaveraldine is described. This study includes observations on the cleavage of the methoxyl groups in the dimethyl ethers of some of these compounds and synthetic intermediates, and evidence for the structure of partially cleaved ether derivatives.

In continuation of a study of nuclear substitution in norepinephrine and related pharmacodynamic drugs,[2] several 2-chloro- and 2-methyl-3,4-dihydroxyphenethylamine and -β-aminophenylpropane derivatives have been prepared. The corresponding 3,4-dimethoxy compounds may be regarded as structural analogs of 2,3,4-trimethoxyphenethylamine, a hallucinogenically interesting isomer[3] of the alkaloid mescaline. Replacement of all three methoxyl groups in mescaline by chlorine gives, in 3,4,5-trichlorophenethylamine, a compound which exhibits the sympathomimetic but not the psychogenic properties of the model alkaloid.[4] A comparison of methyl and chlorine substituted compounds in this series appeared especially interesting since approximative calculations based on accurately constructed models[5–7] indicate that the volumes of the chlorine atom (14.087 Å.$^3$) and the methyl group (14.126 Å.$^3$) are almost the same, and biological differences between such isosteres must be due to electronic effects only.

2-Methylveratraldehyde, previously obtained by a Gattermann reaction from 3-methylveratrole,[8] was prepared conveniently by a Sommelet reaction on 3-methyl-4-chloromethylveratrole,[2] and condensed with nitromethane and nitroethane, respectively. The resulting α,β-unsaturated nitro compounds were reduced with lithium aluminum hydride, and the ether groups of 2-methyl-3,4-dimethoxyphenethylamine (I) and 1-(2-methyl-3,4-dimethoxyphenyl)-2-aminopropane (II) were cleaved with hydrobromic acid. The catecholic amines III and IV were isolated as the stable hydrobromide salts.



V, R = $CH_3$; X = Cl; Y = H
VI, R = Y = $CH_3$; X = Cl
VII, R = H; X = Cl; Y = $CH_3$
I, R = X = $CH_3$; Y = H
II, R = X = Y = $CH_3$
III, R = Y = H; X = $CH_3$
IV, R = H; X = Y = $CH_3$

Starting with 2-chloroveratraldehyde,[2] the amines V and VI were prepared by a similar synthetic sequence. The two ether groups of VI were cleaved with hydrobromic acid, and 1-(2-chloro-3,4-dihydroxyphenyl)-2-aminopropane (VII) was isolated as the hydrobromide. Treatment of V with hydrobromic acid in an atmosphere of nitrogen gave only dark uncrystallizable gums. Therefore, attempts were renewed to demethylate 2-chloroveratraldehyde to 2-chloroprotocatechuic aldehyde, and to use this compound in the synthesis of 2-chloro-3,4-dihydroxyphenethylamine. However, as observed previously[2] 2-chloroveratraldehyde could be only monodemethylated; the re-

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[1] Parke, Davis and Company Fellow, 1953–1955.

[2] E. D. Hornbaker and A. Burger, THIS JOURNAL, **77**, 5314 (1955).

[3] K. H. Slotta and J. Müller, *Z. physiol. Chem.*, **238**, 14 (1936).

[4] S. Chiavarelli, *Gazz. chim. ital.*, **85**, 1405 (1955).

[5] Arthur S. LaPine Co., Chicago, Ill.

[6] A. Stuart, "Die Physik der Hochpolymeren. I. Die Struktur des freien Moleküls." Springer, Vienna, 1952.

[7] G. Briegleb, *Fortschr. chem. Forsch.*, **1**, 642 (1950).

[8] R. I. T. Cromartie and J. Harley-Mason, *J. Chem. Soc.*, 1052 (1952).