(2 H, d, J = 9 Hz, 3′-H and 5′-H), 3.05 (1 H, s, 6-H), and 2.84 (2 H, d, J = 9 Hz, 2′-H and 6′-H). The oxalate formed colorless needles (from ethanol–ether), mp 177–178°.

Anal. Calcd for $C_{20}H_{24}BrNO_3 \cdot C_2H_2O_4$: C, 53.23; H, 5.28; Br, 16.10; N, 2.82. Found: C, 53.05; H, 5.32; Br, 15.86; N, 3.01.

1,2,3,4-Tetrahydro-8-hydroxy-7-methoxy-1-(4-methoxyphenethyl)-2-methylisoquinoline (3).—A solution of 30 mg of the bromoisoquinoline **9** in 40 ml of ethanol was shaken in a current of hydrogen on 10 mg of Raney nickel at room temperature and atmospheric pressure. After absorption of the calculated amount of hydrogen, the catalyst was filtered off and the filtrate was concentrated *in vacuo*. The residue was basified with 10% ammonia and extracted with chloroform. The extract was washed with water, dried over Na_2SO_4, and evaporated *in vacuo* to give 20 mg (83.3%) of *N*-norhomopetaline (**3**) as a viscous syrup: mass spectrum m/e 327 (M^+); ir ($CHCl_3$) 3520 cm^{-1}; uv (EtOH) 279.5 and 284 nm (log ϵ 3.41 and 3.40); nmr τ ($CDCl_3$) 7.57 (3 H, s, NMe), 6.25 (3 H, s, OMe), 6.16 (3 H, s, OMe), 4.47 (1 H, broad signal, OH), 3.44 (1 H, d, J = 8.5 Hz, 6-H), 3.27 (1 H, d, J = 8.5 Hz, 5-H), 3.23 (2 H, d, J = 9 Hz, 3′H and 5′-H), and 2.86 (2 H, d, J = 9 Hz, 2′-H and 6′-H). The oxalate formed pale brown needles (from methanol–ether), mp 171–172°.

Anal. Calcd for $C_{20}H_{25}NO_3 \cdot C_2H_2O_4 \cdot 0.25H_2O$: C, 62.62; H, 6.45; N, 3.32. Found: C, 62.51; H, 6.36; N, 3.33.

6-Ethoxycarbonylamino-1,2,3,4-tetrahydro-7,8-dimethoxy-1-(4-methoxyphenethyl)-2-methylisoquinoline (13).—A mixture of 2 g of 6-ethoxycarbonylamino-3,4-dihydro-7,8-dimethoxy-1-(4-methoxyphenethyl)isoquinoline[11] (**11**), 1.5 ml of methyl iodide, and 25 ml of methanol was refluxed for 2.5 hr and allowed to stand at room temperature overnight. After evaporation of the solvent *in vacuo*, the residue was washed with ether and taken up in 50 ml of methanol. To this solution was added 1 g of sodium borohydride in small portions at 0° with stirring during 30 min; stirring was continued at 0° for 30 min. After the mixture had been set aside at room temperature overnight, the excess of reagent was decomposed with acetic acid and the solvent was distilled off *in vacuo*. The residue was basified with 10% ammonia and extracted with chloroform. The extract was washed with water, dried over K_2CO_3, and evaporated *in vacuo* to leave 2 g (96.5%) of the tetrahydroisoquinoline **13** as a brown viscous syrup: mass spectrum m/e 428 (M^+); ir ($CHCl_3$ 3410 and 1732 cm^{-1}; uv (EtOH) 279.5 and 286 nm (log ϵ 3.80 and 3.75); nmr τ ($CDCl_3$) 8.67 (3 H, t, J = 7.0 Hz, CH_3CH_2), 7.58 (3 H, s, NMe), 6.27 (3 H, s, OMe), 6.23 (3 H, s, OMe), 6.17 (3 H, s, OMe), 5.76 (2 H, q, J = 7.0 Hz, CH_3CH_2), 3.18 (2 H, d, J = 9.0 Hz, 3′-H and 5′-H), 2.89 (1 H, NH), 2.80 (2 H, d, J = 9.0 Hz, 2′-H and 6′-H), and 2.40 (1 H, s, 5-H). The oxalate was recrystallized from methanol–ether to give colorless needles, mp 159–160°.

Anal. Calcd for $C_{24}H_{32}N_2O_5 \cdot C_2H_2O_4$: C, 60.22; H, 6.61; N, 5.40. Found: C, 60.05; H, 6.91; N, 5.26.

6-Amino-1,2,3,4-tetrahydro-7,8-dimethoxy-1-(4-methoxyphenethyl)-2-methylisoquinoline (14).—A mixture of 480 mg of the 6-ethoxycarbonylaminoisoquinoline **13**, 1.5 g of potassium hydroxide, and 30 ml of methanol was refluxed for 5.5 hr and the solvent was then removed by distillation *in vacuo*. The residue was extracted with chloroform, and the extract was washed with water, dried over K_2CO_3, and evaporated *in vacuo* to give 350 mg (87.5%) of the 6-aminoisoquinoline **14** as a pale brown viscous syrup: mass spectrum m/e 356 (M^+); ir ($CHCl_3$) 3450, 3360, and 1620 cm^{-1}; uv (EtOH) 280.5 and 286.5 nm (log ϵ 3.79 and 3.80); nmr τ ($CDCl_3$) 7.58 (3 H, s, NMe), 6.24 (9 H, s, 3 OMe), 3.75 (1 H, s, 5-H), 3.18 (2 H, d, J = 8.5 Hz, 3′-H and 5′-H), and 2.81 (2 H, d, J = 8.5 Hz, 2′-H and 6′-H). The oxalate gave pale brown needles (from methanol–ether), mp 151–152°.

Anal. Calcd for $C_{21}H_{28}N_2O_3 \cdot C_2H_2O_4 \cdot 0.5H_2O$: C, 60.64; H, 6.86; N, 6.15. Found: C, 61.05; H, 6.90; N, 6.10.

1,2,3,4-Tetrahydro-7,8-dimethoxy-1-(4-methoxyphenethyl)-2-methylisoquinoline (15).—To a solution of 310 mg of the aminoisoquinoline **14** in 8 ml of 1 *N* sulfuric acid was added dropwise 1.2 ml of 10% sodium nitrite with stirring at 0–5° during 15 min; the mixture was stirred at 0° for 1 hr. To this solution was added 0.6 ml of 30% hypophosphorous acid at 0°; the mixture was stirred at 0° for 2 hr, then set aside at room temperature for 2 days, basified with concentrated ammonia, and extracted with chloroform. The extract was washed with water, dried over K_2CO_3, and evaporated *in vacuo* to leave 287 mg of a pale brown viscous syrup, which was subjected to chromatography on 3.0 g of silica gel, eluting with ether to give 166 mg (56.0%) of the 7,8-dimethoxyisoquinoline **15** as a pale brown viscous syrup: mass spectrum m/e 341 (M^+); nmr τ ($CDCl_3$) 7.54 (3 H, s, NMe), 6.28 (3 H, s, OMe), 6.22 (3 H, s, OMe), 6.16 (3 H, s, OMe), 3.20 (2 H, s, 5-H and 6-H), 3.16 (2 H, d, J = 9.0 Hz, 3′-H and 5′-H), and 2.78 (2 H, d, J = 9.0 Hz, 2′-H and 6′-H). The oxalate was recrystallized from methanol–ether to give colorless needles: mp 164–165°; uv (EtOH) (oxalate) 279.5 and 285.5 nm (log ϵ 3.82 and 3.80).

Anal. Calcd for $C_{21}H_{27}NO_3 \cdot C_2H_2O_4$: C, 64.02; H, 6.77; N, 3.25. Found: C, 63.91; H, 6.77; N, 3.26.

Demethylation of 15 (Formation of *N*-Norhomopetaline).—A mixture of 500 mg of the above isoquinoline **15** and 20 ml of 20% hydrochloric acid was heated at 120° for 2 hr and then evaporated *in vacuo* to leave a gum, which was basified with 10% ammonia and extracted with chloroform. The extract was washed with water, dried over Na_2SO_4, and evaporated *in vacuo* to leave 440 mg of a brown viscous syrup, which was chromatographed on 20 g of silica gel. Evaporation of the first chloroform–methanol (97:3, v/v) eluate *in vacuo* gave 95 mg (19.8%) of *N*-norhomopetaline (**3**) as a pale brown viscous syrup, whose spectroscopic data were superimposable on those of the authentic sample. The oxalate gave pale brown needles (from methanol–ether), mp and mmp 170–171.5°. The second eluate gave 50 mg (10.8%) of the 4′,8-dihydroxyisoquinoline **16** as a red viscous oil: mass spectrum m/e 313 (M^+); ir ($CHCl_3$) 3570 and 3510 cm^{-1}; nmr τ ($CDCl_3$) 7.57 (3 H, s, NMe), 6.18 (3 H, s, OMe), 4.91 (2 H, broad signal, 2 OH), 3.45 (1 H, d, J = 8.0 Hz, 6-H), 3.35 (2 H, d, J = 8.5 Hz, 3′-H and 5′-H), 3.26 (1 H, d, J = 8.0 Hz, 5-H), and 3.01 (2 H, d, J = 8.5 Hz, 2′-H and 6′-H); m/e 192 (base peak) [$M^+ - (CH_2)_2C_6H_4OH$].

Registry No.—**3**, 28116-36-1; **3** oxalate, 28116-37-2; **6**, 28116-38-3; **7**, 28116-39-4; **9**, 28116-40-7; **9** oxalate, 28116-41-8; **13**, 28116-42-9; **13** oxalate, 28201-46-9; **14**, 28116-43-0; **14** oxalate, 28116-44-1; **15**, 28116-45-2; **15** oxalate, 28116-46-3; **16**, 28116-47-4.

Acknowledgment.—We thank Mr. M. Yamazaki and Dr. M. Kawazu, Tanabe Seiyaku Co. Ltd., for their encouragements and Mr. S. Hirata, Miss A. Kawakami, Miss C. Yoshida, Miss R. Kato, Miss T. Yoshida, and Miss Y. Tadano, Pharmaceutical Institute, Tohoku University, for microanalyses and for spectral measurements. We also thank the Analytical Centre of Organic Chemistry Research Laboratory, Tanabe Seiyaku Co. Ltd., for microanalyses and spectral determinations.

Studies on the Syntheses of Heterocyclic Compounds. CCCXCVI.[1] An Alternative Total Synthesis of (±)-Galanthamine

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Received September 21, 1970

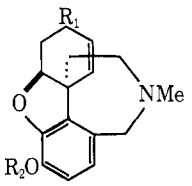
Galanthamine,[2] an *Amaryllidaceae* alkaloid isolated from *Lycoris radiata*, was assigned structure **1** by Barton.[3] A synthesis based on biogenetic lines was also carried out. Recently, some of the present authors reported total syntheses of (±)-galanthamine (**1**) and

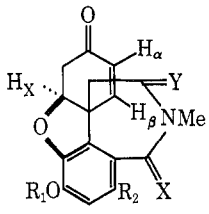
(1) Part CCCXCV: T. Kametoni, K. Fukumoto, and M. Fujihara, *J. Org. Chem.*, **36**, 1293 (1971).

(2) W. C. Wildman, *Alkaloids*, **11**, 348 (1968), and references cited therein; T. Kametani, "The Chemistry of the Isoquinoline Alkaloids," Hirokawa Publishing Co., Tokyo, and Elsevier, Amsterdam, 1968, pp 196, 296.

(3) D. H. R. Barton and G. W. Kirby, *J. Chem. Soc.*, 806 (1962).

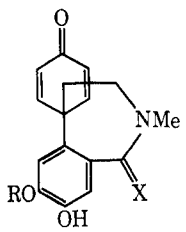
(±)-epigalanthamine (**2**) by the reduction of the narwedine-type enones (**3**) and (**4**) prepared from the amides **5** and **6**, respectively.[4-6] Since natural and synthetic galanthamines appear to possess analgesic activity[5,7] comparable to that of morphine, we report an alternative total synthesis of (±)-galanthamine.





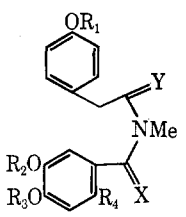
1, R_1 = ⁃OH; R_2 = Me
2, R_1 = ---OH; R_2 = Me

3, R_1 = Me; R_2 = Br; X = O; Y = H_2
4, R_1 = Me; R_2 = Br; X = H_2; Y = O
8, R_1 = Me; R_2 = H; X = O; Y = H_2

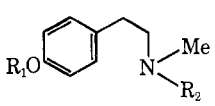


9, R = Me; X = O

The oxidation of 3-hydroxy-*N*-(4-hydroxyphenethyl)-4-methoxy-*N*-methylbenzamide (**7**) was studied, since this compound was more readily available than the amides **5** and **6**. It was expected that coupling might occur at two positions, ortho and para to the hydroxy group, with the formation of narwedine-type enone **8** and dienone **9**. Schotten–Baumann reaction of 4-benzyloxy-*N*-methylamine (**10**) with 3-benzyloxy-4-methoxybenzoyl chloride afforded the corresponding amide **11**, whose debenzylation gave the diphenolic amide **7**.



5, R_1 = R_2 = H; R_3 = Me; R_4 = Br; X = O; Y = H_2
6, R_1 = R_2 = H; R_3 = Me; R_4 = Br; X = H_2; Y = O
7, R_1 = R_2 = R_4 = H; R_3 = Me; X = O; Y = H_2
11, R_1 = R_2 = CH_2Ph; R_3 = Me; R_4 = H; X = O; Y = H_2



10, R_1 = CH_2Ph; R_2 = H

Phenolic oxidation of **7** with potassium ferricyanide gave a 5% yield of **8**. The nmr spectrum showed the α- (τ 4.13) and β-olefinic protons (τ 3.63) in accordance with the expected coupling mode and signals of aromatic protons similar to those of **3** at 3.11 and 2.51 as a doublet. A second compound, **9**, was obtained in 10% yield, whose nmr spectrum showed the α- and β-olefinic protons as an AB quartet and two aromatic protons as singlets. Although this dienone, **9**, had previously been obtained on oxidation of the amide **5** as a colorless syrup,[4] we could here obtain the dienone **9** as pure crystals. Reduction of **8** with lithium aluminum hydride gave (±)-galanthamine (**1**) and (±)-epigalanthamine (**2**). Thus, an alternative synthesis of (±)-galanthamine has been accomplished from compound **7**, more simple and more easily available than the starting materials **5** and **6** used in the previous papers.[4-6] Phenolic oxidation of the amide **7** with vanadium oxytrichloride[8] gave **8** and **9** in 2 and 2.5% yields, respectively, but in the case of short reaction time only the ortho-coupled compound **9** was obtained.

Experimental Section[9]

3-Benzoyloxy-*N*-(4-benzyloxyphenethyl)-4-methoxy-*N*-methylbenzamide (11).—To a stirred suspension of 2 g of 4-benzyloxy-*N*-methylphenethylamine (**10**) in a mixture of 4.5 ml of 10% sodium hydroxide solution and 50 ml of chloroform was added dropwise a solution of 3-benzyloxy-4-methoxybenzoic acid chloride (prepared from 2 g of the acid by the usual way) in 50 ml of chloroform at room temperature. After the stirring had been continued for 0.5 hr, the organic layer was washed with water, dried over Na_2SO_4, and evaporated to give 3 g of the amide **11** as colorless needles (from *n*-hexane), mp 78–78.5°.

Anal. Calcd for $C_{31}H_{31}NO_4$: C, 77.31; H, 6.49; N, 2.91. Found: C, 77.77; H, 6.30; N, 3.24.

3-Hydroxy-*N*-(4-hydroxyphenethyl)-4-methoxy-*N*-methylbenzamide (7).—(a) A mixture of 6 g of the preceding amide **11**, 120 ml of 48% hydrobromic acid, and 200 ml of ethanol was warmed at 55–60° on a water bath for 1 hr. The solvent was evaporated *in vacuo* and the remaining residue was extracted with chloroform. The extract was washed with sodium hydrogen carbonate solution and water and dried over Na_2SO_4. Evaporation of the solvent afforded 1.5 g of the amide **7** as colorless prisms (from *n*-hexane), mp 185–186°.

Anal. Calcd for $C_{17}H_{19}NO_4$: C, 67.76; H, 6.36. Found: C, 67.32; H, 6.54.

(b) A solution of 6 g of the amide **11** in 100 ml of methanol was shaken in a current of hydrogen with 2.5 g of 10% palladium/charcoal until the uptake of hydrogen ceased. After the catalyst had been filtered off, the solvent was evaporated to give 3 g of the phenolic amide, mp 185–186° (from *n*-hexane), which was identical with the authentic specimen, prepared by procedure a, by comparison of spectroscopic data and mixture melting point.

Phenol Oxidation of 7.—(a) To a solution of 2.3 g of **7** in 500 ml of chloroform was added rapidly a mixture of 9.8 g of potassium ferricyanide and 100 ml of 5% sodium hydrogen carbonate solution with vigorous stirring at 55–60°; the stirring was continued for 1.5 hr. The chloroform layer was separated, washed with water, dried over Na_2SO_4, and evaporated to give 1 g of a brown syrup, which was chromatographed on 20 g of silica gel with chloroform as eluent. Evaporation of the first chloroform eluate gave 120 mg of the narwedine-type enone **8** as colorless prisms (from ethanol): mp 269–271°, ir ($CHCl_3$) 1683, 1639, and 1620 cm^{-1}; nmr τ ($CDCl_3$) 6.79 (3 H, s, NMe), 6.10 (3 H, s, OMe), 5.15 (1 H, m, H_x), 4.13 (1 H, d, J = 10.0 Hz, H_α), 3.63 (1 H, s, J = 10.0 and 2 Hz), 3.11, 2.51 (2 H, each d, J = 8.0 Hz, Ar H); mass spectrum (70 eV) m/e 299 (M^+).

Anal. Calcd for $C_{17}H_{17}NO_4$: C, 68.21; H, 5.73; N, 4.68. Found: C, 68.53; H, 5.77; N, 5.02.

(4) T. Kametani, K. Yamaki, H. Yagi, and K. Fukumoto, *J. Chem. Soc., C*, 2602 (1969).

(5) T. Kametani, K. Yamaki, C. Seino, S. Shibuya, K. Fukumoto, K. Kigasawa, M. Hiiragi, F. Satoh, and T. Hayasaka, *ibid.*, in press.

(6) T. Kametani, K. Yamaki, S. Shibuya, K. Fukumoto, K. Kigasawa, F. Satoh, M. Hiiragi, and T. Hayasaka, *ibid.*, in press.

(7) W. C. Wildman, *Alkaloid*, **6**, 376 (1960).

(8) M. A. Schwartz and R. A. Holton, *J. Amer. Chem. Soc.*, **92**, 1090 (1970), and references cited therein.

(9) Ir spectra were measured with a Type EPI-3 Hitachi recording spectrometer and nmr spectra with a Hitachi R-20 spectrometer with deuteriochloroform as solvent and tetramethylsilane as internal reference unless otherwise noted. Mass spectra were taken with a Hitachi RMU-7 mass spectrometer.

Elution with 1% methanol–chloroform gave 300 mg of the dienone **9** as colorless needles (from ethanol): mp 265–267°; ir ($CHCl_3$) 3510, 1660, 1630 cm^{-1}; nmr τ ($CDCl_3$) 6.80 (3 H, s, NMe), 6.13 (3 H, s, OMe), 3.73 (1 H, d, J = 10 Hz, H_α), 2.92 (1 H, d, J = 10 Hz, H_β), 3.39, 2.55 (2 H, each s, Ar H); mass spectrum (70 eV) m/e 299 (M^+) and 256 ($M^+ - 43$).

Anal. Calcd for $C_{17}H_{17}NO_4$: C, 68.21; H, 5.73; N, 4.68. Found: C, 68.49; H, 5.59; N, 4.95.

(b) To a stirred solution of 1 g of **7** in 50 ml of chloroform was added dropwise 1.5 g of vanadium oxytrichloride at room temperature. After the mixture had been stirred for 4 hr, the excess of vanadium oxytrichloride was decomposed with water, and the separated chloroform layer was washed with water, dried over Na_2SO_4, and evaporated to give 0.5 g of a brownish syrup, which was chromatographed on 10 g of silica gel. Elution with chloroform gave 20 mg of the enone **8** as colorless prisms, mp 269–271°, whose spectroscopic data were identical with those of the authentic sample **8**. Removal of the eluent with 1% methanol–chloroform (20 ml) afforded 25 mg of the dienone **9** as colorless needles, mp 265–267°, and, finally, successive elution with the same eluent gave 100 mg of the starting material **7** as colorless needles, mp 167–169°.

In this case when the above reaction was carried out for a short time (2 hr), the para-coupled compound **9** was not observed.

(±)-Galanthamine (1) and (±)-Epigalanthamine (2).—To a stirred suspension of 50 mg of lithium aluminum hydride in 20 ml of tetrahydrofuran was added dropwise a solution of 22 mg of **8** in 50 ml of tetrahydrofuran at room temperature. The mixture was refluxed on a water bath for 10 hr. The mixture was then decomposed with 20% sodium hydroxide solution. The inorganic substance was removed by filtration and the solvent was evaporated to give 18 mg of a colorless syrup which was chromatographed on 0.6 g of alumina. Elution with ethyl acetate–benzene (1:1) gave 13 mg of (±)-galanthamine (**1**) as colorless needles (from ether), mp 121–123°, whose spectroscopic data and chromatographic behavior were identical with those of the authentic (±)-galanthamine and natural (−)-galanthamine. Subsequent elution with ethanol–chloroform (1:9) gave a small amount of material whose chromatographic data were identical with those of authentic (±)-epigalanthamine, but the substance could not be isolated in the pure state.

Registry No.—**1**, 23173-12-8; **7**, 28129-09-1; **8**, 28129-07-9; **9**, 27994-91-8; **11**, 28129-10-4.

Acknowledgment.—We thank Professor S. Uyeo, Kyoto University, and Dr. A. Brossi, Hoffmann-La Roche, Inc., for a gift of natural galanthamine. We also thank Mr. S. Hirata for mass spectral determination, Miss A. Kawakami and Miss C. Yoshida for microanalysis, and Miss Y. Tadano for the nmr measurements.

Spectral Effects Attributable to Conjugation with Trivalent Phosphorus among Some 2-Phospholenes[1]

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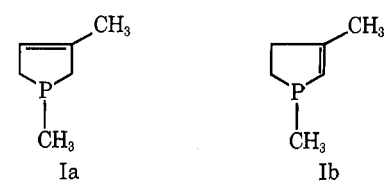
Received September 15, 1970

Synthetic work in this laboratory with phospholenes has made available pairs of isomers which differ in the position of the double bond. In compiling spectral data for these compounds, we have observed consistent differences which can be associated with conjugation of phosphorus with the double bond of the 2-phospholene system. The differences to be described have apparently not been reported upon previously; in part, this may be due to nonavailability of a series of vinylic–allylic models, although the differences appear particularly strong in our cyclic compounds. The existence of a conjugative effect for trivalent phosphorus and the relative importance of utilization of its d or p orbitals have remained points of uncertainty; the opinion has been expressed that there may be a weak involvement of the lone pair on phosphorus in delocalization,[2] but the view has also been taken that acceptance of electrons in the d orbitals of phosphorus may be more significant.[3]

The spectral differences we have encountered so far (infrared and ^{31}P and ^1H nmr) are particularly well displayed by the isomeric 1,3-dimethylphospholenes (Ia[4] and Ib[5]). The conjugative effect is clearly revealed by



Ia Ib

characteristics of the C=C stretching band in the ir spectra. For the allylic isomer Ia, this band appears at 1658 cm^{-1}, while the vinylic isomer Ib has a band of considerably greater intensity at lower frequency (1613 cm^{-1}). The frequency and intensity differences are those expected for diminished double-bond character and polarization in the vinylic isomer through delocalization involving phosphorus. The low electronegativity of phosphorus suggests that the effect is not due to induction. Enamines exhibit similar intensification of the C=C absorption,[6] but apparently this has not been previously observed for vinylphosphine derivatives. In the Raman spectrum, the C=C absorption of di-*n*-butylvinylphosphine is at considerably lower frequency than that of 1-hexene, but the relative intensities are similar.[7] This observation was interpreted to indicate that little, if any, p_π–p_π conjugation prevails among vinylphosphines.[3]

That the conjugative effect is in the direction to endow phosphorus with some positive character is suggested by the nmr spectra of compounds Ia and Ib. The ^{31}P signal for the vinylic compound is at considerably lower field than that of the allylic isomer (Ia, +32.6; Ib, +15.2). Acyclic vinylphosphines do not exhibit appreciable chemical shift differences from their saturated counterparts; for example, trivinylphosphine has a value of +20.7 ppm,[8] while that of triethylphosphine is +20.4 ppm.[9] It is apparent that the phospholene system is unique; in view of the conjugative effect

(1) Supported by Public Health Service Research Grant CA-05507 from the National Cancer Institute.

(2) A. J. Kirby and S. G. Warren, "The Organic Chemistry of Phosphorus," Elsevier, Amsterdam, 1967, p 3.

(3) E. N. Tsvetkov, D. I. Lobanov, M. M. Makhamatkhanov, and M. I. Kabachnik, *Tetrahedron*, **25**, 5623 (1969).

(4) L. D. Quin, J. P. Gratz, and T. P. Barket, *J. Org. Chem.*, **33**, 1034 (1968).

(5) D. K. Myers and L. D. Quin, *ibid.*, **36**, 1285 (1971).

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