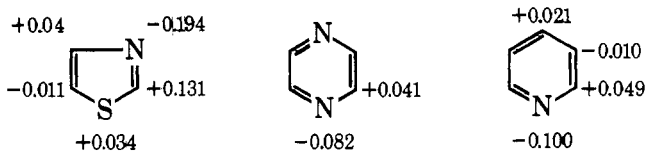

Figure 1. Charge distribution in nitrogen heterocycles. Electron density: −, excess; +, deficiency.

isosteric pyridines and thiazoles do exhibit distinct similarities.

Another factor influencing odor quality is charge distribution. Application of molecular orbital calculations to the unsubstituted thiazole molecule has shown that the charge distribution is nonuniform (Palmer, 1967). The carbon atoms in the 2 and 4 positions tend to be π-electron deficient and are separated by the electron-attracting nitrogen atom; the ring nitrogens of pyrazine and pyridine exert a similar effect (see Figure 1). However, the carbon atom of position 5 of the thiazole ring tends to be π-electron rich and is adjacent to an electron-deficient sulfur (due to its donation of two electrons to the π system). Thus, functional groups on C-5 of the thiazole ring are influenced by a different electron distribution or environment from those situated at C-2 or C-4, the latter positions approximating the C-2 positions of pyridine and pyrazine. The charge distribution undoubtedly plays an important role in determining the orientation of the thiazole ring and its substituent(s) at the nasal receptor site through the creation of a polarized odorant–receptor complex (Klopping, 1971), although the precise charge distribution and orientation of the odorant molecule in the transaction state must at present remain speculative.

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Flavor Properties of Phenylpentenals

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A number of phenylpentenals, isomeric with respect to double bond location and the position of phenyl substitution, have been prepared and their flavor properties have been described.

Phenylalkenals **1a, b,** and **c** were first isolated and identified from a steam distillate of cocoa nibs (van Praag *et al.*, 1968) and subsequently found in peanut (Johnson *et al.*, 1971; Walradt *et al.*, 1971) and in filbert (Kinlin *et al.*, 1972).

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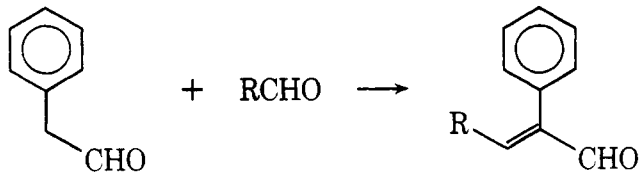
It was suggested (van Praag *et al.*, 1968) that the phenylalkenals arose by aldol condensation of phenylacetaldehyde with acetaldehyde, isobutyraldehyde, and isovaleraldehyde, followed by dehydration to the respective enals **1a, b,** and **c** (Figure 1). In fact these materials were synthesized by classical aldol methods and proved to be of considerable value as flavoring agents (van Praag and Stein, 1971).



1a, R = $-CH_3$

b, R = $-CH(CH_3)_2$

c, R = $-CH_2CH(CH_3)_2$

Figure 1. Formation of phenylalkenals *via* aldol condensation.

In a study of homologous aldol condensates, we found that 2-phenyl-2-pentenal (**1d**) (Figure 2) had the most interesting flavor properties of the series. This led us to investigate the preparation of a number of phenylpentenals, isomeric with respect to position of the phenyl substituent and location of the double bond.

Preparation of the Phenylpentenals. Syntheses of many of the phenylpentenals have already been described (2-phenyl-2-pentenal: Veux (1939), Prevost and Robert (1944), Bouget (1965); 2-phenyl-4-pentenal: Elkik and Francesch (1969), Fitzpatrick *et al.* (1969); 3-phenyl-2-pentenal: Finici and Normant (1964); 3-phenyl-4-pentenal: Burgstahler *et al.* (1963); 5-phenyl-2-pentenal: Delahy (1932)). However, for present purposes more convenient synthetic methods were often employed. Figure 2 outlines the procedures used.

Condensation of phenylacetaldehyde with propionaldehyde yielded 2-phenyl-2-pentenal (**1d**). The same starting material, phenylacetaldehyde, was converted to 2-phenyl-4-pentenal (**2**) *via* its enamine, which was alkylated essentially according to Elkik and Francesch (1969), who demonstrated that alkylation occurs first on nitrogen as shown.

3-Phenyl-2-pentenal (**4**) was obtained by a modified aldol condensation developed by Wittig (Wittig and Hesse, 1970). The cyclohexylimine of acetaldehyde was treated with a suitable base (lithium salt of a secondary amine) to form the lithium salt **3**. Propiophenone was added to give the intermediate shown, which was hydrolyzed and dehydrated to provide a mixture of (*E*)- and (*Z*)-**4**. These were isolated by preparative gc and their structures were assigned on the basis of their nmr spectra. Treatment of cinnamyl alcohol with ethyl vinyl ether followed by thermal Claissen–Cope rearrangement provided 3-phenyl-4-pentenal (**5**) (Burgstahler *et al.*, 1963). This compound was converted to its dimethyl acetal and treated with strong base to move the double bond into conjugation with the phenyl group. Mild two-phase hydrolysis of the isomerized acetal afforded 3-phenyl-3-pentenal (**6**). Only one of the two possible isomers was cleanly separated by preparative gc. It is probably the isomer shown but the assignment is tentative, based on nmr spectra of the crude aldehyde and acetal mixtures. Because this compound and the mixture from which it was isolated lacked any special organoleptic properties we were not inclined to investigate the structures of the isomers further.

4-Phenyl-2-pentenal (**7**) was prepared *via* a modified aldol condensation using lithium salt **3** and hydratropic aldehyde. In this case one might predict that normal aldol condensation would yield the desired product but in practice it did not. The preparation of 4-phenyl-4-pentenal (**8**) illustrates the alkylation of lithium salt **3** to give an imine which, on hydrolysis, yields an elaborated aldehyde. The requisite alkylating agent, α-bromomethylstyrene, was prepared by treatment of α-methylstyrene with *N*-bromosuccinimide (Reed, 1965). Reaction of phenylpropionaldehyde with the weakly reactive Wittig reagent formylmethylenetriphenylphosphorane (Trippett and Walker, 1961) provided 5-phenyl-2-pentenal (**9**). Finally, alkylation of **3** with cinnamyl bromide gave, after hydrolysis, 5-phenyl-4-pentenal (**10**).

Organoleptic Determinations. The phenylpentenals were tasted in water at dilutions which allowed the best differentiation of their flavor properties. The set of descriptions in Table I was prepared with the intention of emphasizing the observed differences in character.

RESULTS AND DISCUSSION

The descriptions in Table I suggest an interesting effect of structure on taste. When the phenyl substituent is adjacent to the aldehyde function, the double bond location has a much greater influence on organoleptic character than when phenyl is remote from the aldehyde. Similarly, when the double bond is remote from the carbonyl group, the position of phenyl substitution has the greater effect on organoleptic properties. It may be significant that the most potent of the compounds examined was 3-phenyl-4-pentenal, in which the three functional groups are as far removed from each other as possible. Such observations are qualitative and must be supported by many similar examples of polyfunctional compounds before any conclusions are drawn. Our results are somewhat reminiscent of Bedoukian's (1971) report on the organoleptic properties of hexenols. The observed differences in character between the cis and trans isomers of a given double bond position were greater as the double bond was farther removed from the oxygen-containing functional group.

EXPERIMENTAL SECTION

Ir spectra of neat samples were determined on a Perkin-Elmer model 621 instrument. Several characteristic bands are given. Nmr spectra of $CDCl_3$ solutions were recorded on a Varian HA-100 spectrometer. Chemical shifts are reported in parts per million downfield from tetramethylsilane internal standard. Mass spectra were determined on a CEC 21-103C instrument and gc–ms analyses were performed on a F&M 5750 gas chromatograph coupled to a Hitachi RMU-6 spectrometer *via* a Watson–Biemann separator. The most intense ions are given along with their relative abundances; parent ions are underscored.

All reactions which involved strongly basic reagents were carried out under nitrogen.

2-Phenyl-2-pentenal (1d). Phenylacetaldehyde (18.3 g), propionaldehyde (10.0 g), sodium acetate (6.0 g), and 40 ml of methanol were combined and heated at reflux for about 13 hr. The alcohol was evaporated and the residue was partitioned between water and ether. The organic layer was dried over sodium sulfate and evaporated. The residue was distilled without fractionation to give (11.3 g) colorless material which was 80–85% product by gc. Redistillation gave 5.2 g of material which was greater than 98% pure: bp 80–82° (0.4 mm); ir 1675, 1623, 1598, 2700 cm^{-1}; nmr δ 1.09 (t, J = 7.5 Hz, 3 H), 2.36 (m, 2 H), 6.67 (t, J = 7.5 Hz, 1 H), 7.05–7.55 (m, 5 H), 9.60 (s, 1 H); mass spectra m/e 160 (100), 91 (94), 117 (71), 29 (63), 131 (61), 115 (60).

2-Phenyl-4-pentenal (2). 2-Phenyl-4-pentenal was prepared essentially according to Elkik and Francesch (1969). Material for spectral and organoleptic determination was obtained by preparative gc (SE-30 column): ir 1714, 910, 987, 1637, 2703, 1595 cm^{-1}; nmr δ 2.28–2.92 (m, 2 H), 3.54 (t, J = 7 Hz, 1 H), 4.88–5.06 (m, 2 H), 5.46–5.87 (m, 1 H), 7.08–7.62 (m, 5 H), 9.65 (d, J = 1.5 Hz, 1 H); mass spectra m/e 131 (100), 91 (95), 39 (28), 29 (26), 116 (24), 51 (21), 160 (5).

3-Phenyl-2-pentenals (4). A solution of lithium salt **3** was prepared from 12.5 g of the cyclohexylimine of acetaldehyde and treated with 9.0 ml of propiophenone following the method of Wittig and Hesse (1970). Steam distillation of the adduct from aqueous oxalic acid provided 7.3 g of a mixture comprised of propiophenone and the (*E*) and (*Z*) isomers of 3-phenyl-2-pentenal in the approxi-

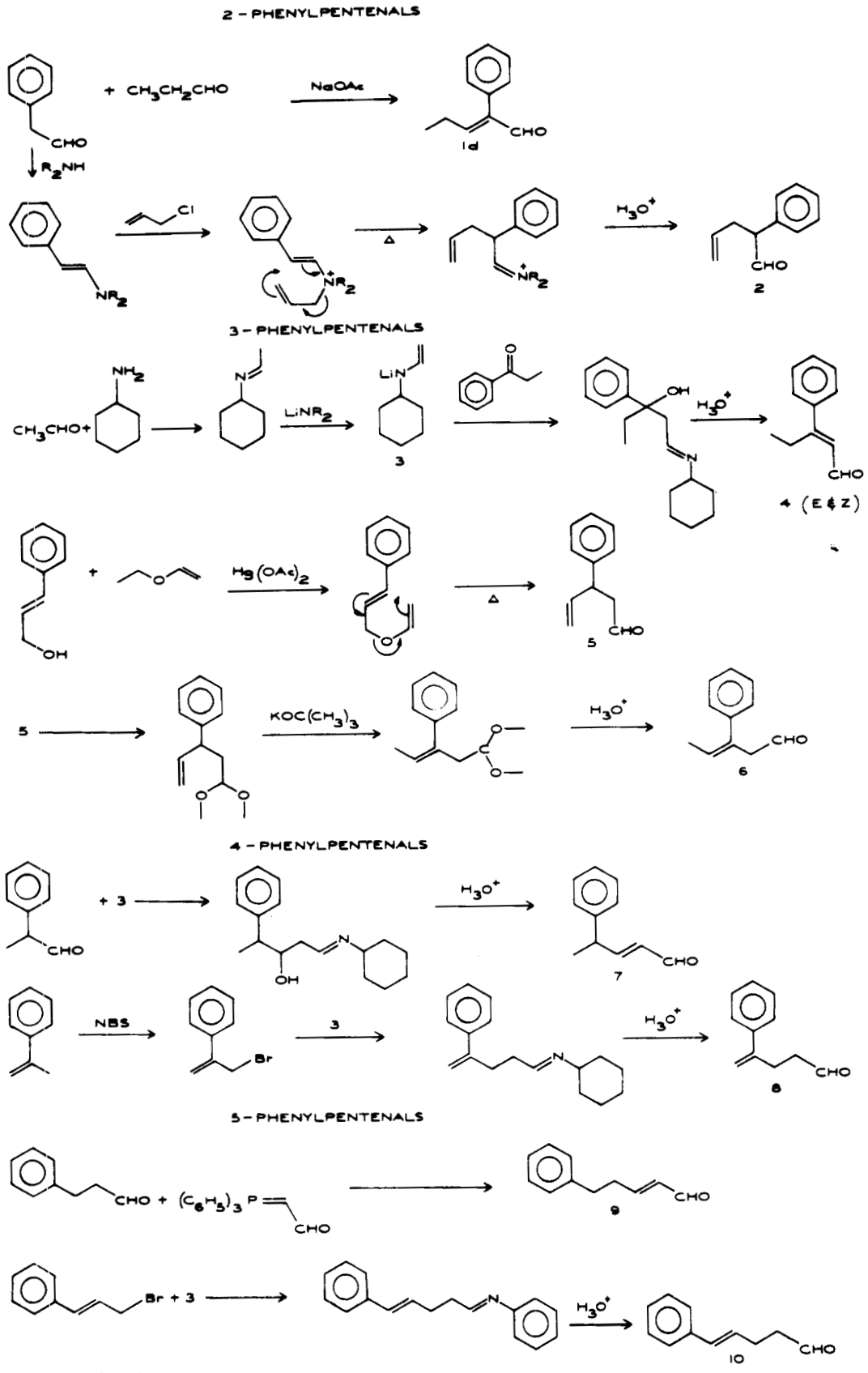
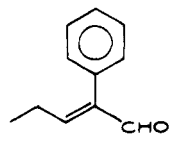
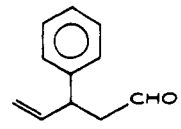
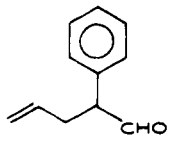
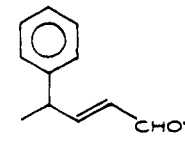
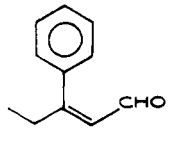
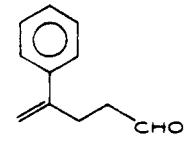
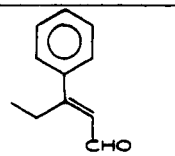
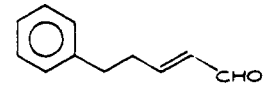
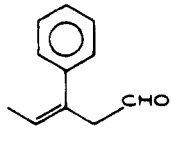
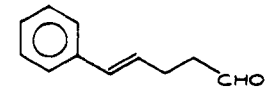


Figure 2. Preparation of phenylpentenals.

mate ratio 2:1 as determined by nmr. The two isomers were isolated by preparative gc (SE-52 column). The (*E*) isomer had: nmr δ 1.07 (t, J = 7.5 Hz, 3 H), 2.60 (q of d, J = 7.5 and 2 Hz, 2 H), 6.07 (d of d, J = 8 and 2 Hz, 1 H), 7.08–7.52 (m, 5 H), 9.43 (d, J = 8 Hz, 1 H). The (*Z*) isomer had: nmr δ 1.15 (t, J = 7.5 Hz, 3 H), 3.03 (q, J = 7.5 Hz, 2 H), 6.22 (d, J = 8 Hz, 1 H), 7.15–7.60 (m, 5 H), 10.14 (d, J = 8 Hz, 1 H). Gc–ms indicated that the two isomers had virtually the same mass spectra: m/e 159 (100), 160 (97), 131 (58), 91 (51), 77 (43), 51 (41).

3-Phenyl-4-pentenal (5). 3-Phenyl-4-pentenal, prepared according to Burgstahler *et al.* (1963), had the following spectral characteristics: ir 1720, 915, 1630, 2710, 1595 cm^{-1}; nmr δ 2.80 (m, 2 H), 3.93 (br q, J = 7 Hz, 1 H),

Table I. Flavor Properties of Phenylpentenals

 2-PHENYL-2-PENTENAL	LIGHT ROSY	 3-PHENYL-4-PENTENAL	COCOA POWDER
 2-PHENYL-4-PENTENAL	COOKED TOMATO, METALLIC	 4-PHENYL-2-PENTENAL	WEEDY GREEN, MELON
 (Z)-3-PHENYL-2-PENTENAL	SWEET, CEDARWOOD-LIKE	 4-PHENYL-4-PENTENAL	WATERMELON, WALNUT, WALNUT HULL AROMA
 (E)-3-PHENYL-2-PENTENAL	LEAFY GREEN, SLIGHTLY METALLIC	 5-PHENYL-2-PENTENAL	CITRUS, ESPECIALLY GRAPEFRUIT, FRUITY
 3-PHENYL-3-PENTENAL	GREEN, ROSY	 5-PHENYL-4-PENTENAL	GRAPEFRUIT JUICE, MELON NOTES, CHLORINE-WATER AROMA

4.90–5.20 (m, 2 H), 5.76–6.18 (m, 1 H), 7.06–7.43 (m, 5 H), 9.79 (t, J = 2 Hz, 1 H); mass spectra m/e 117 (100), 115 (51), 91 (49), 27 (31), 29 (30), 51 (28).

3-Phenyl-4-pentenal Dimethyl Acetal. To a solution of 3-phenyl-4-pentenal (180 g) in about 100 ml of methanol was added 1 ml of acetyl chloride and then 16.0 g of 3A molecular sieves. After 2 hr of occasional agitation at room temperature the solution was decanted and distilled. Since the product contained some starting aldehyde the entire distillate was reprocessed as above. Distillation then gave 19.2 g of colorless oil: bp 72–73° (0.5 mm); ir 1050, 1120, 677, 2930, 910 cm^{-1}; mass spectra m/e 75 (100), 117 (55), 115 (36), 142 (27), 91 (25), 29 (19), 206 (1).

3-Phenyl-3-pentenal Dimethyl Acetal. 3-Phenyl-4-pentenal (15.0 g) was dissolved in 35 ml of dimethyl sulfoxide (DMSO) and 1.5 g of potassium *tert*-butoxide was added. After 1.5 hr the mixture was partitioned between water and ether. The organic layer was dried over sodium sulfate and evaporated. Gc (SE-30 column) suggested that some starting material remained. The mixture was therefore treated again with potassium *tert*-butoxide in DMSO and reisolated to give 13.9 g of orange oil; 8.9 g of the mixture was fractionally distilled to give 5.6 g of product, bp 80–83° (0.1 mm). Gc-ms (SE-30 column) and nmr strongly suggested the presence of both cis-trans isomers. Only the major product was readily obtained in pure form by preparative gc: nmr δ 1.82 (d, J = 7 Hz, 3 H), 2.83 (d, J = 6 Hz, 2 H), 3.24 (s, 6 H), 4.63 (t, J = 6 Hz, 1 H), 5.82 (q, J = 7 Hz, 1 H), 7.15–7.45 (m, 5 H); mass spectra m/e 75 (100), 47 (13), 91 (7), 115 (6), 31 (6), 76 (5), 206 (1).

3-Phenyl-3-pentenal (6). The distilled acetal mixture (2.3 g) from the previous section was stirred overnight with 10 ml of water and 1 ml of 37% HCl. The product was extracted with ether, washed with aqueous Na_2CO_3, dried over sodium sulfate, and evaporated to give 1.8 g of light yellow oil. Isolation of the major component by preparative gc (SE-30 column) gave the desired product: ir 1718, 1660, 1595, 2710 cm^{-1}; nmr δ 1.82 (d, J = 7 Hz, 3 H), 3.57 (d, J = 2.5 Hz, 2 H), 6.14 (q, J = 7 Hz, 1 H), 7.15–7.50 (m, 5 H), 9.62 (t, J = 2.5 Hz), 6.14 (q, J = 7 Hz, 1 H), 7.15–7.50 (m, 5 H), 9.62 (t, J = 2.5 Hz, 1 H); mass spectra m/e 91 (100), 160 (88), 29 (77), 117 (66), 131 (63), 159 (58).

4-Phenyl-2-pentenal (7). A solution of lithium salt 3 (prepared from 2.60 g of imine) was treated with 2.68 g of hydratropic aldehyde and worked up as described for 3-phenyl-2-pentenal to give 2.10 g of crude material. The product was isolated by preparative gc (SE-30): ir 1683, 1828, 1597, 2720 cm^{-1} ; nmr δ 1.42 (d, J = 7 Hz, 3 H), 3.71 (m, 1 H), 6.07 (m, 1 H), 6.92 (m, 1 H), 7.07–7.66 (m, 5 H), 9.51 (d, J = 8 Hz, 1 H); mass spectra m/e 131 (100), 29 (79), 91 (76), 115 (66), 160 (55), 51 (44).

4-Phenyl-4-pentenal (8). A solution of lithium salt 3 (from 2.50 g of imine) was cooled in a Dry Ice bath and treated with 4.00 g of α-bromomethylstyrene (Reed, 1965). The mixture was then kept at 5° overnight; 10 ml of water was added followed by 4 ml of 37% HCl to give pH 1. After ½ hr of stirring the two-phase mixture, the crude material was isolated from the organic layer. The product was unstable to preparative gc but was readily purified

via Girard's P reagent to give 0.5 g of light yellow oil which was 98+% pure by analytical gc (DC-710 column): ir 1720, 896, 1623, 2710, 1570, 1596 cm^{-1}; nmr δ 2.35–3.00 (m, 4 H), 5.06 (s, 1 H), 5.30 (s, 1 H), 7.32 (m, 5 H), 9.77 (s, 1 H); mass spectra *m/e* 118 (100), 29 (48), 117 (43), 103 (32), 91 (30), 77 (30), 160 (2).

5-Phenyl-2-pentenal (9). A solution of 1.34 g of 3-phenylpropionaldehyde and 3.25 g of formylmethylenetriphenylphosphorane (Trippett and Walker, 1961) in 10 ml of benzene was heated at reflux overnight. The solvent was evaporated and the residue was extracted several times with isopentane. Evaporation of the combined extracts gave 0.90 g of yellow oil from which the major component was isolated by preparative gc (W-98 column): ir 1686, 1632, 1599, 2720 cm^{-1}; nmr δ 2.45–3.00 (m, 4 H), 6.09 (d of d, J = 16 and 8 Hz, 1 H), 6.81 (d of t, J = 16 and 7 Hz, 1 H), 7.05–7.45 (m, 5 H), 7.46 (d, J = 8 Hz, 1 H); mass spectra *m/e* 91 (100), 116 (18), 65 (15), 92 (10), 160 (7).

5-Phenyl-4-pentenal (10). A solution of the lithium salt 3 (from 1.30 g of imine) was treated at Dry Ice temperature with 2.00 g of cinnamyl bromide. After 5 hr at room temperature, water was added followed by 10% H_2SO_4 to give pH 1. After 15 min of stirring, the crude product was isolated from the separated organic layer and purified *via* Girard's P reagent to provide 0.64 g of yellow oil which was 99.5% pure by gc (DC-710): ir 1720, 963, 2720, 1595 cm^{-1}; nmr δ 2.54 (m, 4 H), 6.12 (m, 1 H), 6.42 (d, J = 16 Hz, 1 H), 7.25 (m, 5 H), 9.78 (s, 1 H); mass spectra *m/e* 104 (100), 91 (55), 29 (51), 117 (46), 115 (44), 160 (39).

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The Synthesis and Properties of Alkylated Five- and Six-Membered Alicyclic Pyrazines

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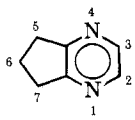
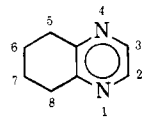
A series of mono-, di-, and trialkyl derivatives of 6,7-dihydro-5*H*-cyclopentapyrazine and 5,6,7,8-tetrahydroquinoxaline was prepared either by condensation of α,β-dicarbonyls with α,β-diamines and subsequent oxidative aromatization or by alkylation of the bicyclic pyrazines. The gas chromatographic retention indices and ir, uv, nmr, and mass spectral data of these derivatives are presented, together with a summary of their natural occurrence to date.

During our gas chromatographic and mass spectroscopic investigations of the volatiles of roasted peanuts and roasted filberts, we encountered a series of compounds which appeared to be pyrazine derivatives with molecular weights two units lower than the alkyl-substituted pyrazines, namely 120, 134, 148, and 162. The data suggested that these compounds probably contained either an unsaturated side chain or else possessed an alicyclic structure. Johnson *et al.* (1971) had encountered similar components in roasted peanut volatiles, and from the mass spectral and uv data they tentatively assigned structures of isopropenyl- and methyl isopropenylpyrazine to the compounds of mol wt 120 and 134, respectively, and suggested also that a methyl-substituted cyclopentapyrazine (mol wt 134) was present. However, when a comparison was made of authentic isopropenylpyrazine, synthesized from ethylpyrazine *via* the Mannich base (Kamal *et al.*, 1962), its mass fragmentation and gc retention time were quite different from the mol wt 120 compound reported by Johnson *et al.* but were identical with our data for an earlier eluting roasted peanut component. Because of the lack of similarity between the properties of the isopropenylpyrazine and the roasted peanut and filbert "unknowns," we concluded that the latter probably were in fact unique bicyclic pyrazines. Various alkyl derivatives of five- and six-membered alicyclic pyrazines (structures I and X, respectively) were synthesized and their gas chromatographic and spectral properties determined. With the availability of these reference data it has been possible to establish the natural occurrence of bicyclic pyrazines not only in roasted peanuts (Walradt *et al.*, 1971) and filberts (Kinlin *et al.*, 1972) but also in cooked beef (Mussinan *et al.*, 1973) and cooked pork liver (Mussinan and Walradt, 1973).



6,7-dihydro-5*H*-cyclopentapyrazine
I



5,6,7,8-tetrahydroquinoxaline
X

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