The infrared signals (Nujol) appeared at 1715 (*p*-nitrobenzoyl carbonyl), 1600 (aromatic), 1517 and 1335 ($-NO_2$), 1263, 1112 and 1099 (ν_{CO}), and 717 cm^{-1} (aromatic).

Methylurea.—The chloroform-insoluble crystalline material and the combined fractions 58–110 were pooled and recrystallized from methanol–methylene chloride mixture to afford colorless needles which showed a homogeneous spot (R_f 0.53) by thin layer chromatography in solvent system B, were positive toward modified Ehrlich reagent, and had mp 100.5–101.5° and a yield of 0.55 g (93.3–95.9%).

Anal. Calcd for $C_2H_6N_2O$: C, 32.42; H, 8.16; N, 37.82. Found: C, 32.33; H, 8.07; N, 37.51.

The infrared spectrum (Nujol) gave signals at 3509, 3390 and 3268 ($-NH_2$ and $>NH$), 1684 (shoulder), 1639 and 1567 cm^{-1} ($-NHCONH_2$). The product was identical with an authentic specimen of methylurea with regard to infrared spectrum and R_f value (tlc).

Methylurea Nitrate.—The above methylurea was dissolved in 10% nitric acid and the solution was evaporated under reduced pressure. The crystalline residue was recrystallized from methanol to afford colorless rods, mp 129.5–131° dec.

Hydrogenolysis of Prominal (XXXV).—To a solution of 2.0 g of prominal in 200 ml of 50% aqueous methanol was added 1.228 g (4 equiv) of sodium borohydride. After 43 hr at room temperature the reaction mixture was worked up according to the general procedure. The reduced product was chromatographed on silica gel (column: 24 × 270 mm) and the column eluted with chloroform–methanol (9:1). The fractions (5 ml each) gave the following distribution: fractions 28–29, mp 179–179.5° (117 mg), recovered starting material (5.9%); fractions 30–33, crystalline (mp 189–190°) (unidentified); fractions 65–75, crystalline (mp 183–184°), positive toward modified Ehrlich reagent (unidentified); fractions 78–135, crystalline, positive toward modified Ehrlich reagent (methylurea).

Fractions 30–33 on evaporation yielded a crystalline residue. Recrystallization from ether gave colorless prisms: mp 189–190° dec; yield 35 mg; negative toward modified Ehrlich test; infrared signals (Nujol) at 3509, 3226, 3106, 1686 cm^{-1}. Fractions 65–75 which showed a positive color test in the modified Ehrlich reagent were pooled and evaporated, and the crystalline residue was recrystallized from acetone to afford colorless needles: mp 183–184°; yield 20 mg; infrared signals (Nujol) at 3448, 2336 (shoulder), 1626 cm^{-1}.

Methylurea from Prominal.—Methylurea was eluted into fractions 78–135. After evaporation the residue was recrystallized from methanol–methylene chloride to yield colorless needles, mp 100.5–101.5°, with a yield of 315 mg (51.8%).

Anal. Calcd for $C_2H_6N_2O$: C, 32.42; H, 8.16; N, 37.82. Found: C, 32.26; H, 7.93; N, 37.56.

Hydrogenolysis of Hydantoin.—A solution of 5.004 g of hydantoin in 500 ml of ethanol was reduced with 7.56 g (4 equiv) of sodium borohydride. After 60 hr at room temperature the reaction mixture was worked up as described above. There was 4.209 g (84.1%) of starting material recovered. The mother liquor was chromatographed on a silica gel column (20 × 270 mm). The column was eluted with chloroform–methanol (7:3). The fractions, 5 ml each, showed the following distribution: fractions 11–12, yellowish crystals (trace); fractions 21–22, mixture of two components (0.19 g); fractions 24–27, oil, positive toward modified Ehrlich reagent.

β-Ureidoethanol.—Fractions 24–27 were collected and evaporated to leave an oily residue which was homogeneous (tlc, solvent system B), yield 0.391 g (7.5%). The modified Ehrlich reagent gave a positive test. The infrared spectrum (liquid film) gave signals at 3425 ($-OH$, $-NH_2$, and $>NH$), 1653, 1605 and 1558 ($-NHCONH_2$), 1063 cm^{-1} (ν_{CO}). Nmr signals (D_2O) appeared at 3.24 (t, J = 5 cps) (DO–CH_2–CH_2–ND), 3.63 ppm (t, J = 5 cps) (DO–CH_2–CH_2–ND–). Chemical shifts are based on 3-(triethylsilyl)-1-propanesulfonic acid as reference.

β-Ureidoethanol O,N-Bis-*p*-nitrobenzoate.—A solution of 122 mg of β-ureidoethanol was allowed to react with *p*-nitrobenzoyl chloride (0.434 g) in dry pyridine at 50° for 30 hr. The O,N-bis-*p*-nitrobenzoate was isolated and recrystallized from ethanol to give yellow needles, mp 244–246° dec.

Anal. Calcd for $C_{17}H_{14}N_4O_8$: C, 50.75; H, 3.51; N, 13.93. Found: C, 50.96; H, 3.69; N, 13.66.

The infrared spectrum (Nujol) gave signals at 3322 (shoulder), 3257 and 3135 ($>NH$), 1727 and 1706 (*p*-nitrobenzoyl carbonyl), 1675 (ureido carbonyl), 1597 (aromatic), 1511 and 1348 ($-NO_2$), 1269 and 1098 (ν_{CO}), and 718 cm^{-1} (aromatic).

Registry No.—Sodium borohydride, 1303-74-8; II, 15025-14-6; III, 15025-15-7; VII, 15025-16-8; VIII, 15025-17-9; X, 15025-18-0; XI, 15077-29-9; XIV, 15083-68-8; XV, 15025-19-1; XVI, 87-41-2; phthalyl alcohol, 612-14-6; XVIII, 15025-21-5; XIX, 15025-22-6; XX, 118-29-6; XXII, 15025-23-7; XXIII, 15026-23-0; *p*-nitrobenzoate of XXIII, 15026-24-1; XXV, 15025-24-8; XXVI, 15025-25-9; *p*-nitrobenzoate of XXVI, 15025-26-0; XXVIII, 927-60-6; *p*-nitrobenzoate of XXVIII, 15025-27-1; XXXI, 115-76-4; β,β-diethylpropylene glycol di-*p*-nitrobenzoate, 15025-29-3; XXXIII, 598-50-5; XXXIV (R = $COC_6H_4NO_2$), 15077-28-8; methylurea nitrate, 598-11-8; β-ureidoethanol, 2078-71-9; β-ureidoethanol O,N-bis-*p*-nitrobenzoate, 15025-32-8.

The Formation of N-Substituted Pyrazoles from the Pyrolysis of Certain α,β-Unsaturated Azines[1]

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Cinnamaldehyde azine and derivatives of this azine were pyrolyzed at temperatures near 200° to give homogeneous isomeric products in high yield. Chemical degradation and spectroscopic analysis show that these products are N-propenylated pyrazoles. For example, cinnamaldehyde azine was converted pyrolytically in 90% yield to 1-(*cis*-3-phenylpropenyl)-5-phenylpyrazole. This pyrolytic synthesis allows the preparation of a previously unreported class of pyrazoles in high yield.

The thermochemical instability of azines was first observed by Curtius, who reported that benzaldehyde azine, on pyrolysis, yielded stilbene.[2] This reaction was subsequently shown to be fairly typical of azines (excluding aryl ketazines), but these studies were limited to structurally uncomplicated substrates.[3] However, the mechanism of the reaction reported by Curtius[2] remained obscure until recently, when Zimmerman and Somasekhara demonstrated an ionic chain process, in which the chain-transfer agent is an aryldiazomethane.[4] This mechanism was established by demon-

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[1] (a) This paper is a portion of a thesis submitted by J. G. K. in partial fulfillment of the requirements of Northeastern University for the degree of Doctor of Philosophy. (b) First presented at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966, p S105.

[2] T. Curtius and R. Jay, *J. Prakt. Chem.*, **39**, 45 (1889).

[3] J. Meisenheimer and F. Helm, *Ann.*, **355**, 274 (1907); P. Pascal and L. Normand, *Bull. Soc. Chim. France*, **9**, 1029, 1059 (1910); **11**, 21 (1912); L. B. Howard and G. E. Hilbert, *J. Am. Chem. Soc.*, **54**, 3628 (1932).

[4] H. E. Zimmerman and S. Somasekhara, *ibid.*, **82**, 5865 (1960).

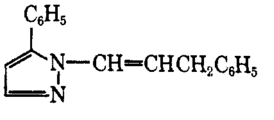
strating that the reaction was intermolecular, catalyzed by phenyldiazomethane, and unaffected by radical trapping agents. The study by Zimmerman[4] was carried out in the molten state, but the decomposition was examined in solution by Overberger and Chien, who found the reaction to be unchanged mechanistically.[5]

Recently, analogous pyrolytic reactions have been reported for furfuraldehyde azine[6] and α- or β-naphthaldehyde azine.[7] Of particular interest is the observation of Hirsch that aryl ketazine pyrolysis follows a different pathway.[8] He reported that benzophenone azine, on pyrolysis at 375–500°, yields benzhydrylidine imine, benzonitrile, and 6-phenylphenanthridine as major products, accompanied by lesser amounts of benzene, biphenyl, diphenylmethane, and benzhydrylidine aniline. The author claims that this reaction is a free-radical process.

Results and Discussion

While examining the thermal double-bond isomerizations of cinnamaldehyde azine, Zechmeister and Dale[9] observed significant amounts of decomposition product(s), which were not examined further. We have reexamined this reaction, and have found that cinnamaldehyde azine, on pyrolysis in solution or in melt at temperatures from 170–250°, is converted in high yield to a single, homogeneous isomer. This compound on oxidation with permanganate yields benzoic acid, 3(5)-phenylpyrazole, and 2 equiv of carbon dioxide. Assuming that the above-mentioned pyrazole is a "normal" oxidation product, the pyrolysis product must be a derivative of 3(5)-phenylpyrazole.

When the cinnamaldehyde azine isomer was hydrogenated with a palladium catalyst, a dihydro derivative was formed, indicating the probable presence of one double bond. This dihydro derivative on oxidation with permanganate yielded the same product mixture as previously obtained from the thermal isomer. Spectral analysis of the pyrolysis product demonstrated the absence of amino hydrogen, and from this result it can be concluded that this compound is one of the four N-phenylpropenylated pyrazoles (**1**–**4**) (neglecting geometrial isomerism for the time being).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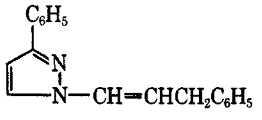
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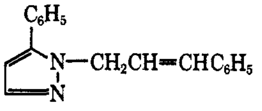
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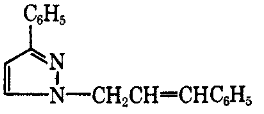
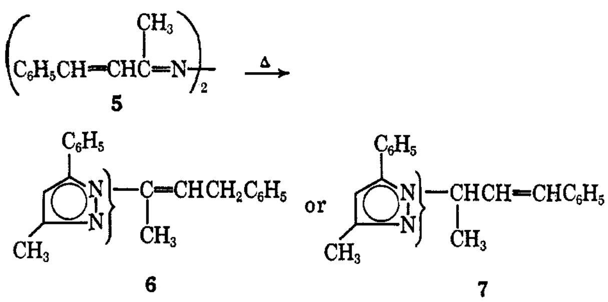

4

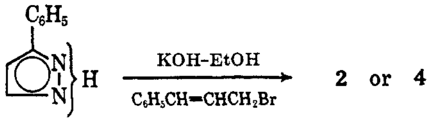
On ozonolysis the isomer yielded phenylacetaldehyde, but not benzaldehyde. On this basis it is clear that the nine-carbon substituent on nitrogen is in fact —CH=CHCH$_2$C$_6$H$_5$. The conclusion reached above, concerning the structure of the side chain on nitrogen, was confirmed by examining the pyrolysis of the azine derived from benzalacetone (**5**).[10] The two possible modes of decomposition of this azine are indicated in eq 1. It can be seen that if compound **6** were the structure of the pyrolysis product, there should be two allylic protons observable in the nmr spectrum, whereas the spectrum of compound **7** would show only one such proton. When compound **5** was pyrolyzed at 190° for 30 min, a 90% yield of a pyrazole was obtained. The nmr spectrum (see Experimental Section) of this pyrazole clearly showed adsorption due to two benzylic protons at τ 7.07, and a single olefin protonic adsorption at 4.50. Thus, the exclusion of structures **2** and **4** for the thermal isomer is warranted.



(1)

The experimental distinction between structures **1** and **3** proved to be difficult. The position of N-alkylation could not be decided on the basis of a routine analysis of the proton nmr spectrum of this compound, since the observed spectrum was apparently consistent with either of the two possible structures. However, Tensmeyer and Ainsworth[11] have recently shown in an nmr study of a large number of substituted pyrazoles, that when either α position of 3(5)-phenylpyrazole is substituted, the aromatic protons on the benzene ring appear as a sharp singlet in the nmr. Conversely, when the aryl group is not adjacent to some substituent on nitrogen or carbon, these aromatic protons appear as a complex multiplet. Since, in the nmr spectrum of the pyrolytic isomer, the adsorption due to the aryl protons on the benzene ring directly attached to the pyrazole ring were observed as a sharp singlet at τ 2.60, it is concluded that the correct structure for the pyrolysis product is in fact that indicated by structure **1**.

The above conclusion is supported by the following experiment. We examined the product of the reaction between cinnamyl bromide and the potassium salt of 3(5)-phenylpyrazole. There are two possible products of this reaction (eq 2), depending on the position of N-alkylation. The proton nmr spectrum of compound **5** is consistent only with the normal SN reaction mode, and since the aryl protons appear as a multiplet centered about τ 2.60 it is felt that the conclusion drawn above about the position of N-alkylation in compound **1** is correct (*i.e.*, the product of this reaction is in fact **4**,



(2)

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[5] C. G. Overberger and P. Chien, *J. Am. Chem. Soc.*, **82**, 5874 (1960).

[6] N. I. Shuikin, M. V. Yushkevich, and G. S. Belikova, *Sb. Statei Obshch. Khim., Akad. Nauk SSSR*, **2**, 1112 (1953).

[7] N. P. Shimanskaya, L. Ya. Malkes, and V. O. Bezuglyi, *J. Gen. Chem. USSR*, **33**, 2040 (1963).

[8] S. S. Hirsch, Abstracts, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966, Paper S106.

[9] J. Dale and L. Zechmeister, *J. Am. Chem. Soc.*, **75**, 2379 (1953).

[10] S. G. Beach, J. H. Turnbull, and W. Wilson, *J. Chem. Soc.*, 4686 (1952).

[11] L. G. Tensmeyer and C. Ainsworth, *J. Org. Chem.*, **31**, 1878 (1966).

TABLE I

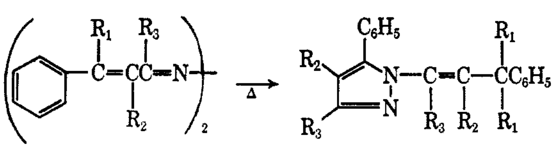
PYROLYSIS OF DERIVATIVES OF CINNAMALDEHYDE AZINE (EQUATION 1)

R_1	R_2	R_3	Temp, °C	Solvent	% yield of pyrazole product	Reacn time, min
H	H	H	170–250	None	90	20
H	H	H	170–250	Benzyl alcohol	95	20
H	H	H	170–250	Triglyme	90	20
H	H	H	170–250	Triphenylmethane	95	20
H	H	H	200	2-Ethoxynaphthalene	95	30
H	H	CH_3	190–200	None	90	30
H	C_6H_5	H	200	None	85	20
CH_3	H	H	250	None	No reaction	20
C_6H_5	H	H	250	None	No reaction	20

and not 2). Compound **4** was hydrogenated, and the dihydro derivative obtained from this reaction proved to be nonidentical with the dihydro derivative obtained from the pyrolysis product, as expected. This reaction (preferential formation of the less hindered pyrazole derivative) is in accord with previous findings of Williams on pyrazole substitution reactions.[12]

The geometry of the carbon–carbon double bond in the side chain of the pyrazole **1** can be deduced from the observed olefinic coupling constant in the proton nmr spectrum of 9 Hz. Compound **1** is in fact an enamine. Sauer and Prahl have found in a study of the nmr spectra of geometrically isomeric enamines that *trans*-enamines exhibit coupling constants of *ca.* 14 Hz, while *cis*-enamines have values for the olefinic coupling constant of about 9 Hz.[13] We thus conclude that the geometry of the double bond in compound **1** is most probably *cis*.

Having established the structure of the pyrolysis product of cinnamaldehyde azine as 1-(*cis*-3-phenylpropenyl)-5-phenylpyrazole, we next elected to examine the generality of the reaction. The general case would be that shown in eq 3.



(3)

The results of pyrolysis experiments on a number of substituted cinnamaldehyde azine derivatives of the type indicated in eq 3 are given in Table I. Examination of this table reveals that the only apparent limitation of the reaction is that the substituent R_1 must be hydrogen. Substitution at either of the other two carbon atoms (R_2 or R_3) in the carbon chain does not alter in any way the course of the reaction. Thus, with the limitation indicated above, azines of the type shown in eq 3 yield a previously unreported class of pyrazoles nearly quantitatively on pyrolysis.

The syntheses of the azines in Table I were effected by conventional routes which are described in the Experimental Section. These pyrolysis reactions are now being studied from a mechanistic point of view. The results of these experiments will be reported at a later time.

Experimental Section[14]

Pyrolysis of Cinnamaldehyde Azine.—Cinnamaldehyde azine (26.0 g, 0.10 mole) was placed in a flask and heated at 200° in an oil bath for 20 min. The resulting dark brown liquid was distilled *in vacuo* to give 25 g of light yellow oil. This was treated with decolorizing charcoal in benzene and redistilled to give 23 g (90 mmoles) of the colorless product ultimately identified as 1-(*cis*-3-phenylpropenyl)-5-phenylpyrazole in 90% yield: $n^{25}\text{D}$ 1.6218; bp 142° (0.01 mm).

Anal. Calcd for $C_{18}H_{16}N_2$: C, 83.04; H, 6.20; N, 10.82; mol wt, 260. Found: C, 82.82; H, 6.25; N, 10.93; mol wt, 230.

The nmr spectrum at 60 MHz in $CDCl_3$ showed a doublet at τ 2.32 (J = 2.0 Hz), a singlet at 2.60, a singlet at 2.78, a doublet at 3.31 (J = 9.0 Hz), a doublet at 3.61 (J = 2.0 Hz), a quartet at 4.50 (J = 9.0 Hz), and a quartet at 6.09 (J = 9.0 Hz) in a weight ratio of 1:5:5:1:1:1:2.

Identical results were obtained when the pyrolysis was carried out in the following solvents: benzyl alcohol, triglyme, triphenylmethane, and 2-ethoxynaphthalene. It was found that at temperatures from 170 to 250° the pyrolysis proceeded smoothly and gave in all cases good yields of product.

Hydrogenation of the Pyrolysis Product.—The thermal isomer (1.25 g, 1.90 mmoles) was hydrogenated in methanol with 5% Pd-C catalyst at 23° and atmospheric pressure. Hydrogen uptake was complete after 1 hr at which time 1.90 mmoles (corrected) of hydrogen had been taken up. The solution was filtered, and the methanol removed on a rotary evaporator. The colorless, liquid dihydro derivative was distilled *in vacuo:* picrate mp 106°, $n^{25}\text{D}$ 1.5891.

Anal. Calcd for $C_{18}H_{18}N_2$: C, 82.36; H, 6.91; N, 10.73. Found: C, 82.53; H, 6.86; N, 10.79.

Potassium Permanganate Oxidation of the Thermal Isomer.—The pyrazole **1** (2.6 g, 1.0 mmole) was dissolved in refluxing acetone and potassium permanganate added until a slight pink color persisted. The solution was filtered and evaporated to dryness leaving 1.2 g (0.84 mmole, 84%) of 3(5)-phenylpyrazole. The manganese dioxide precipitate was washed with hot water. The extracts were cooled and acidified, and 1.1 g (0.90 mmole, 90%) of benzoic acid was collected and identified.

Quantitative Determination of CO_2 Evolution During the $KMnO_4$ Oxidation of 1.—A solution of potassium permanganate (5 g) in water (100 ml) was refluxed in a 500-ml, three-neck flask equipped with gas inlet, reflux condenser, and rubber septum, until gas evolution was no longer evident. The system was flushed with nitrogen for 5 min, and the top of the reflux condenser was connected to a vessel containing 40 ml of 0.100 *N* sodium hydroxide such that any carbon dioxide evolved would bubble through the standard base. Compound **1** (0.228 g, 0.875 mmole) was injected through the septum, and the mixture refluxed until no more carbon dioxide was evolved. The system

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[12] J. K. Williams, *J. Org. Chem.*, **29**, 1377 (1964).

[13] J. Sauer and H. Prahl, *Tetrahedron Letters*, 2863 (1966).

[14] All organic chemicals were used as received; cinnamaldehyde azine, from Matheson Coleman and Bell; all other reagents, Aldrich Chemical Co.; solvents were routinely distilled prior to use. All infrared spectra were taken on a Beckman IR-8 instrument with sodium chloride optics. Ultraviolet spectra were recorded in ethanol on a Bausch and Lomb Spectronic 505 instrument. Nuclear magnetic resonance spectra were obtained on a Varian A-60 instrument using tetramethylsilane as an internal standard in deuteriochloroform. All melting points are corrected, while boiling points are uncorrected. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y., and by Galbraith Laboratories, Knoxville, Tenn. Molecular weights were determined by the Rast method in D-camphor.

was flushed with nitrogen for 5 min, and the sodium hydroxide solution was titrated with standard hydrochloric acid to phenolphthalein and methyl orange end points. The theoretical yield of carbon dioxide was 175 mmoles and that found was 180 mmoles which corresponds to 2.06 moles of carbon dioxide from 1 mole of the pyrazole **1**.

Permanganate Oxidation of the Dihydro Derivative.—The dihydro derivative (0.70 g, 2.7 mmoles) was suspended in a solution of potassium permanganate (4.0 g, 25 mmoles) in water (50 ml). The mixture was refluxed for 1 hr and cooled and sodium bisulfite added to destroy the manganese dioxide which had formed. The solution was acidified and extracted with ether. The ether extract was washed with 10% sodium bicarbonate solution. The aqueous layer was acidified, and the resulting precipitate collected by filtration. It was identified as benzoic acid by comparison of the infrared spectrum and melting point with those of an authentic sample. The amount obtained was 0.30 g (2.4 mmoles, 95%). The ether layer was washed with water and dried over magnesium sulfate. The ether was evaporated to leave 0.35 g (88%, 2.4 mmoles) of a material shown to be 3(5)-phenylpyrazole by comparison of the infrared spectrum to that of an authentic sample.

Ozonolysis of the Thermal Isomer 1.—A stream of oxygen containing 2% ozone was passed through a solution of **1** (5 g) in ethyl acetate (200 ml) with stirring for a period of 2 hr. A small amount of 10% Pd–C catalyst was added and the solution stirred in an atmosphere of hydrogen until hydrogen uptake had ceased. The solution was filtered and the solvent evaporated. The residue was dissolved in ethanol (20 ml) and the solution treated with 2,4-dinitrophenylhydrazine reagent. The precipitate which formed was collected (1 g) and recrystallized from ethanol, mp 123–124°, $\lambda_{\max}^{\mathrm{EtOH}}$ 2600 A (log ϵ 4.38). The melting point given in the literature for the 2,4-dinitrophenylhydrazone of phenylacetaldehyde is 122–123°.[15] The literature melting point for the 2,4-dinitrophenylhydrazone of benzaldehyde is 237–239°[15] ($\lambda_{\max}^{\mathrm{EtOH}}$ 2570 A (log ϵ 4.37)[16] and $\lambda_{\max}^{\mathrm{EtOH}}$ 2770 A (log ϵ 4.48)[16]).

1-(3-Phenylpropenyl)-3-phenylpyrazole (4).[17]—A solution of potassium hydroxide (1.4 g, 25 mmoles) in 15 ml of ethanol was added to 3(5)-phenylpyrazole (3.8 g, 25 mmoles) in 5 ml of ethanol and left to stand for 30 min. Cinnamyl bromide (7.4 g, 40 mmoles) in 8 ml of ethanol was added with cooling maintaining room temperature. The mixture was refluxed for 1 hr, cooled, and filtered to remove the potassium bromide. Fractional distillation resulted in 4.5 g (17 mmoles, 70%) of a yellow liquid, bp 170° (0.01 mm), which solidified on cooling. The product (mp 90–92°) was recrystallized from petroleum ether (60–110°).

Anal. Calcd for $C_{18}H_{16}N_2$: C, 83.04; H, 6.20; N, 10.76. Found: C, 83.19; H, 6.26; N, 10.69.

The nmr spectrum at 60 MHz in $CDCl_3$ showed a doublet at τ 2.21 (J = 2.0 Hz), a multiplet at 2.60, a singlet at 2.69, a doublet at 3.41 (J = 2.0 Hz), a multiplet at 3.49, and a doublet at 3.41 (J = 2.0 Hz) in a weight ratio of 1:5:5:1:2:2.

Pyrolysis of Benzalacetone Azine.—Benzalacetone azine (**5**,[10] 10 g) was held at 190° for 30 min. The resulting dark brown liquid was distilled to yield 9.0 g (90%) of a yellow liquid, 1-(1-methyl-3-phenylpropenyl)-3-methyl-5-phenylpyrazole (**6**): bp 157° (0.02 mm), $n^{25}\mathrm{D}$ 1.5940, $\lambda_{\max}^{\mathrm{EtOH}}$ 2500 A (log ϵ 4.22).

Anal. Calcd for $C_{20}H_{20}N_2$: C, 83.29; H, 6.99; N, 9.72. Found: C, 83.26; H, 7.10; N, 9.67.

The nmr spectrum at 60 MHz in $CDCl_3$ showed a singlet at τ 3.83, a triplet at 4.50 (J = 7.0 Hz), a doublet at 7.07 (J = 7.0 Hz), a singlet at 7.70, and a doublet at 7.99 (J = 1.0 Hz) in a weight ratio of 1:1:2:3:3.

β-Phenylcinnamyl Alcohol.—β-Phenylcinnamic acid,[18] mp 162° (15 g, 67 mmoles), was placed in a flask with 400 ml of ether. The mixture was stirred at 0°, and lithium aluminum hydride (2.2 g, 58 mmoles) added in small portions over 1 hr. The mixture was stirred overnight. Water was added to destroy the excess hydride, and the mixture was poured into cold, dilute sulfuric acid. The ether layer was separated, and the aqueous layer extracted with ether. The ether solutions were combined and washed with sodium carbonate solution and water, dried over magnesium sulfate, and evaporated to leave 7.0 g (33 mmoles, 50%) of the alcohol.

β-Phenylcinnamaldehyde.[19]—β-Phenylcinnamyl alcohol (7.0 g, 33 mmoles) in 10 ml of pyridine was added in one portion to chromium trioxide (10.5 g) in 115 ml of pyridine. (This solution is best made by adding the solid chromium trioxide to the pyridine at 0°). The mixture was stirred for 30 min and left standing overnight. It was then poured into 500 ml of water and extracted with ether. The ether extracts were combined and washed with 10% hydrochloric acid, 10% sodium carbonate solution, and water. The solution was dried over magnesium sulfate and evaporated to leave 8 g of the crude aldehyde. The 2,4-dinitrophenylhydrazone had mp 204° (lit.[15] mp 207°).

β-Phenylcinnamaldehyde Azine.—The crude residue from above was dissolved in ethanol and treated with 1 ml of 95% hydrazine. The solution was refluxed for 4 hr and evaporated to dryness. The residue was recrystallized from petroleum ether (60–110°) to yield 5.0 g (70%) of azine, mp 203°.

Anal. Calcd for $C_{30}H_{24}N_2$: C, 87.34; H, 5.86; N, 6.79. Found: C, 87.49; H, 6.06; N, 6.47.

β-Methylcinnamaldehyde Azine.[17]—This compound was made from β-methylcinnamic acid by the same methods used for β-phenylcinnamaldehyde azine. The yield was 75% from the aldehyde, mp 131–132° (petroleum ether).

Anal. Calcd for $C_{20}H_{20}N_2$: C, 83.29; H, 6.99; N, 9.72. Found: C, 83.19; H, 7.05; N, 9.61.

Registry No.—**1** (*cis*), 14949-51-0; **1** (dihydro derivative, picrate), 15320-65-7; **4**, 14949-52-1; **6**, 14949-53-2; β-phenylcinnamaldehyde azine, 14949-54-3; β-methylcinnamaldehyde azine, 14947-18-3.

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[15] R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1956, p 283.

[16] G. D. Dodson, *J. Am. Chem. Soc.*, **75**, 2720 (1953).

[17] Adapted from the method of I. L. Finar and K. Utting, *J. Chem. Soc.*, 5272 (1960).

[18] D. Lipkin and T. D. Stewart, *J. Am. Chem. Soc.*, **61**, 3295 (1939).

[19] Adapted from the method of J. R. Holum, *J. Org. Chem.*, **26**, 4814 (1961).