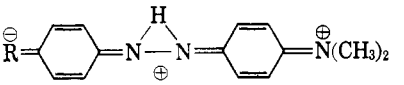
state energy of the molecule is a very good possibility. The K_T data indicate that in the first conjugate acid the form present in major proportions is the azonium form (II). Since pK_2 is the pK_a of the azonium form, it could be expected that pK_{a2} would be quite close to pK_2. This was found to be the case. The results of the least squares analysis are shown in Table IV.

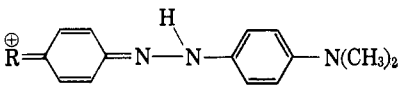
It should be noted that the Hammett plots of pK_3 and pK_2 are quite good straight lines. This is in contrast to work of Zollinger[3f] and Heilbronner[3g] who could obtain good fits only when points representing the more active substituents such as 4′-nitro and 4′-cyano were omitted. This is due to their basic assumption that K_T can be estimated by the spectroscopic method of Sawicki,[3c] as discussed above.

When the Hammett equation was applied to log K_T it was found that, with σ^+, a correlation coefficient of 0.916, and with $\sigma^+\sigma^-$, one of 0.968, could be obtained. The appropriate data are shown in more detail in Table IV and a graphical representation is shown in Fig. 6. That the use of $\sigma^+\sigma^-$ constants yields the better fit can be rationalized on the basis of the resonance forms



VI

and



VII

In structure VI substituents capable of exerting an electron-withdrawing effect by resonance would tend to make the dimethylamino group less basic, leaving the azo group effectively uncharged. This would tend to increase K_T and would require σ^--values. Structures such as VII would demonstrate the effect of electron-donating groups in increasing the basicity of the azo group and leaving the dimethylamino group effectively uncharged. Such structures would lead to a fit with σ^+. Both structures tend to substantiate the view that the tautomer protonated on the azo group should be predominant.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF ARIZONA STATE UNIVERSITY, TEMPE, ARIZ.]

Enamines as Dipolarophiles in 1,3-Dipolar Addition Reactions[1]

BY MORTON E. MUNK AND YUNG KI KIM[2]

RECEIVED JANUARY 13, 1964

The investigation of the reaction of phenyl azide with a series of enamines clearly demonstrates that the exclusive products of 1,3-dipolar addition, 1-phenyl-5-amino-4,5-dihydro-1,2,3-triazoles, are the result of electronic control. The negative end of the azide dipole, *i.e.*, the nitrogen bearing phenyl, is directed to that carbon atom of the unsaturated linkage bearing the electron-releasing amino group. The fact that conjugation with an amino group "activates" the olefinic linkage toward 1,3-dipolar addition supports the electrophilic nature of the reaction.

Of the varied olefinic dipolarophiles successfully employed in intermolecular 1,3-dipolar addition reactions, the predominant number involve an unsaturated linkage that is either strained or conjugated to aromatic and/or electron-withdrawing groups.[3,4] However, only relatively few isolated examples of the successful utilization of dipolarophiles in which the olefinic linkage is conjugated to an electron-releasing group have appeared in the literature.[5] The present report, describing the addition of phenyl azide to a series of enamines,[6] clearly demonstrates the important role that an electron-releasing substituent at the site of unsaturation can play in determining the course of 1,3-dipolar additions.

The directive influence of the amino group was established on the basis of the isomeric 5-(1-piperidino)-4,5-dihydro-1,2,3-triazoles,[7] IIa (70% yield) and IIb (91% yield), respectively, arising from the addition of phenyl azide to the isomeric piperidine enamines of acetophenone and phenylacetaldehyde (Ia and Ib, respectively). Thus the nitrogen atom of the azide dipole bearing phenyl is directed to that carbon of the unsaturated linkage bearing the amino group. Reaction was conveniently effected by mixing equimolar amounts of reactants at room temperature in the absence of solvent.

Triazoline structures IIa and IIb were assigned on the basis of elemental analysis and their facile conversion, in yields greater than 90%, to the known triazoles, 1,5-diphenyl-1,2,3-triazole (IIIa)[8] and 1,4-diphenyl-1,2,3-triazole (IIIb),[8] respectively, upon treatment with refluxing 2 *N* methanolic potassium hydroxide. It appears that the stabilization of the transition state of the elimination step provided by the incipient aromaticity of the 1,2,3-triazole system accounts for the rather facile departure of a poor leaving group. It is interesting to note that dilute aqueous acid promotes a similar quantitative elimination of piperidine in the case of triazoline IIa; the isomeric triazoline IIb gives rise to more deep-seated decomposition products under these conditions (*vide infra*).

(1) Presented before the Division of Organic Chemistry at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept. 10, 1963.

(2) Supported by a Parke, Davis and Co. Research Scholarship.

(3) The facile intramolecular cycloaddition of nitrones to "unactivated" olefinic linkages to yield fused bicyclic isoxazolidines has been reported by N. A. LeBel and J. J. Whang, *J. Am. Chem. Soc.*, **81**, 6334 (1959).

(4) R. Huisgen, *Angew. Chem.*, **75**, 604 (1963), provides a recent and comprehensive review of the entire field of 1,3-dipolar addition reactions.

(5) (a) K. Alder and G. Stein, *Ann.*, **501**, 1 (1933), suggest that the reactions of cyclohexanone and cyclopentanone anil with phenyl azide are explicable in terms of a 1,3-dipolar addition to the tautomeric enamine forms. (b) R. Huisgen, M. Seidel, G. Wallbillich, and H. Knupfer, *Tetrahedron*, **17**, 3 (1962), report the cycloaddition of diphenylnitrilimine to ketene diethyl acetal. (c) R. Huisgen, *Angew. Chem.*, **75**, 604 (1963), reports the successful addition of *p*-nitrophenyl azide to 2,3-dihydropyran.

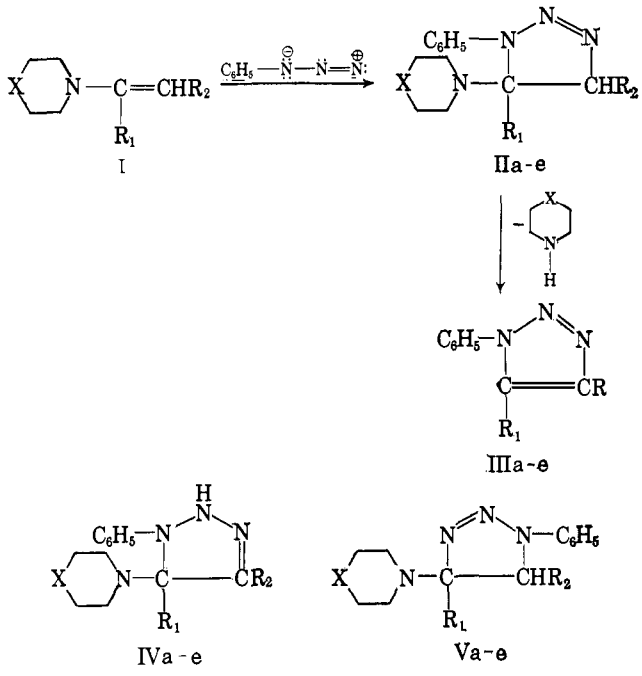
(6) Recent papers by R. Fusco, G. Bianchetti, and D. Pocar, *Gazz. chim. ital.*, **91**, 849 (1961) [*Chem. Abstr.*, **56**, 14019 (1962)], and G. Nathansohn, E. Testa, and N. Dimola, *Experientia*, **18**, 57 (1962), which appeared after the inception of the study described in this manuscript, report the successful condensation of aromatic azides with enamines.

(7) 4,5-Dihydro-1,2,3-triazoles will hereafter be designated as "triazolines."

(8) W. Kirmse and L. Horner, *Ann.*, **614**, 1 (1958).

Assignment of triazoline structures IIa and IIb, rather than the tautomeric structures IVa and IVb, respectively, was made on the basis of the absence of N–H stretching absorption in the infrared and their nuclear magnetic resonance spectra. The presence of a quartet—centered at 4.4 δ (J = 17 c.p.s.) with a total area corresponding to two protons—characteristic of an AB system[9] is consistent with the formulation of triazoline structure IIa in which two ring protons appear at position 4. Likewise, the presence of a pair of doublets (each with a total area corresponding to one proton) centered at 4.6 and 5.3 δ (J = 3.5 c.p.s.) is compatible with the assignment of triazoline structure IIb in which positions 4 and 5 each bear a single proton. The value of the coupling constant, J = 3.5 c.p.s., is suggestive of a *trans* configurational relationship for the two ring hydrogens (dihedral angle of ~120°[10]), but such an assignment of stereochemistry is considered strictly tentative.

The specificity of the cycloaddition is demonstrated by the fact that in each case the triazolines IIa and IIb are the exclusive products of 1,3-dipolar addition; all attempts to detect the presence of isomeric triazolines Va and Vb, respectively, failed. In addition, treatment of the mother liquors from the isolation of IIa and IIb with methanolic potassium hydroxide failed to produce detectable amounts of triazoles IIIa and IIIb, respectively.



a, R_1 = C_6H_5, R_2 = H, X = CH_2
b, R_1 = H, R_2 = C_6H_5, X = CH_2
c, R_1 = CH_3, R_2 = CH_2CH_3, X = O
d, R_1 = CH_2CH_3, R_2 = CH_3, X = O
e, R_1 = H, R_2 = CH_3, X = CH_2

Additional evidence to support the suggested influence of the amino group on the direction of addition was obtained by a similar sequence of reactions employing the isomeric morpholine enamines of 2-pentanone and 3-pentanone, 2-(4-morpholino)-2-pentene (Ic),[11] and 3-(4-morpholino)-2-pentene (Id), respectively. Triazolines IIc and IId are the *exclusive* products of 1,3-dipolar addition of phenyl azide to enamines Ic and Id, respectively; all attempts to detect the isomeric triazolines Vc and Vd, respectively, failed. Structure assignment of triazolines IIc and IId was again founded on base-induced conversion to the corresponding 1,2,3-triazoles IIIc and IIId, respectively, neither of which are recorded in the literature. The structure of triazole IIIc was established by comparison with an authentic sample prepared by a Wolff-Kishner reduction of the known 1-phenyl-4-acetyl-5-methyl-1,2,3-triazole.[12] This transformation also establishes the structure of the isomeric triazole arising from triazoline IId as 1-phenyl-4-methyl-5-ethyl-1,2,3-triazole (IIId).

The reaction of phenyl azide with isobutyrophenone-piperidine enamine (VI) required a temperature of 100° as compared to room temperature for the cycloadditions reported above and undoubtedly reflects increased steric compression in the transition state.[13] The crystalline solid, isolated in 50% yield, was assigned structure VII on the basis of elemental analysis and the products of acid hydrolysis. Treatment of the product of 1,3-dipolar addition with 3 N hydrochloric acid led to the immediate evolution of nitrogen. A vapor phase chromatographic analysis of the neutral fraction arising from an ether extract of the acidic solution indicated the presence of three components identified (by comparison of infrared spectra and retention times of authentic samples) as 2-chloro-2-methylpropiophenone (IX), 2-hydroxy-2-methylpropiophenone (X), and α-methylacrylophenone (XI) in yields of 15, 19, and 49%, respectively. The basic fraction was shown to consist of piperidine and aniline.

It is suggested that the products of acid hydrolysis can best be accommodated in terms of triazoline structure VII. Hydrolysis is pictured as proceeding *via* an acid-catalyzed cleavage of the triazene linkage of the triazoline ring, followed by solvolysis and hydrolysis of the resulting α-diazoketimine VIII.[14] Following a similar course of acid hydrolysis, the isomeric triazoline XII would be expected to give rise to 2-anilino-2-methylpropiophenone, which in an independent experiment was shown to be stable under the conditions of acid hydrolysis. Triazoline VII proved to be the exclusive product of 1,3-dipolar addition and all attempts to detect the isomeric compound XII in the mother liquors or 2-anilino-2-methylpropiophenone in the acid hydrolysate thereof failed.

The experimental results clearly indicate that the "negative end" of the azide dipole, *i.e.*, the nitrogen

(9) L. M. Jackman, "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, p. 89.

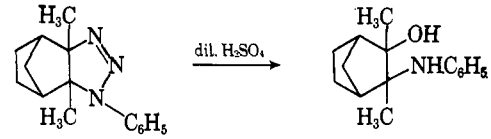
(10) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

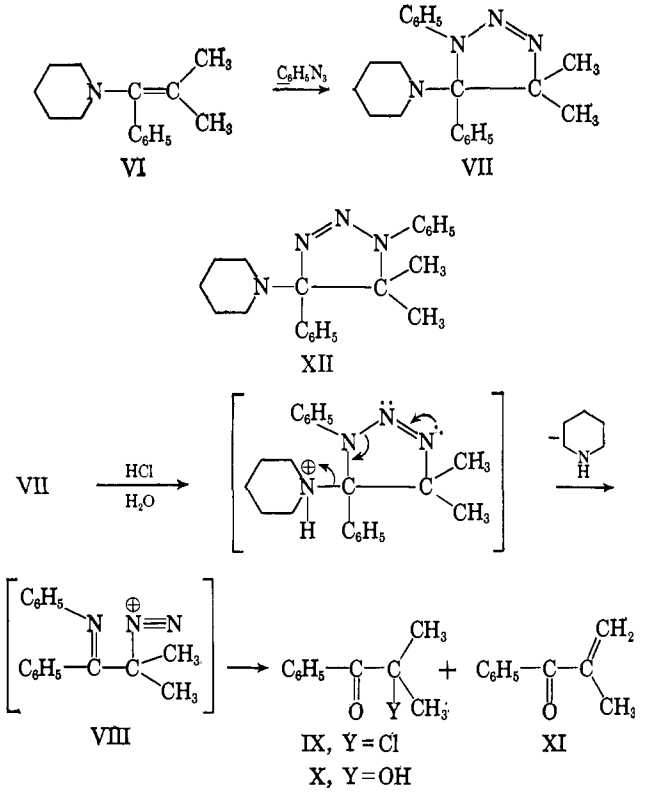
(11) The n.m.r. spectrum of the gas chromatographically pure compound (see Experimental) is compatible with that of the isomeric 2-(4-morpholino)-2-pentene structure and incompatible with that of the isomeric 2-(4-morpholino)-1-pentene structure.

(12) O. Dimroth, *Ber.*, **35**, 1029 (1902).

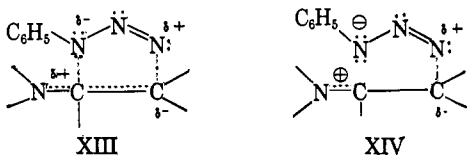
(13) The "additional" steric compression in this particular example may, in part, be due to the decrease in bond angle between the *gem*-methyl groups that results as rehybridization from sp^2 to sp^3 occurs; see A. Streitwieser, Jr., *Chem. Rev.*, **56**, 683 (1956).

(14) The merit of such a description is illustrated by its ability to rationalize the formation of the products of acid hydrolysis of 1-phenyl substituted triazolines arising from the cycloaddition of phenyl azide to a series of strained olefins[6a]; *e.g.*





bearing phenyl,[15] is directed to that carbon atom of the unsaturated linkage bearing the electron-releasing amino group.[16] The directive influence of the amino group is compatible with a transition state, *e.g.*, XIII or XIV, in the rate-determining step which possesses considerable ionic character and suggests that the mode of orientation observed is the result of electronic control. Specifically, addition occurs in the direction which generates positive charge on the carbon atom best able to sustain



it—that bearing the amino group. No distinction between a concerted addition (transition state XIII) and a two-step process (transition state XIV) is intended at this time.[17] If a concerted addition is operative in the examples studied, the mode of orientation is particularly interesting since the data suggest that electronic control subjugates steric control. This point is best illustrated by the exclusive formation of triazoline IIa upon addition of phenyl azide to the enamine Ia. In a one-step process the transition state in which nitrogen bearing phenyl joins with carbon bearing a phenyl and piperidino group is clearly sterically least favored, thus demonstrating the importance of electronic stabilization.

The orientation observed is striking in view of the importance of steric control suggested by Huisgen[5b] in a study of the cycloaddition of diphenylnitrilimine, $C_6H_5C{=}\overset{\oplus}{N}{-}\overset{\ominus}{N}C_6H_5$, to the "electron poor" double bonds of acrylonitrile and ethyl acrylate. In each case a single 2-pyrazoline was isolated which proved to be isomeric with that anticipated on the basis of electronic control.

The role of the amino group in directing the course of the reactions reported suggests that the cycloaddition is electrophilic in nature, *i.e.*, conjugation with an electron-releasing group "activates" the dipolarophile toward 1,3-dipolar addition. This conclusion finds support in the observation that under reaction conditions which lead to the formation of triazoline IIb in high yield the reaction of phenyl azide with styrene or methyl cinnamate leads to an almost quantitative recovery of starting materials. Similar findings were observed in a comparison of the reactivity of the "electron-rich" dipolarophile, propionaldehydepiperidine enamine (Ie), and the "electron-poor" dipolarophile, ethyl crotonate. Whereas a 54% yield of analytically pure triazoline IIe was obtained with the enamine, no reaction could be detected in the case of the α,β-unsaturated ester.

Experimental[18]

Preparation of Enamines. A. Ketone Enamines.—The procedure of Stork[19] was employed in all cases. *p*-Toluenesulfonic acid was added as a catalyst.

Isobutyrophenonepiperidine Enamine (VI).—After 75 days of refluxing in benzene the enamine was obtained in 63% yield, b.p. 91–92° (0.4 mm.), $n^{25}D$ 1.5395. The infrared spectrum of the gas chromatographically pure enamine (column temperature 200°, gas pressure 9 p.s.i.) showed a weak band at 1640 (C=C) and no absorption at 1685 cm.$^{-1}$ (C=O).

Anal. Calcd. for $C_{15}H_{21}N$: C, 83.66; H, 9.83; N, 6.51. Found: C, 83.49; H, 9.82; N, 6.53.

The perchlorate salt of VI crystallized from ethyl acetate–methanol; m.p. 156–157°.

Anal. Calcd. for $C_{15}H_{22}NClO_4$: C, 57.05; H, 7.02; N, 4.43; O, 20.27. Found: C, 56.91; H, 7.18; N, 4.18; O, 20.52.

Acetophenonepiperidine Enamine (Ia).—After 6 days of refluxing the enamine was obtained in 63% yield, b.p. 78–79° (0.3 mm.), $n^{25}D$ 1.5540. The infrared spectrum of the gas chromatographically pure enamine (column temperature 200°, gas pressure 15 p.s.i.) showed a doublet at 1575 and 1600 (C=C) and no absorption at 1695 cm.$^{-1}$ (C=O).

Anal. Calcd. for $C_{13}H_{17}N$: C, 83.37; H, 9.15; N, 7.48. Found: C, 83.31; H, 9.23; N, 7.20.

The perchlorate salt of Ia crystallized from ethyl acetate–methanol; m.p. 130–131°.

(15) Such an assignment appears to reflect best the chemical reactivity of the azide and is compatible with the quantum mechanical calculations of J. D. Roberts, *Ber.*, **94**, 273 (1963). For example, the acid hydrolysis of phenyl azide to *p*-aminophenol [P. Friedländer and M. Zeitlin, *ibid.*, **27**, 192 (1894)] is explicable in terms of an anionic center at the nitrogen bearing phenyl. Phenylhydroxylamine, which can arise from protonated phenyl azide, $C_6H_5\overset{\oplus}{N}HN{\equiv}N$:, in aqueous solution, is known to rearrange to *p*-aminophenol under acidic conditions [E. Bamberger, *ibid.*, **27**, 1347 (1894)]. The reaction of phenyl azide with cyanide ion and methylmagnesium iodide, respectively, to yield 3-cyano-1-phenyltriazene($C_6H_5N{=}NNHCN$) and 3-methyl-1-phenyltriazene [see J. H. Boyer and F. C. Canter, *Chem. Rev.*, **54**, 1 (1954) for a review of this chemistry] is indicative of the electrophilic nature of the terminal nitrogen of the dipole not bearing phenyl.

(16) This mode of orientation is in contrast to that suggested by Alder and Stein[3a] and in accord with the findings of Fusco.[6]

(17) R. Huisgen, *Proc. Chem. Soc.*, 357 (1961), presents evidence in support of the concerted addition of phenyl azide to a strained olefin.

(18) Melting points were taken in open capillaries on a Thomas-Hoover apparatus and are uncorrected. Boiling points are also uncorrected. Infrared spectra of liquids and solids were determined (as liquid films and potassium bromide pellets, respectively) on a Perkin–Elmer Model 137 or 237 Infracord. Nuclear magnetic resonance spectra were taken in carbon tetrachloride or chloroform-*d* on a Varian Associates A-60 spectrometer with tetramethylsilane as an internal standard and are reported in δ-values (p.p.m.).

Gas chromatographic analyses were carried out on 6-ft. glass columns using a thermal conductivity detection system and helium as the carrier gas. The packing was prepared with Dow Corning 550 silicone, 20% on Anakrom ABS. Column temperature and helium pressure is indicated in each case.

Microanalyses were performed by Midwest-Microlab, Inc., Indianapolis, Ind.

(19) G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrell, *J. Am. Chem. Soc.*, **85**, 207 (1963).

Anal. Calcd. for $C_{13}H_{18}NClO_4$: C, 54.26; H, 6.31; N, 4.87. Found: C, 54.25; H, 6.43; N, 4.89.

2-Pentanonemorpholine Enamine (Ic).—After 4 days of refluxing the enamine was obtained in 36% yield, b.p. 78–79° (8 mm.), $n^{25}D$ 1.4762.

Anal. Calcd. for $C_9H_{17}NO$: C, 69.63; H, 11.04; N, 9.02; O, 10.31. Found: C, 69.88; H, 10.98; N, 8.84; O, 10.19.

Catalytic hydrogenation of the enamine in ethyl acetate over platinum oxide gave 4-(2-pentyl)morpholine, b.p. 196–198° (739 mm.), $n^{25}D$ 1.4474 (reported[20] b.p. 193–194° (744 mm.), $n^{25}D$ 1.4475).

The infrared spectrum of the gas chromatographically pure enamine (column temperature 145°, gas pressure 7 p.s.i.) showed a band at 1600 cm.$^{-1}$ (C=C) and no absorption in the carbonyl region (1730 cm.$^{-1}$). The nuclear magnetic resonance spectrum ($CDCl_3$) showed a triplet at 4.40 δ (J = 6.5 c.p.s.) with a total area corresponding to one proton. This is consistent with the presence of a single vinylic proton interacting with an adjacent $-CH_2-$ moeity.

3-Pentanonemorpholine Enamine (Id).—After 66 hr. of refluxing, the enamine was obtained in 41% yield, b.p. 78° (9 mm.) (reported[19] b.p. 77–78° (9 mm.)). The infrared spectrum showed a strong band at 1650 (C=C) and no absorption at 1730 cm.$^{-1}$ (unconjugated C=O).

B. **Aldehyde enamines** were prepared according to the procedure of Mannich and Davidsen.[21]

Phenylacetaldehydepiperidine enamine (Ib) was obtained in 44% yield, b.p. 109–111° (0.35 mm.), m.p. 28–30° (reported[21] b.p. 174–175° (15 mm.), m.p. 29–30°). The infrared spectrum showed a strong band at 1640 cm.$^{-1}$ (C=C) and no carbonyl absorption (1735 cm.$^{-1}$).

Propionaldehydepiperidine enamine (Ie) was obtained in 65% yield, b.p. 53–55° (10 mm.), $n^{25}D$ 1.4795 (reported[22] b.p. 53–55° (12 mm.), $n^{20}D$ 1.4688, and b.p. 51–53° (10 mm.)[23]). The infrared spectrum showed a strong band at 1670 cm.$^{-1}$ (C=C) and no absorption in the carbonyl region (1740 cm.$^{-1}$).

Anal. Calcd. for $C_8H_{15}N$: C, 76.73; 12.08; N, 11.19. Found: C, 76.50; H, 12.14; N, 11.36.

1,5-Diphenyl-5-(1-piperidino)-4,5-dihydro-1,2,3-triazole (IIa).—A solution containing 9.35 g. (0.050 mole) of the piperidine enamine of acetophenone and 5.95 g. (0.050 mole) of phenyl azide in a stoppered flask was allowed to react in the absence of light for 48 hr. at room temperature. The brown solid mass was dissolved in boiling *n*-pentane, treated with decolorizing charcoal, filtered, and cooled to yield 9.25 g. of a crude solid material, m.p. 98–103°. The mother liquor was concentrated to produce additional solid raising the total yield of crude material to 10.65 g. (70%). Repeated recrystallization from *n*-pentane gave 7.48 g. (49%) of an analytically pure crystalline solid, m.p. 109–110.5°.

Anal. Calcd. for $C_{19}H_{22}N_4$: C, 74.48; H, 7.24; N, 18.28. Found: C, 74.61; H, 7.30; N, 18.46.

A paper chromatogram (*n*-heptane system) of the pure triazoline indicated a single spot. All attempts to isolate a compound corresponding to the isomeric triazoline Va failed. Treatment of the mother liquors from the isolation of triazoline IIa with 2 *N* methanolic potassium hydroxide (*vide infra*) yielded 0.20 g. of 1,5-diphenyl-1,2,3-triazole (IIIa), m.p. 112–113° (reported[8] m.p. 110–111°), and no detectable 1,4-diphenyl-1,2,3-triazole (IIIb).

1,4-Diphenyl-5-(1-piperidino)-4,5-dihydro-1,2,3-triazole (IIb).—A solution containing 0.94 g. (0.0050 mole) of the piperidine enamine of phenylacetaldehyde and 0.60 g. (0.0050 mole) of phenyl azide was allowed to react in the absence of light for 54 hr. at room temperature. The resulting yellow solid was dissolved in boiling Skellysolve B[24] and cooled to yield 1.39 g. (91%) of a crude solid material, m.p. 94–97°. Repeated recrystallization from Skellysolve B yielded 1.13 g. (74%) of an analytically pure white crystalline solid, m.p. 99–101°. The pure triazoline showed a single spot on paper (*n*-heptane system). A reduction in reaction time to 3 hr. led to the formation of a 60% yield of analytically pure material.

Anal. Calcd. for $C_{19}H_{22}N_4$: C, 74.48; H, 7.24; N, 18.28. Found: C, 74.67; H, 7.06; N, 17.98.

All attempts to detect the isomeric triazoline Vb failed. Treatment of the mother liquors from the isolation of IIb with 2 *N* methanolic potassium hydroxide (*vide infra*) yielded 0.05 g. of 1,4-diphenyl-1,2,3-triazole (IIIb), m.p. 181–183° (reported[8] m.p. 180–183°), and no detectable 1,5-diphenyl-1,2,3-triazole.

1-Phenyl-4-ethyl-5-methyl-5-(4-morpholino)-4,5-dihydro-1,2,3-triazole (IIc).—A solution containing 6.00 g. (0.038 mole) of the morpholine enamine of 2-pentanone and 4.76 g. (0.040 mole) of phenyl azide was allowed to react in the absence of light for 24 hr. at room temperature. The resulting light yellow sirup was dissolved in a boiling mixture of Skellysolve B and cyclohexane and cooled to yield 3.40 g. of a crude solid, m.p. 90–95°. Additional solid from the mother liquor raised the yield to 5.00 g. (47%). Recrystallization yielded 4.63 g. (44%) of an analytically pure white crystalline solid, m.p. 98–100°. The paper chromatogram (*n*-heptane system) of the pure triazoline showed only a single spot. None of the isomeric triazoline Vc could be detected.

Anal. Calcd. for $C_{15}H_{22}N_4O$: C, 65.66; H, 8.09; N, 20.42. Found: C, 65.83; H, 8.20; N, 20.68.

1-Phenyl-4-methyl-5-ethyl-5-(4-morpholino)-4,5-dihydro-1,2,3-triazole (IId).—A solution containing 5.20 g. (0.034 mole) of the morpholine enamine of 3-pentanone and 4.05 g. (0.034 mole) of phenyl azide was allowed to react in the absence of light for 12 hr. at room temperature. Work-up in the fashion indicated above yielded 8.20 g. (89%) of a crude solid material, m.p. 75–79°. Repeated recrystallization from Skellysolve B gave 6.30 g. (69%) of an analytically pure white crystalline solid, m.p. 81–82.5°. None of isomeric triazoline Vd was detected.

Anal. Calcd. for $C_{15}H_{22}N_4O$: C, 65.66; H, 8.09; N, 20.42; O, 5.83. Found: C, 65.86; H, 8.22; N, 20.35; O, 5.73.

1-Phenyl-4-methyl-5-(1-piperidino)-4,5-dihydro-1,2,3-triazole (IIe).—A solution containing 0.63 g. (0.0050 mole) of the piperidine enamine of propionaldehyde and 0.60 g. (0.0050 mole) of phenyl azide was occasionally cooled in a cold-water bath for the first half-hour in order to maintain the reaction at room temperature and then allowed to stand at room temperature in the absence of light for 54 hr. The usual work-up yielded 0.76 g. (62%) of a crude solid material, m.p. 57–60°. Repeated recrystallization from *n*-pentane yielded 0.65 g. (53%) of an analytically pure solid, m.p. 64–65°. The paper chromatogram of the pure triazoline showed a single spot (*n*-heptane system).

Cutting the total reaction time to 3 hr. resulted in the formation of 53% of crude material and 42% of analytically pure material.

Anal. Calcd. for $C_{14}H_{20}N_4$: C, 68.82; H, 8.25; N, 22.93. Found: C, 69.10; H, 8.00; N, 23.22.

Treatment of the mother liquors from the isolation of triazoline IIe with 2 *N* methanolic potassium hydroxide (*vide infra*) yielded 0.03 g. of 1-phenyl-4-methyl-1,2,3-triazole (IIIe), m.p. 80–81° (reported[25] m.p. 81°), and no detectable 1-phenyl-5-methyl-1,2,3-triazole.

1,5-Diphenyl-4,4-dimethyl-5-(1-piperidino)-4,5-dihydro-1,2,3-triazole (VII).—A solution containing 14.40 g. (0.067 mole) of piperidine enamine of isobutyrophenone and 10.0 g. (0.084 mole) of phenyl azide was heated in an autoclave for 60 hr. at 100°. The brown solid was dissolved in boiling *n*-hexane, treated with decolorizing charcoal, filtered, and cooled, to yield 12.50 g. (56%) of a crude solid material, m.p. 144–148°. Repeated recrystallization from *n*-hexane gave 11.20 g. (50%) of an analytically pure white crystalline solid, m.p. 149–151°. Thin layer alumina chromatograms in three systems (acetone–benzene (20:80 v./v.), acetone–pentane (2:98 v./v.), and benzene) produced a single spot in each case.

Anal. Calcd. for $C_{21}H_{28}N_4$: C, 75.41; H, 7.84; N, 16.75. Found: C, 75.62; H, 8.03; N, 16.98.

1,5-Diphenyl-1,2,3-triazole (IIIa). A. Base-Induced Elimination.—A solution of 0.76 g. (0.0025 mole) of triazoline IIa in 15 ml. of 2 *N* methanolic potassium hydroxide was refluxed for 2 hr. After evaporation to dryness *in vacuo*, the residue was taken up in water and extracted three times with ether. Evaporation of the dried ether solution yielded 0.54 g. (97%) of a white crystalline solid, m.p. 111–113°. Recrystallization from Skellysolve B yielded 0.46 g. (83%) of analytically pure material, m.p. 112–113° (reported[8] m.p. 110–111°).

Anal. Calcd. for $C_{14}H_{11}N_3$: C, 76.00; H, 5.01; N, 18.99. Found: C, 75.89; H, 4.99; N, 18.73.

(20) R. W. Doskotch and H. A. Lardy, *J. Am. Chem. Soc.*, **79**, 6230 (1957).

(21) C. Mannich and H. Davidsen, *Ber.*, **69**, 2106 (1936).

(22) G. Opitz, H. Hellmann, and H. W. Schubert, *Ann.*, **623**, 112 (1959).

(23) R. Adams and J. E. Mahan, *J. Am. Chem. Soc.*, **64**, 2588 (1942).

(24) Skellysolve B is a petroleum ether fraction, boiling range 63–67°, marketed by Skelly Oil Co.

(25) A. Bertho, *Ber.*, **58B**, 859 (1925).

B. **Acid-Catalyzed Elimination.**—A solution of 0.82 g. (0.0027 mole) of triazoline IIa in 25 ml. of 10% sulfuric acid was permitted to remain at room temperature for 15 hr. The resulting white solid precipitate was collected by filtration; 0.59 g. (99%), m.p. 112–113°. A mixture melting point with the compound resulting from base elimination produced no depression.

1,4-Diphenyl-1,2,3-triazole (IIIb).—Following procedure A outlined above, 1.07 g. (0.0035 mole) of triazoline IIb was converted to 0.74 g. (95%) of the corresponding triazole IIIb, m.p. 181–183° (reported[8] m.p. 180–183°).

1-Phenyl-4-ethyl-5-methyl-1,2,3-triazole (IIIc). A. From Triazoline IIc.—Following procedure A outlined above for the preparation of triazole IIIa, 0.30 g. (0.0011 mole) of triazoline IIc was converted to 0.19 g. (92%) of the crude oily triazole IIIc. The triazole was isolated as its picrate salt (0.30 g., 66% based on triazoline IIc), m.p. 128.5–130°.

Anal. Calcd. for $C_{11}H_{13}N_3 \cdot C_6H_3N_3O_7$: C, 49.04; H, 3.87; N, 20.19. Found: C, 49.34; H, 4.06; N, 19.90.

The triazole arising from 0.30 g. of triazoline IIc could also be isolated as its perchlorate salt in 54% yield based on starting triazoline, m.p. 118–120°.

Anal. Calcd. for $C_{11}H_{13}N_3 \cdot HClO_4$: C, 45.92; H, 4.90; N, 14.61. Found: C, 46.00; H, 4.83; N, 14.45.

B. **Independent Synthesis.**—A solution of 0.20 g. (0.010 mole) of 1-phenyl-4-acetyl-5-methyl-1,2,3-triazole (*vide infra*), 1.25 g. of sodium hydroxide, and 1.2 ml. of hydrazine (95%) in 20 ml. of triethylene glycol was refluxed for 1 hr. With the condenser removed the solution was heated until the temperature reached 195–200°. The solution was then cooled, diluted with water, and extracted with benzene. Evaporation of the dried benzene solution yielded 0.16 g. of the oily triazole IIIc, isolated as its picrate (49% yield), m.p. 128.5–130°. A mixture melting point with the triazole picrate derived from A above was undepressed.

The infrared spectra of the triazole picrates from both sources were superimposable.

1-Phenyl-4-methyl-5-ethyl-1,2,3-triazole (IIId).—Following procedure A outlined above for the preparation of triazole IIIa, 5.00 g. (0.018 mole) of triazoline IId was converted to 2.80 g. (82%) of analytically pure triazole IIId, m.p. 55–56.5° (Skellysolve B–acetone).

Anal. Calcd. for $C_{11}H_{13}N_3$: C, 70.56; H, 7.00; N, 22.44. Found: C, 70.37; H, 7.01; N, 22.68.

Picrate of triazole IIId, m.p. 144–145.5°.

Anal. Calcd. for $C_{11}H_{13}N_3 \cdot C_6H_3N_3O_7$: C, 49.04; H, 3.87; N, 20.19. Found: C, 49.26; H, 4.14; N, 20.45.

Perchlorate of triazole IIId, m.p. 161–163°.

Anal. Calcd. for $C_{11}H_{13}N_3 \cdot HClO_4$: C, 45.92; H, 4.90; N, 14.61. Found: C, 46.19; H, 5.17; N, 14.83.

1-Phenyl-4-methyl-1,2,3-triazole (IIIe).—Following procedure A outlined above for the preparation of triazole IIIa, 0.88 g. (0.0036 mole) of triazoline IIe was converted to 0.42 g. (73%) of analytically pure triazole IIIe, m.p. 80–81° (Skellysolve B; reported[25] m.p. 81°).

Acid Hydrolysis of Triazoline VII.—Dissolution of 2.70 g. (0.0081 mole) of triazoline VII in 70 ml. of 3 *N* hydrochloric acid led to the immediate and gradual evolution of a gas (presumably nitrogen). After remaining at room temperature for 12 hr. the solution was extracted with ether. The ether extract was washed with water, dried over anhydrous magnesium sulfate, and evaporated *in vacuo* to yield 1.05 g. of a light amber liquid. A gas chromatographic analysis (column temperature 185°, helium pressure 10 p.s.i.) of this liquid indicated the presence of only three components whose retention times were identical with those of authentic samples of α-methylacrylophenone,[26] 2-hydroxy-2-methylpropiophenone,[26] and 2-chloro-2-methylpropiophenone[26] (in order of increasing retention times). A quantitative analysis of the relative ratio of components present in the mixture led to the conclusion that the three compounds listed above were formed in 49, 19, and 15% yields, respectively, based on starting triazoline. A comparison of the infrared spectrum of the mixture with that of an authentic mixture of the three components revealed no differences with a single exception. A weak band at 1500 cm.$^{-1}$ present in the spectrum of the neutral components from the hydrolysis could not be detected in the spectrum of the authentic mixture.

The aqueous acidic solution was next made basic with sodium hydroxide and extracted with ether. The ether extract was shown to contain piperidine and aniline by comparison of retention times with authentic samples.

A solution of 18 mg. of 2-anilino-2-methylpropiophenone[27] in 5 ml. of 3 *N* hydrochloric acid was stirred at room temperature for 24 hr., then made basic with sodium hydroxide, and extracted with ether. Evaporation of the dried ether solution gave 16 mg. (89%) of unreacted 2-anilino-2-methylpropiophenone, m.p. 137–138°.

Reaction of Phenyl Azide with Styrene.—A mixture of 1.04 g. (0.010 mole) of styrene and 1.20 g. (0.010 mole) of phenyl azide was allowed to react at room temperature in the absence of light for 72 hr. The volatile components (1.89 g.) were collected by a *rapid* distillation (20 min.) under 3.5–5 mm. pressure. The bath temperature was not permitted to exceed 70°. A gas chromatographic analysis (column temperature 150°, gas pressure 7 p.s.i.) of the distillate indicated a 97% recovery of styrene and a 76% recovery of phenyl azide. The presence of an adduct could not be detected.

Reaction of Phenyl Azide with Methyl Cinnamate.—A mixture of 0.81 g. (0.0050 mole) of methyl cinnamate and 0.60 g. (0.0050 mole) of phenyl azide was allowed to react at room temperature for 84 hr. at room temperature in the absence of light. The volatile components (1.2 g.) were collected by a rapid distillation (20 min.) at 0.3 mm. pressure (bath temperature less than 100°). A gas chromatographic analysis (column temperature 190°, gas pressure 10 p.s.i.) of the distillate indicated an 86.5% recovery of methyl cinnamate and an 83.5% recovery of phenyl azide. No adduct could be detected.

Reaction of Phenyl Azide with Ethyl Crotonate.—A mixture of 1.14 g. (0.010 mole) of ethyl crotonate and 1.20 g. (0.010 mole) of phenyl azide was allowed to react at room temperature for 4 hr. in the absence of light. The volatile components (1.85 g.) were collected by a rapid distillation (20 min.) at 4–5 mm. pressure (bath temperature less than 70°.) A gas chromatographic analysis (column temperature 140°, gas pressure 10 p.s.i.) of the distillate indicated a 95% recovery of ethyl crotonate and a 75% recovery of phenyl azide. No adduct could be detected.

1-Phenyl-4-acetyl-5-methyl-1,2,3-triazole.—A solution of 2.50 g. (0.012 mole) of 1-phenyl-5-methyl-1,2,3-triazole-4-carboxylic acid (prepared from phenyl azide and ethyl acetoacetate[28]) in 500 ml. of anhydrous ether was added dropwise, in a nitrogen atmosphere, to a stirred solution of methyllithium prepared from 1.47 g. (0.21 mole) of lithium. After standing overnight, the solution was poured into ice water, and the ether layer was separated. Evaporation of the dried ether solution yielded 0.77 g. (31%) of a white crystalline solid, m.p. 92–96°. Recrystallization from Skellysolve B and acetone raised the melting point to 98–99° (reported[29] m.p. 99–100°).

Acknowledgment.—The generous financial support of Parke, Davis and Co. is gratefully acknowledged. We are indebted to Dr. Irwin Klundt for carrying out some of the very early experiments in this investigation.

(26) C. L. Stevens and B. V. Ettling, *J. Am. Chem. Soc.*, **77**, 5412 (1955).

(27) J. Gilbert, M.S. Thesis, Arizona State University, 1963.

(28) O. Dimroth, *Ber.*, **35**, 1029 (1902).

(29) W. Borsche, H. Hahn, and M. Wagner-Roemmich, *Ann.*, **554**, 15 (1943).